Photochemical Reactions of *N*-Acyldithiocarbamates and *N*-Acylthiocarbamates

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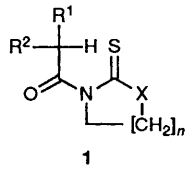
Photochemical hydrogen abstraction from *N*-acyltetrahydro-1,3-thiazine-2-thiones, *N*-acyloxazolidine-2-thiones and *N*-acyltetrahydro-1,3-oxazine-2-thiones have been studied. Irradiation of *N*-(diphenylacetyl)-and *N*-(alkoxyacetyl)tetrahydro-1,3-thiazine-2-thiones in benzene at 40 °C gave bicyclic lactams, 5,7-dithia-1-azabicyclo[4.3.0]nonan-9-ones, accompanied by Norrish Type-II cleavage products, whereas *N*-acetyl and *N*-isobutyryl derivatives gave only cleavage products. Photolysis of *N*-(diphenylacetyl)-, *N*-(methoxyacetyl)-and *N*-(ethoxyacetyl)-tetrahydro-1,3-thiazine-2-thiones at 0 °C followed by acetylation afforded cepham analogues, 6-acetylthio-5-thia-1-azabicyclo[4.2.0]octan-8-ones. *N*-Acyloxazolidine-2-thiones underwent Norrish Type-II cleavage to give oxazolidine-2-thione and the corresponding esters (*O*-acylmethanols) as the sole products on irradiation in methanol. *N*-Acetyl- or *N*-isobutyryltetrahydro-1,3-oxazine-2-thiones underwent only Norrish Type-II cleavage whereas *N*-(alkoxyacetyl)tetrahydro-1,3-thiazine-2-thiones underwent cleavage and also gave 5-oxa-7-thia-1-azabicyclo[4.3.0]nonan-9-ones.

Photochemical hydrogen abstraction of thiones[1] and thioesters[2] have been well studied. For thiocarbonyl compounds adjacent to a nitrogen atom, *i.e.* thioamides and thioimides, the photochemistry has received much attention from both mechanistic and synthetic viewpoints.[3] Hydrogen abstraction from a compound with a thioacarbonyl group interposed by two heteroatoms has been studied only a little. Thioparabanate, which possesses a thiourea moiety, led to intermolecular hydrogen abstraction on irradiation to yield thiols.[4] Photolysis of *N*-acylthiazolidine-2-thiones gave Norrish Type-II cleavage products efficiently.[5] We have already reported that the photolysis of acyclic *N*-acylthiocarbamates gave mercapto-β-lactams and/or thioxo-β-lactams by γ-hydrogen abstraction by the thiocarbonyl group.[6] In this connection, we now report the photochemical reactivity and the ring-size effects of *N*-acyldithiocarbamates and *N*-acylthiocarbamates.[7]

Results and Discussion

All *N*-acyltetrahydro-1,3-thiazine-2-thiones **1a–e**, *N*-acyloxazolidine-2-thiones **1f–h** and *N*-acyltetrahydro-1,3-oxazine-2-thiones **1i**, **1j** were prepared easily by the reaction of the corresponding dithiocarbamates or thiocarbamates with the appropriate acid chloride in the presence of triethylamine.



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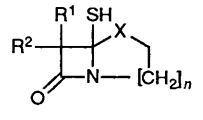
a, n = 2; R^1 = R^2 = H, X = S; **b**, n = 2; R^1 = R^2 = Me, X = S; **c**, n = 2; R^1 = R^2 = Ph, X = S; **d**, n = 2; R^1 = MeO, R^2 = H, X = S; **e**, n = 2; R^1 = EtO, R^2 = H, X = S; **f**, n = 1; R^1 = R^2 = Me, X = O; **g**, n = 1; R^1 = Ph, R^2 = H, X = O; **h** n = 1; R^1 = MeO, R^2 = H, X = O, **i**, n = 2; R^1 = MeO, R^2 = H, X = O; **j**, n = 2; R^1 = EtO, R^2 = H, X = O

When *N*-acetyltetrahydro-1,3-thiazine-2-thione **1a** was irradiated in benzene under argon with a 1 kW high-pressure mercury lamp at 15 °C until the starting material had disappeared, tetrahydro-1,3-thiazine-2-thione **5** was obtained in 50% yield. Photolysis of *N*-isobutyryl derivative **1b** gave similar results (**5**, 62% yield) For the diphenylacetyl derivative **1c**, the IR spectrum of the resulting mixture exhibited a strong carbonyl frequency at 1760 cm^{-1} characteristic of a four-membered lactam (compound **2c**), whereas it was impossible to isolate compound **2c**. Instead, the thioxo-β-lactam **3c** was isolated in 55% yield by silica gel column chromatography. The IR spectrum ($CHCl_3$) of compound **3c** showed a strong absorption at 1800 cm^{-1} assignable to the carbonyl frequency of a four-membered monothioimide.[8] In the photolysis of the alkoxyacetyl derivatives **1d** and **1e**, a small amount of compound **5** and an intractable mixture were obtained, and the mercapto-β-lactams **2d** and **2e** or thioxo-β-lactams **3d** and **3e** were not isolated under the same conditions.



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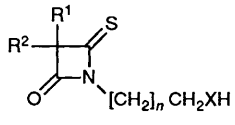

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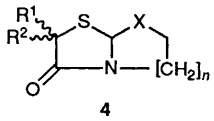

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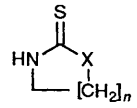
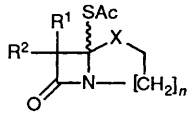


5; n = 2; X = S
6; n = 1; X = O
7; n = 2; X = O

$R^1R^2CHCO_2Me$

8



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Irradiation of compounds **1a** and **1b** at 40 °C gave similar results in the photolysis at 15 °C (Table 1). When compound **1c** was photolysed under the same conditions except that the reaction temperature was 40 °C, 8,8-diphenyl-5,7-dithia-1-azabicyclo[4.3.0]nonan-9-one **4c** was obtained as a main product (51% yield) accompanied by the Norrish Type-II cleavage product **5**. Photolysis of compound **1c** at 70 °C gave similar

Table 1 Photolysis of *N*-acyldithiocarbamates **1a–e** and *N*-acylthiocarbamates **1f–j**

Substrate 1	Solvent	Irradiation temp. (T/°C)	Irradiation time (t/h)	Yield (%) 4	Yield (%) 5, 6 or 7
a	Benzene	15	20	0	50[c]
	Benzene	40	20	0	48[c]
b	Benzene	15	20	0	62[c]
	Benzene	40	20	0	59[c]
c	Benzene	15	8	55[a]	10[c]
	Benzene	40	8	51	11[c]
	Benzene	70	8	49	12[c]
d	Benzene	15	8	0	15[c]
	Benzene	40	8	31 (70:30)[b]	16[c]
e	Benzene	15	8	0	23[c]
	Benzene	40	8	56 (77:23)[b]	26[c]
f	MeOH	15	8	0	99[d] (82)[f]
g	MeOH	15	8	0	91[d] (85)[f]
h	Benzene	15	24	0	62[d]
	MeOH	15	6	0	84[d] (78)[f]
i	Benzene	15	6	37 (70:30)[b]	30[e]
	Benzene	40	6	35 (70:30)[b]	32[e]
j	Benzene	15	6	46 (70:30)[b]	31[e]
	Benzene	40	6	45 (70:30)[b]	30[e]

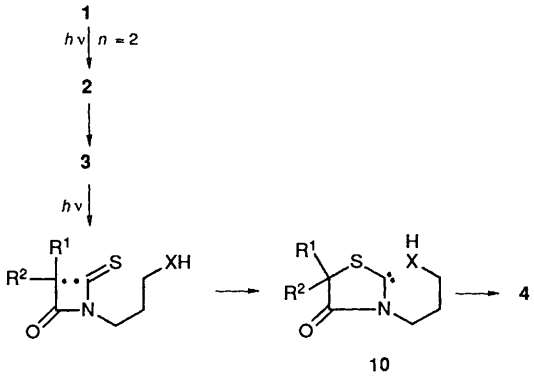
[a] Yield of **3c**. [b] The ratios of the stereoisomers. [c] Yields of **5**. [d] Yields of **6**. [e] Yields of **7**. [f] Yields of esters **8** determined by GLC.

results. For the other dithiocarbamates **1d** and **1e**, 8-alkoxy-5,7-dithia-1-azabicyclo[4.3.0]nonan-9-ones **4d** and **4e** were obtained. The bicyclic lactams **4d** and **4e** were isolated as mixtures of two stereoisomers. The ratios of the isomers are summarised in Table 1. However, it was impossible to determine their stereochemistry. The structure of the bicyclic lactams **4c–e** was determined on the basis of elemental analyses and spectral data. For example, the IR spectrum ($CHCl_3$) of the major isomer of compound **4e** exhibited an absorption at 1690 cm^{-1} due to the carbonyl group. The ^1H NMR spectrum showed two singlet signals, at δ_H 5.59 and 5.63, which were assignable to 8-H and 6-H, respectively. The ^{13}C NMR spectrum exhibited two doublet signals, at δ_C 61.3 (C-6) and 83.1 (C-8); the absence of the thiocarbonyl carbon was suggested.

Next, the photochemical reactions of *N*-acylthiocarbamates **1f–j** were investigated. When *N*-acyloxazolidine-2-thiones **1f–h** were irradiated in benzene, the starting materials were consumed very slowly and oxazolidine-2-thione **6** was obtained. Irradiation of a methanolic solution of compounds **1f–h** gave compound **6** and the corresponding methyl esters **8** efficiently. Photolysis of five-membered-ring thiocarbamates **1f–h** in benzene or methanol did not give Norrish Type-II cyclisation products but instead yielded cleavage products. It is reasonable to suggest that the esters are formed by trapping of ketenes with methanol, the ketenes being generated by the Norrish Type-II cleavage reaction. It was confirmed that *N*-acyloxazolidine-2-thiones **1f–h** were stable in methanol under these conditions; however, prolonged exposure or heating gave the same products almost quantitatively. The Norrish Type-II cleavage reactions of compounds **1f–h** in benzene were quite inefficient because the generated ketenes and oxazolidine-2-thiones reproduce the starting materials **1f–h**.

Irradiation of *N*-(alkoxyacetyl)tetrahydro-1,3-oxazine-2-thiones **1i** and **1j** at 15 °C gave 8-alkoxy-5-oxa-7-thia-1-azabicyclo[4.3.0]nonan-9-ones **4i** and **4j** as the main products accompanied by tetrahydro-1,3-oxazine-2-thione **7**. The structure of the bicyclic lactams **4i** and **4j** was determined on the basis of elemental analysis and spectral data.

For the formation of the bicyclic lactams **4**, we concluded that the thiacarbene **10** was generated by α-cleavage of the thioxo-β-lactam **3** (Scheme 1). When the thioxo-β-lactam **3c** was irradiated in benzene, compound **4c** was obtained in 70% yield as the sole product. Photolysis of compound **3c** in methanol also gave compound **4c**, and the methoxy derivative which was expected to be formed by intermolecular trapping of the thiacarbene was not detected at all. It is known that during photochemical reactions of azetidine-2,4-diones in methanol the substrates undergo ring expansion to produce 5-methoxyisoxazolidinones *via* oxacarbene intermediates.[9] In the photochemistry of thiocarbonyl compounds, Norrish Type-I reactivity (α-cleavage) is not common and has been reported only for strained thioketones and dithioesters.[10] This photoreaction described by us provides one of the very rare examples of α-cleavage reactivity in thiocarbonyl photochemistry.



Scheme 1

It is expected that protection of the mercapto group of the β-lactams **2** would allow their isolation since the β-lactams **2c–e** are stable at low temperature. When the dithiocarbamate **1c** was irradiated at 0 °C in toluene, and acetyl chloride and triethylamine were added to the reaction mixture at −20 °C, acetylthio-β-lactam **9c** was obtained as expected, in 66% yield. In the same manner, cepham analogues **9d** and **9e** were isolated whereas photolysis of compounds **1a** and **1b** under the same conditions gave only cleavage products (Table 2). The β-lactam **9d** was obtained as a mixture of two steroisomers (major : minor 90:10), and compound **9e** as a single stereoisomer. The structures for the β-lactams **9c–e** were determined on the basis of elemental analyses and spectral data. The IR spectrum of the β-lactam **9e** exhibited two strong frequencies for carbonyl

Table 2 Photolysis of substrates **1a–e** followed by acetylation

Substrate 1	Irradiation time (*t*/h)	Yield (%) 9	1a
a	20	0	52
b	20	0	60
c	8	66	10
d	8	57 (90:10)[a]	15
e	8	65 (100:0)[a]	23

[a] The ratios of the stereoisomers.

groups, at 1690 (acetyl carbonyl) and 1765 cm^{-1} (β-lactam carbonyl). The ^1H NMR spectrum showed a new singlet at δ_H 4.76 (1 H, s) assignable to 7-H. For the ^{13}C NMR spectrum the singlet peak due to the thiocarbonyl carbon was not observed, and new singlet and doublet peaks were exhibited at δ_C 77.3 (s, C-6) and 94.1 (d, C-7), respectively. It was too difficult to determine the stereochemistry of the β-lactams **9d** and **9e**.

Attempted trapping of the mercapto group of the β-lactam generated by photolysis of *N*-(alkoxyacetyl)tetrahydro-1,3-oxazine-2-thiones **1i** and **1j** with acetyl chloride was unsuccessful even on photolysis at −78 °C. Instead, the corresponding bicyclic lactams **4i** and **4j** were isolated. It seems that the ring-opening reaction (C–O bond cleavage) of the oxazine ring of mercaptooxacephams is much faster than the C–S bond cleavage of mercaptocephams, and the following photochemical process takes place to produce bicyclic lactams **4**.

In conclusion, photolysis of *N*-(diphenylacetyl)-, *N*-(methoxyacetyl), and *N*-(ethoxyacetyl)tetrahydro-1,3-thiazine-2-thiones followed by acetylation gave cepham analogues **9** in good yield. Photolysis at 40 °C gave 5,7-dithia-1-azabicyclo-[4.3.0]nonan-9-ones **4** *via* several steps including a Norrish Type-II cyclisation, ring opening of the mercapto-β-lactam, and α-cleavage of the resulting thioxo-β-lactam. Irradiation of *N*-acyloxazolidine-2-thiones led only to products of Norrish Type-II cleavage. The bicyclic lactams, 5-oxa-7-thia-1-azabicyclo[4.3.0]nonan-9-ones **2**, were obtained in the photoreaction of *N*-(alkoxyacetyl)tetrahydro-1,3-oxazine-2-thiones. With both types of five-membered-ring *N*-acyldithioacarbamate (thiazolidine-2-thiones)[5] and *N*-acylthiocarbamate (oxazolidine-2-thiones) only the Norrish Type-II cleavage took place on irradiation. It seems likely that steric strain prevents the cyclisation to give penem or oxapenem analogues. Furthermore, we conclude that diphenylacetyl and alkoxyacetyl groups were preferred in Norrish Type-II cyclisation because of the steric bulk or hydrogen bonding between the alkoxy group and the mercapto group in the intermediate.[3m] The present reaction provides not only a useful synthesis of bicyclic lactams (including cepham analogues) but also a very rare example of α-cleavage reactivity in thiocarbonyl compounds.

Experimental

M.p.s were measured on a Yanagimoto micro melting point apparatus and were uncorrected. IR spectra were measured on a JASCO IRA-1 spectrophotometer. The ^1H and the ^{13}C NMR spectra were recorded on an Hitachi R-600, a JEOL GX-270, or a GSX-500 spectrometer with tetramethylsilane as internal standard and $CDCl_3$ as solvent. The chemical shifts were recorded as δ-values with coupling constants (*J*) in Hz; UV spectra were measured on a Shimadzu UV-200A UV-VIS-NIR recording spectrophotometer. An Eikohsya 1 kW high-pressure mercury lamp was used as the irradiation source. Silica gel (Merck; Kieselgel 60, 230–400 mesh) was used for flash column chromatography.

Preparation of N-*Acyltetrahydro*-1,3-*thiazine*-2-*thiones* **1a–e**, *N-Acyloxazolidine*-2-*thiones* **1f–h** *and* N-*Acyltetrahydro*-1,3-*oxazine*-2-*thiones* **1i** *and* **1j**.—All *N*-acyldithiocarbamates **1a–e** and *N*-acylthiocarbamates **1i–j** were prepared by condensation of dithiocarbamates or thiocarbamates with the corresponding acid chloride. The preparation of *N*-acetyltetrahydro-1,3-thiazine-2-thione **1a** is given as an example. Triethylamine (600 mg, 6.0 mmol) was added dropwise to a solution of tetrahydro-1,3-thiazine-2-thione **5** (730 mg, 5.5 mmol) and acetyl chloride (470 mg, 6.0 mmol) in dry tetrahydrofuran (THF) (50 cm^3) at 0 °C under argon and the reaction mixture was then stirred for 2 h. The precipitated triethylamine hydrochloride was removed by filtration through a Celite (545) column, the filtrate was evaporated, and the residual mixture was subjected to chromatography on silica gel [eluent benzene–ethyl acetate 20:1)]. A yellow viscous oil, *N*-acetyltetrahydro-1,3-thiazine-2-thione **1a** (690 mg, 72%, was isolated and was purified by molecular distillation. Other *N*-acyldithiocarbamates and *N*-acylthiocarbamates were synthesized in the same manner. The crystalline compounds were recrystallised from chloroform–hexane.

N-*Acetyltetrahydro*-1,3-*thiazine*-2-*thione* **1a**. Yield 72%; b.p. 55-60 °C/1 mmHg; $\lambda_{max}(C_6H_{12})$/nm 270 (ε 9300 dm^3 mol cm^{-1}), 319 (11 200) and 440 (70); $\nu_{max}(CHCl_3)cm^{-1}$ 1690; δ_H 2.27 (2 H, quint, *J* 6.0, CH_2), 2.70 (3 H, s, Me), 3.07 (2 H, t, *J* 6.0, CH_2) and 4.01 (2 H, t, *J* 6.0, CH_2) (Found: C, 41.0; H, 5.15; N, 7.9. $C_6H_9NOS_2$ requires C, 41.11; H, 5.17; N, 7.99%).

N-*Isobutyryltetrahydro*-1,3-*thiazine*-2-*thione* **1b**. Yield 95%; b.p. 55–60 °C/1 mmHg; $\lambda_{max}(C_6H_{12})$/nm 270 (ε 8300), 319 (9200) and 420 (60); $\nu_{max}(CHCl_3)/cm^{-1}$ 1715; δ_H 1.22 (6 H, d, *J* 6.6, 2 × Me), 2.25 (2 H, quint, *J* 6.0, CH_2), 3.06 (2 H, t, *J* 6.0, CH_2) and 3.7–4.1 [3 H, m, C(=O)CH and CH_2] (Found: C, 47.0; H, 6.3; N, 6.8. $C_8H_{13}NOS_2$ requires C, 47.26; H, 6.44; N, 6.88%).

N-(*Diphenylacetyl*)*tetrahydro*-1,3-*thiazine*-2-*thione* **1c**. Yield 92%; m.p. 124–125 °C; $\lambda_{max}(C_6H_{12})$/nm 277 (ε 8600), 320 (6600) and 440 (30); $\nu_{max}(CHCl_3)/cm^{-1}$ 1715; δ_H 1.93 (2 H, quint, *J* 6.0, CH_2), 2.81 (2 H, t, *J* 6.0, CH_2), 3.67 (2 H, t, *J* 6.0, CH_2), 6.69 [1 H, s, C(=O)CH] and 7.38 (10 H, s, ArH) (Found: C, 66.05; H, 5.25; N, 4.2. $C_{18}H_{17}NOS_2$ requires C, 66.02; H, 5.23; N, 4.27%).

N-(*Methoxyacetyl*)*tetrahydro*-1,3-*thiazine*-2-*thione* **1d**. Yield 82%; b.p. 75–80 °C/1 mmHg; $\lambda_{max}(C_6H_{12})$/nm 269 (ε 12 900), 320 (14 400) and 420 (140); $\nu_{max}(CHCl_3)/cm^{-1}$ 1700; δ_H 2.27 (2 H, quint, *J* 6.0, CH_2), 3.06 (2 H, t, *J* 6.0, CH_2), 3.47 (3 H, s, Me), 4.02 (2 H, t, *J* 6.0, CH_2) and 4.77 [2 H, s, $C(=O)CH_2$] (Found: C, 40.65; H, 5.35; N, 6.8. $C_7H_{11}NO_2S_2$ requires C, 40.95; H, 5.40; N, 6.82%).

N-(*Ethoxyacetyl*)*tetrahydro*-1,3-*thiazine*-2-*thione* **1e**. Yield 86%; b.p. 75–80 °C/1 mmHg; $\lambda_{max}(C_6H_{12})$/nm 270 (ε 7500), 320 (8800) and 420 (110); $\nu_{max}(CHCl_3)/cm^{-1}$ 1700; δ_H 1.25 (3 H, t, *J* 7.0,, CH_2Me), 2.25 (2 H, quint, *J* 6.0, CH_2), 3.05 (2 H, t, *J* 6.0, CH_2), 3.62 (2 H, q, *J* 7.0 CH_2Me), 4.01 (2 H, t, *J* 6.0, CH_2) and 4.79 [2 H, s, $C(=O)CH_2$] (Found: C, 43.7; H, 5.95; N, 6.35. $C_8H_{13}NO_2S_2$ requires C, 43.81; H, 5.95; N, 6.35%).

N-*Isobutyryloxazolidine*-2-*thione* **1f**. Yield 90%; b.p. 45–50 °C/1 mmHg; $\lambda_{max}(C_6H_{12})$/nm 269 (ε 12 000) and 350 (60); $\nu_{max}(CHCl_3)/cm^{-1}$ 1690; δ_H 1.37 (6 H, d, *J* 6.6, 2 × Me) and 3.9–4.9 [5 H, m, C(=O)CH and 2 × CH_2] (Found: C, 48.4; H, 6.4; N, 8.05. $C_7H_{11}NO_2S$ requires C, 48.53; H, 6.40; N, 8.08%).

N-(*Phenylacetyl*)*oxazolidine*-2-*thione* **1g**. Yield 83%; b.p. 120–125 °C/1 mmHg; $\lambda_{max}(C_6H_{12})$/nm 267 (ε 13 000) and 345 (100); $\nu_{max}(CHCl_3)/cm^{-1}$ 1695; δ_H 3.9–4.9 (4 H, m, 2 × CH_2), 4.76 (2 H, s, CH_2Ph) and 7.1–7.5 (5 H, m, Ph) (Found: C, 59.6; H, 5.0; N, 6.3. $C_{11}H_{11}NO_2S$ requires C, 59.7; H, 5.01; N, 6.33%).

N-(*Methoxyacetyl*)*oxazolidine*-2-*thione* **1h**. Yield 88%; m.p. 64.5–66.0 °C; $\lambda_{max}(C_6H_{12})$/nm 276 (ε 8000) and 340 (30);

$\nu_{max}(CHCl_3)/cm^{-1}$ 1700; δ_H 3.51 (3 H, s, Me), 3.9–4.9 (4 H, m, 2 × CH_2) (Found: C, 41.1; H, 5.2; N, 8.0. $C_6H_9NO_3S$ requires C, 41.13; H, 5.17; N, 7.99%).

N-(*Methoxyacetyl*)*tetrahydro*-1,3-*oxazine*-2-*thione* **1i**. Yield 89%; b.p. 75–80 °C/1 mmHg; $\lambda_{max}(C_6H_{12})/nm$ 280 (ε 8500) and 370 (120); $\nu_{max}(CHCl_3)/cm^{-1}$ 1700; δ_H 2.0–2.5 (2 H, m, CH_2), 3.48 (3 H, s, Me), 3.6–4.0 (2 H, m, CH_2), 4.1–4.5 (2 H, m, CH_2) and 4.85 [2 H, s, C(=O)CH_2] (Found: C, 44.4; H, 5.85; N, 7.4. $C_7H_{11}NO_3S$ requires C, 44.43; H, 5.85; N, 7.40%).

N-(*Ethoxyacetyl*)*tetrahydro*-1,3-*oxazine*-2-*thione* **1j**. Yield 78%; b.p. 75–80 °C/1 mmHg; $\lambda_{max}(C_6H_{12})/nm$ 280 (ε 5400) and 370 (85;) $\nu_{max}(CHCl_3)/cm^{-1}$ 1700; δ_H 1.26 (3 H, t, *J* 7.0, CH_2*Me*), 2.24 (2 H, quint, *J* 7.0, CH_2), 3.4–4.0 (4 H, m, OCH_2 and CH_2Me), 4.37 (2 H, t, *J* 7.0, NCH_2) and 4.88 [2 H, s, C(=O)CH_2] (Found: C, 47.25; H, 6.5; N, 6.85. $C_8H_{13}NO_3S$ requires C, 47.27; H, 6.44; N, 6.89%).

General Procedure for the Photochemical Reaction of N-*Acyldithiocarbamates* **1a–e** *and N-Acylthiocarbamates* **1f–j**.—A solution of the carbamate (0.03 mol dm^{-3}) under argon was irradiated with a 1 kW high-pressure mercury lamp at the stated temperature (Table 1) until the starting material had disappeared as determined by TLC. After evaporation of the solvent, the residual mixture was subjected to chromatography on silica gel, with benzene–ethyl acetate as eluent. The crystalline products were recrystallised from chloroform–hexane, and the liquid photoproducts were purified by molecular distillation.

3,3-*Diphenyl*-1-(3′-*mercaptopropyl*)-2-*thioxoacetidin*-4-*one* **3c**. Yield 55%; $\nu_{max}(CHCl_3)/cm^{-1}$ 1800; δ_H 1.98 (2 H, quint, *J* 7.0, CH_2), 2.04 (2 H, t, *J* 7.0, CH_2), 3.73 (2 H, t, *J* 7.0, CH_2) and 7.0–7.3 (10 H, m, ArH); δ_C 21.7 (t, CH_2), 31.0 (t, CH_2), 39.4 (t, CH_2), 81.2 (s, C-3), 126.9 (d, Ph), 128.3 (d, Ph), 128.8 (d, Ph), 135.9 (s, Ph), 171.5 (s, C=O) and 208.9 (s, C=S); *m*/*z* (EI) 327 M^+).

8,8-*Diphenyl*-5,7-*dithia*-1-*azabicyclo*[4.3.0]*nonan*-9-*one* **4c**. Yield 51%; m.p. 136–137 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 1735; δ_H 1.9–2.2 (5 H, m, 3- and 4-H_2 and 2-H), 3.9–4.1 (1 H, m, 2-H), 5.40 (1 H, s, 6-H) and 7.1–7.6 (10 H, m, ArH); δ_C 30.6 (t, C-3), 40.3 (t, C-4), 41.9 (t, C-2), 71.1 (s, C-8), 74.8 (d, C-6), 126.7 (d, Ph), 127.3 (d, Ph), 127.4 (d, Ph), 128.1 (d, Ph), 128.7 (d, Ph), 136.3 (s, Ph), 140.3 (s, Ph) and 168.6 (s, C=O) (Found: C, 65.55; H, 5.25; N, 4.2. $C_{18}H_{17}NOS_2 \cdot 0.1H_2O$) requires C, 65.66; H, 5.26; N, 4.25%).

8-*Methoxy*-5,7-*dithia*-1-*azabicyclo*[4.3.0]*nonan*-9-*one* **4d**. This compound was obtained as a mixture of two stereoisomers. Their ratio was determined from the ^1H NMR spectrum. Yield 31% (major:minor 70:30); b.p. 75–80 °C/1 mmHg; $\nu_{max}(CHCl_3)/cm^{-1}$ 1690 (Found: C, 40.7; H, 5.35; N, 6.8. $C_7H_{11}NO_2S_2$ requires C, 40.95; H, 5.40; N, 6.82%).

Major isomer: δ_H 1.8–1.9 (1 H, m, 3-H), 1.9–2.0 (1 H, m, 3-H), 2.75–2.85 (1 H, m, 4-H), 2.9–3.1 (1 H, m, 2-H), 3.1–3.2 (1 H, m, 4-H), 3.48 (3 H, s, MeO), 4.4–4.6 (1 H, m, 2-H), 5.53 (1 H, s, 8-H), and 5.68 (1 H, s, 6-H); δ_C 25.1 (t, C-3), 30.4 (t, C-4), 44.1 (t, C-2), 55.9 (q, MeO), 60.4 (d, C-6), 84.5 (d, C-8) and 166.1 (s, C=O).

Minor isomer: δ_H 1.8–2.0 (2 H, m, 3-H_2), 2.75–2.85 (1 H, m, 4-H), 2.9–3.1 (1 H, m, 2-H), 3.1–3.2 (1 H, m, 4-H), 3.42 (3 H, s, MeO), 4.4–4.6 (1 H, m, 2-H), 5.63 (1 H, s, 8-H) and 5.76 (1 H, s, 6-H); δ_C 25.0 (t, C-3), 29.8 (t, C-4), 43.4 (t, C-2), 55.9 (q, MeO), 61.3 (d, C-6), 84.0 (d, C-8) and 166.6 (s, C=O).

8-*Ethoxy*-5,7-*dithia*-1-*azabicyclo*[4.3.0]*nonan*-9-*one* **4e**. This compound was obtained as a mixture of two stereoisomers. Their ratio was determined from the ^1H NMR spectrum. Yield 56% (major:minor 77:23); b.p. 75–80 °C/mmHg; $\nu_{max}(CHCl_3)/cm^{-1}$ 1690 (Found: C, 43.65; H, 5.95; N, 6.35. $C_8H_{13}NO_2S_2$ requires C, 43.81; H, 5.97; N, 6.38%).

Major isomer: δ_H 1.29 (3 H, t, *J* 6.9, CH_2*Me*), 1.8–2.0 (2 H, m, 3-H_2), 2.75–2.85 (1 H, m, 4-H), 2.9–3.1 (1 H, m, 2-H), 3.1–3.2 (1 H, m, 4-H), 3.6–3.8 (2 H, m, CH_2Me), 4.4–4.5 (1 H, m, 2-H), 5.59 (1 H, s, 8-H) and 5.63 (1 H, s, 6-H); δ_C 14.7 (q, CH_2*Me*), 25.1 (t, C-3), 30.5 (t, C-4), 44.1 (t, C-2), 61.3 (d, C-6), 64.5 (t, CH_2Me), 83.1 (d, C-8) and 166.3 (s, C=O).

Minor isomer: δ_H 1.26 (3 H, t, *J* 6.9, CH_2*Me*), 1.8–2.0 (2 H, m, 3-H), 2.75–2.85 (1 H, m, 4-H), 2.9–3.1 (1 H, m, 2-H), 3.1–3.2 (1 H, m, 4-H), 3.6–3.8 (2 H, m, CH_2Me), 4.4–4.5 (1 H, m, 2-H), 5.63 (1 H, s, 8-H) and 5.76 (1 H, s, 6-H); δ_C 14.7 (q, CH_2*Me*), 25.0 (t, C-3), 29.8 (t, C-4), 43.4 (t, C-2), 60.5 (d, C-6), 65.2 (t, CH_2Me), 82.7 (d, C-8) and 166.9 (s, C=O).

8-*Methoxy*-5-*oxa*-7-thia-1-*azabicyclo*[4.3.0]*nonan*-9-*one* **4i**. This compound was obtained as a mixture of two stereoisomers. Their ratio was determined from the ^1H NMR spectrum. Yield 37% (major:minor 70:30); b.p. 75–80 °C/1 mmHg; $\nu_{max}(CHCl_3)/cm^{-1}$ 1690 (Found: C, 44.2; H, 5.8; N, 7.4. $C_7H_{11}NO_3S_2$ requires C, 44.43; H, 5.85; N, 7.40%).

Major isomer: δ_H 1.55–1.65 (1 H, m, 3-H), 1.8–2.0 (1 H, m, 3-H), 3.05–3.1 (1 H, m, 2-H), 3.45 (3 H, s, MeO), 3.8–3.9 (1 H, m, 4-H), 4.2–4.3 (1 H, m, 4-H), 4.35–4.45 (1 H, m, 2-H), 5.54 (1 H, s, 8-H) and 5.84 (1 H, s, 6-H); δ_C 24.5 (t, C-3), 41.8 (t, C-2), 54.9 (q, MeO), 68.5 (t, C-4), 83.9 (d, C-8), 89.2 (d, C-6) and 166.6 (s, C=O).

Minor isomer: δ_H 1.55–1.65 (1 H, m, 3-H), 1.8–2.0 (1 H, m, 3-H), 3.05–3.1 (1 H, m, 2-H), 3.41 (3 H, s, MeO), 3.8–3.9 (1 H, m, 4-H), 4.2–4.3 (1 H, m, 4-H), 4.35–4.45 (1 H, m, 2-H), 5.64 (1 H, s, 8-H) and 6.03 (1 H, s, 6-H); δ_C 23.9 (t, C-3), 40.9 (t, C-2), 55.8 (q, MeO), 68.1 (t, C-4), 84.4 (d, C-8), 89.2 (d, C-6) and 166.5 (s, C=O).

8-*Ethoxy*-5-*oxa*-7-*thia*-1-*azabicyclo*[4.3.0]*nonan*-9-*one* **4j**. This compound was obtained as a mixture of two stereoisomers. Their ratio was determined from the ^1H NMR spectrum. Yield 46% (major:minor 70:30); b.p. 75–80 °C/1 mmHg; $\nu_{max}(CHCl_3)/cm^{-1}$ 1690 (Found: C, 47.0; H, 6.4; N, 6.85. $C_8H_{13}NO_3S$ requires C, 47.27; H, 6.44; N, 6.89%).

Major isomer: δ_H 1.27 (3 H, t, *J* 7.0, CH_2*Me*), 1.55–1.65 (1 H, m, 3-H), 1.8–2.0 (1 H, m, 3-H), 3.1–3.2 (1 H, m, 2-H), 3.65–3.85 (2 H, m, CH_2Me), 3.85–3.95 (1 H, m, 4-H), 4.2–4.3 (1 H, m, 4-H), 4.35–4.45 (1 H, m, 2-H), 5.57 (1 H, s, 8-H) and 5.83 (1 H, s, 6-H); δ_C 14.7 (q, CH_2*Me*), 24.5 (t, C-3), 41.8 (t, C-2), 63.7 (CH_2Me), 68.4 (t, C-4), 82.6 (d, C-8), 89.2 (d, C-6) and 166.8 (s, C=O).

Minor isomer: δ_H 1.26 (3 H, t, *J* 7.0, CH_2*Me*), 1.55–1.65 (1 H, m, 3-H), 1.8–2.0 (1 H, m, 3-H), 3.1–3.2 (1 H, m, 2-H), 3.65–3.85 (2 H, m, CH_2Me), 3.85–3.95 (1 H, m, 4-H), 4.2–4.3 (1 H, m, 4-H), 4.35–4.45 (1 H, m, 2-H), 5.65 (1 H, s, 8-H) and 6.02 (1 H, s, 6-H); δ_C 14.7 (q, CH_2*Me*), 23.9 (t, C-3), 40.8 (t, C-2), 65.1 (CH_2Me), 68.1 (t, C-4), 83.2 (d, C-8), 89.3 (d, C-6) and 166.8 (s, C=O).

General Procedure for the Photochemical Reaction of N-*Acyldithiocarbamates* **1a–e** *at* 0 °C *followed by Acetylation*.—A toluene solution of a dithiocarbamate **1a–e** was irradiated in the presence of molecular sieves (4 Å) at 0 °C until the starting material had disappeared. Then to the photolysate at −20 °C were added acetyl chloride (3 mol equiv.) and triethylamine (3 mol equiv.) and the mixture was stored overnight at 0 °C. Precipitated triethylamine hydrochloride was filtered off and the filtrate was concentrated under reduced pressure. The residual mixture was chromatographed on silica gel. The crystalline products were recrystallised from chloroform–hexane.

6-*Acetylthio*-7,7-*diphenyl*-5-*thia*-1-*azabicyclo*[4.2.0]*octan*-8-*one* **9**. Yield 65%; m.p. 161–162 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 1755 and 1690; δ_H 1.5–2.0 (2 H, m, 3-H_2), 1.96 (3 H, s, Ac), 2.6–3.4 (3 H, m, 2-H and 4-H_2), 3.9–4.2 (1 H, m, 2-H) and 7.0–7.6 (10 H, m, ArH); δ_C 23.6 (t, C-3), 28.5 (t, C-4), 30.4 [q, MeC(=O)], 37.3 (t, C-2), 81.1 (s, C-6 or -7), 81.7 (s, C-7 or -6), 127.6 (d, Ph),

127.8 (d, Ph), 128.3 (d, Ph), 128.7 (d, Ph), 136.5 (s, Ph), 137.5 (s, Ph), 165.0 (s, NC=O) and 192.8 (s, SC=O) (Found: C, 64.85; H, 5.2; N, 3.75. $C_{20}H_{19}NO_2S_2$ requires C, 65.01; H, 5.18; N, 3.80%).

6-Acetylthio-7-methoxy-5-thia-1-azabicyclo[4.2.0]octan-8-one **9**. This material was obtained as a mixture of two stereoisomers. Their ratio was determined from the ^1H NMR spectrum. Yield 57% (major:minor 90:10); $\nu_{max}(CHCl_3)/cm^{-1}$ 1765 and 1695.

Major isomer: δ_H 1.6–1.8 (1 H, m, 3-H), 1.8–2.0 (1 H, m, 3-H), 2.35 (3 H, s, Ac), 2.75–2.9 (1 H, m, 4-H), 2.9–3.0 (1 H, m, 2-H), 3.2–3.3 (1 H, m, 4-H), 3.55 (3 H, s, OMe), 3.9–4.0 (1 H, m, 2-H) and 4.68 (1 H, s, 7-H); δ_C 23.3 (t, C-3), 27.2 (t, C-4), 30.9 [q, MeC(=O)], 37.3 (t, C-2), 60.9 (q, MeO), 77.2 (s, C-6), 94.6 (d, C-7), 161.7 (s, NC=O) and 193.6 (s, SC=O).

Minor isomer: δ_H 1.6–1.8 (1 H, m, 3-H), 1.8–2.0 (1 H, m, 3-H), 2.34 (3 H, s, Ac), 2.75–2.9 (1 H, m, 4-H), 2.9–3.0 (1 H, m, 2-H), 3.2–3.3 (1 H, m, 4-H), 3.67 (3 H, s, OMe), 3.9–4.0 (1 H, m, 2-H) and 4.97 (1 H, s, 7-H); δ_C 23.7 (t, C-3), 25.6 (t, C-4), 30.8 [q, MeC(=O)], 36.4 (t, C-2), 60.5 (q, MeO), 75.6 (s, C-6), 95.4 (d, C-7), 162.9 (s, NC=O) and 194.3 (s, SC=O).

6-*Acetylthio*-7-*ethoxy*-5-*thia*-1-*azabicyclo*[4.2.0]*octan*-8-*one* **9e**. Yield 65%; m.p. 83–84 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 1765 and 1695; δ_H 1.22 (3 H, t, *J* 6.9, CH_2Me), 1.6–2.1 (2 H, m, 3-H_2), 2.34 (3 H, s, Ac), 2.7–3.4 (3 H, m, 2-H and 4-H_2), 3.72 (2 H, q, *J* 6.9, CH_2Me), 3.8–4.1 (1 H, m, 2-H) and 4.76 (1 H, s, 7-H); δ_C 15.1 (q, CH_2Me), 23.4 (t, C-3), 27.3 (t, C-4), 30.9 [q, MeC(=O)], 37.3 (t, C-2), 69.1 (t, CH_2Me), 77.3 (s, C-6), 94.1 (d, C-7), 162.0 (s, NC=O) and 193.5 (s, SC=O) (Found: C, 46.0; H, 5.85; N, 5.4. $C_{10}H_{15}NO_3S_2$ requires C, 45.95; H, 5.78; N, 5.35%).

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