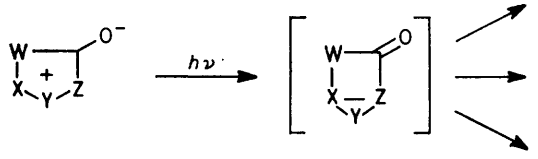
Photochemical Transformations. Part 36.† Synthesis and Photolytic Ring Contraction of Mesoionic 2-Alkylthiothiazol-4-ones; a New Route to β-Lactams

By **Derek H. R. Barton,* Ernst Buschmann, Johannes Haüsler, Cedric W. Holzapfel, Tuvia Sheradsky, and Derryck A. Taylor,** Chemistry Department, Imperial College, London SW7 2AY

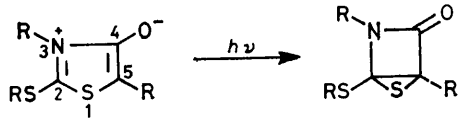
A number of mesoionic 2-alkylthiothiazol-4-ones (6) were prepared by alkylation of rhodanines or by the reaction of α-bromomalonates with dithiocarbamates. The photolysis of these mesoionic compounds proceeds *via* a highly strained, bicyclic, ring contraction product which rearranges to a thiazolin-2-one (14), loses sulphur, affording a β-aminoacrylate (11), or is trapped by methanol giving methoxy-β-lactams (12) and (13).

THE photochemistry of certain classes of five-membered mesoionic heterocycle has been generally rationalized in terms of a mechanism which involves a transient four-membered carbonyl-containing ring [1,2] formed by photolytically induced ring contraction (Scheme 1). This process presents an attractive possibility for β-lactam synthesis from mesoionic thiazolones, imidazolones, or oxazolones.

New syntheses of β-lactams are always designed with a view to their application in the synthesis of penicillins and cephalosporins. This requires a polyfunctional precursor. Accordingly the known 2-alkylthiothiazolium-4-olates [3] (Scheme 2), having the alkylthio-



SCHEME 1

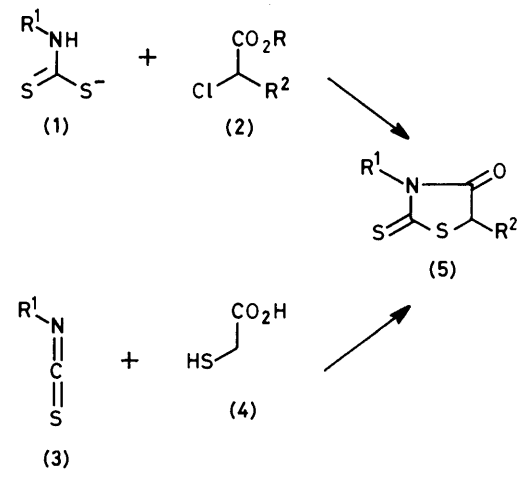


SCHEME 2

group in the desired position, were considered to be good models for a photolytically induced cephalosporin or penicillin synthesis.

The appropriate substituent on C-5 of the mesoion would be an amido-group. However, all attempts up to now to prepare amido-substituted mesoionic thiazolones of type (6) have failed.

Since the conversion of carboxy-β-lactams into amino-β-lactams has been described,[4] another useful substituent in position 5 would be a carboxy-group. We were, in fact, able to prepare such 5-carboxy-substituted mesoions. Mesoionic 2-alkylthiothiazol-4-ones of type (6) can be prepared by alkylation of rhodanines (2-thioxothiazolidin-4-ones).[3] The required rhodanines (5) are readily synthesized by standard procedures.[5]



(5a)* R^1=H, R^2=H
(5b)† R^1=H, R^2=CO_2Et
(5c) R^1=Me, R^2=CO_2Et
(5d)* R^1=Me, R^2=Ph
(5e) R^1=$CH_2 \cdot CO_2Et$, R^2=CO_2Et
(5f)* R^1=$CH_2 \cdot CH{:}CH_2$, R^2=H
(5g) R^1=$CH_2 \cdot CH(OMe)_2$, R^2=H

SCHEME 3 * Ref. 4. † J. J. D'Amico and M. W. Harman, *J. Amer. Chem. Soc.*, 1955, **77**, 476

Alkylation of dithiocarbamate anions (1) with α-chloro-carboxylic esters (2), or addition of thioglycolic acid (4) to alkyl isothiocyanates (3) gave the desired rhodanines (5) (Scheme 3).

The 5-acylrhodanines (5h—k) were conveniently prepared by acylation of the rhodanines (5a, f, and g)

† Part 35, D. H. R. Barton and L. A. Hulshof, preceding paper.

[1] C. H. Krauch, J. Kuhls, and H. J. Piek, *Tetrahedron Letters*, 1966, 4043; H. Kato, M. Kawamura, T. Shiba, and M. Ohta, *Chem. Comm.*, 1970, 959; H. Kato, T. Shiba, H. Yoshida, and S. Fujimori, *ibid.*, p. 1591; C. S. Angadiyavar, and M. V. George, *J. Org. Chem.*, 1971, **36**, 1589; R. Moriarty, R. Mukherjee, O. L. Chapman, and D. Eckroth, *Tetrahedron Letters*, 1971, 397; H. Gotthardt, *Chem. Ber.*, 1972, **105**, 188; A. Holm, N. Harrit, K. Beechgaard, O. Buchardt, and S. E. Harnung, *J.C.S. Chem. Comm.*, 1972, 1125; I. R. Dunkin, M. Poliahoff, J. T. Turner, N. Harrit, and A. Holm, *Tetrahedron Letters*, 1976, 873; H. Kato, *J.C.S. Perkin I*, 1976, 863.

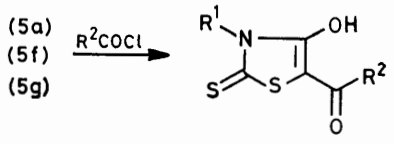
[2] O. Buchardt, J. Domanus, N. Harrit, A. Holm, G. Isaksson, and J. Sandstrom, *J.C.S. Chem. Comm.*, 1974, 376.

[3] J. Sandstrom, *Arkiv Kemi*, 1955, **9**, 127; S. Abrahamsson, A. Westerdahl, G. Isaksson, and J. Sandstrom, *Acta Chem. Scand.*, 1967, **21**, 442.

[4] A. K. Bose, J. Kapur, B. Dayal, and M. S. Manhas, *Tetrahedron Letters*, 1973, 3797; D. H. Brunwin, G. Lowe, and J. Parker, *Chem. Comm.*, 1971, 865.

[5] F. C. Brown, *Chem. Rev.*, 1961, **61**, 463, and references therein.

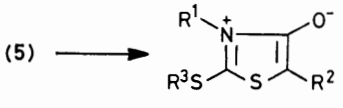
with acid chlorides in the presence of a base (Scheme 4). We envisaged that these 5-carbonyl compounds should be convertible into the appropriate amide derivatives by rearrangement of the derived oximes. In contrast to the rhodanines (5a—g), the ethoxalyl- and phenylacetyl-rhodanines (5h—k) exist as enol tautomers (u.v. and n.m.r. spectra).



(5h) R^1=H, R^2=$PhCH_2$
(5i) R^1=$CH_2{\cdot}CH{:}CH_2$, R^2=CO_2Et
(5k) R^1=$CH_2{\cdot}CH(OMe)_2$, R^2=CO_2Et

SCHEME 4

Alkylation of the anions derived from 3,5-disubstituted rhodanines (5) gave 2-alkylthiothiazolium-4-olates (6) in good yields (Scheme 5). The rhodanines (5b) and



(6)

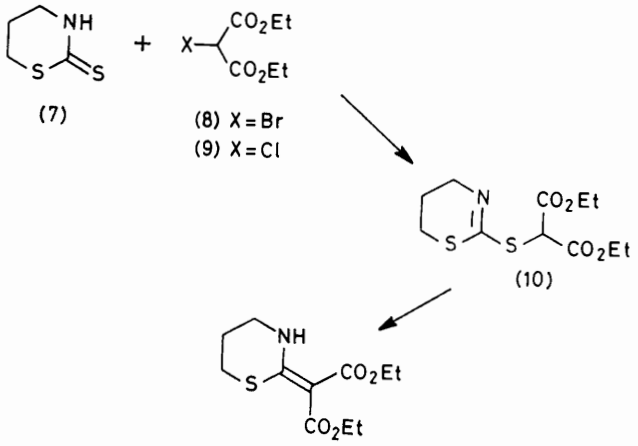
(6a)* R^1=R^3=Me, R^2=Ph
(6b) R^1=R^3=Me, R^2=CO_2Et
(6c) R^1=R^3=$CH_2{\cdot}CO_2Et$, R^2=CO_2Et
(6d) R^1=$CH_2{\cdot}CH{:}CH_2$, R^2=$CO{\cdot}CO_2Et$, R^3=Me
(6e) R^1=$CH_2{\cdot}CH(OMe)_2$, R^2=$CO{\cdot}CO_2Et$, R^3=Me
(6f) R^1R^3=$[CH_2]_3$, R^2=CO_2Et
(6g) R^1R^3=$[CH_2]_3$, R^2=$CO{\cdot}CH_2Ph$
(6h) R^1R^3=$[CH_2]_4$, R^2=CO_2Et
(6i) R^1=Me, R^2=CO_2Et, R^3=Et
(6k) R^1=$CH_2{\cdot}CO_2Et$, R^2=CO_2Et, R^3=Me
(6l) R^1=$CH_2{\cdot}CH{:}CH_2$, R^2=$CO{\cdot}CO_2Et$, R^3=Bu
(6m) R^1=$CH_2{\cdot}CH{:}CH_2$, R^2=CO_2Et, R^3=Bu
(6n) R^1=Me, R^2=CO_2Et, R^3=$HO{\cdot}CH_2{\cdot}CH_2$

* Ref. 2

SCHEME 5

(5h) reacted with 1,3-dibromopropane, 1,4-dibromobutane, or 2 equiv. of methyl iodide in the presence of base giving the mesoionic thiazolones (6b) and (6f—h).

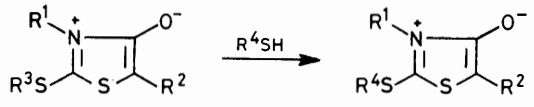
Alkylation of dithiocarbamates of type (7) with diethyl bromomalonate (8) was found to be an alternative route to some mesoions of type (6) (Scheme 6). Bromomalonate, however, is known to react with thiolates giving disulphides and tetraethyl ethane-1,1,2,2-tetracarboxylate.[6] This redox reaction resulted in low yields of the mesoions (6). Alkylation of the dithiocarbamate (7) with diethyl chloromalonate (9) in the presence of base led, *via* the intermediate (10), to the Eschenmoser sulphur elimination[7] product (11a) in 35% yield (Scheme 6). Only traces of the mesoion (6f) were formed in this case.



(7) (8) X=Br (9) X=Cl (10) (11a)

SCHEME 6

The alkylthio-substituent of the mesoions (6) can easily be exchanged by addition of an excess of thiol (Scheme 7).

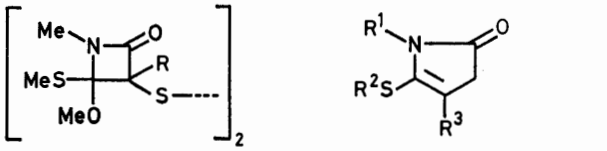


(6l) R^1=$CH_2{\cdot}CH(OMe)_2$, R^2=CO_2Et, R^4=Bu
(6m) R^1=$CH_2{\cdot}CO_2Et$, R^2=CO_2Et, R^4=Bu
(6n) R^1=Me, R^2=CO_2Et, R^4=$[CH_2]_2{\cdot}OH$

SCHEME 7

This offers the possibility of introducing alkylthio-substituents which can not be incorporated by other synthetic routes.

(12a) (12b)



(13a) R=Ph
(13b) R=CO_2Et

(14a) R^1=R^2=Me, R^3=Ph
(14b) R^1=R^2=Me, R^3=CO_2Et
(14c) R^1R^2=$[CH_2]_3$, R^3=CO_2Et

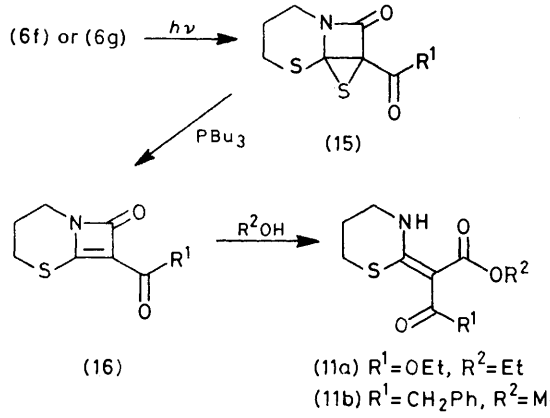
Photolysis of the mesoions (6a and f) was carried out in methanolic solution. Intense i.r. absorptions at 1 760 and 1 780 cm^{-1}, respectively, suggested β-lactam formation. T.l.c. and n.m.r. spectra however showed that the

[6] P. Weygand and H. G. Peine, *Rev. Chim.* (*Acad. R. P. R.*), 1962, **7**, 1379, (*Chem. Abs.*, 1964, **61**, 4208).

[7] M. Roth, P. Dubs, E. Gotschi, and A. Eschenmoser, *Helv. Chim. Acta*, 1971, **54**, 710.

crude material was a complex mixture. Treatment of the crude product with nickel boride or tributylphosphine, followed by chromatographic work-up, afforded the desulphurised β-lactams (12a and b) in 19 and 9% yield, respectively. The products were mixtures of stereoisomers which equilibrated so easily that they could not be separated.

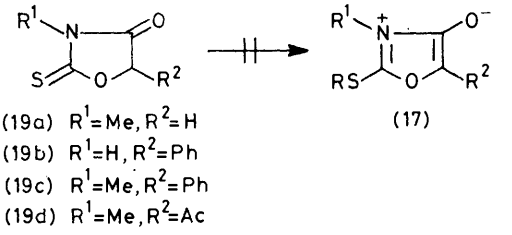
Addition of alkyl iodides to the methanolic solutions of the mesoions before photolysis afforded a cleaner photoreaction. This might have resulted from a heavy atom effect.[8] T.l.c. and n.m.r. spectra of the crude photolysate of the mesoions (6a and b) showed that a smaller number of products were formed. β-Lactams, for which we suggest the disulphide structures (13a and b), were



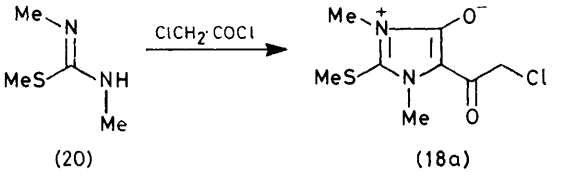
SCHEME 8

isolated in 25 and 21% yield, respectively. In addition to β-lactam (13b) the isomeric thiazol-2-one (14b) was isolated in 14% yield. Photolysis of the mesoion (6a) in ethanol has been reported to give the analogous thiazolone (14a).[2] The mesoion (6f) on irradiation in dioxan gave (14c) *via* a similar photoisomerisation.

Under identical conditions of photolysis the bicyclic mesoions (6f and g) reacted much more slowly than the mesoions (6a and b) to give lower yields of β-lactams (i.r. evidence). The additional ring obviously increases the strain in the β-lactam–thiiran intermediate of type (15) with consequent ready loss of sulphur. The resulting unsaturated lactams of type (16) are known to undergo



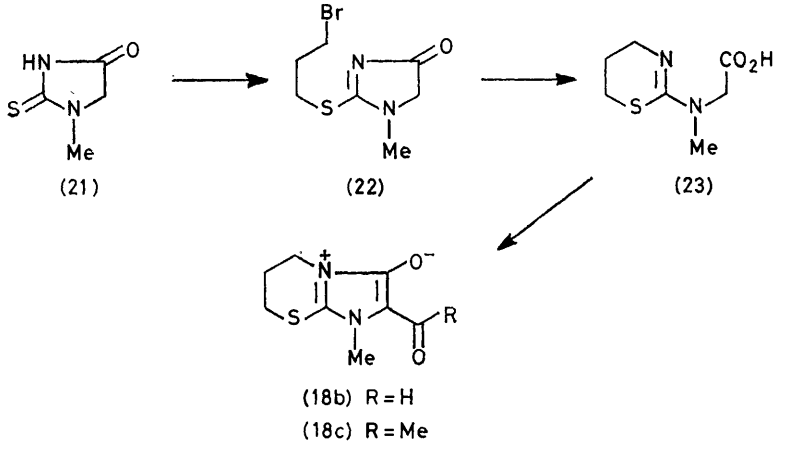
SCHEME 9



SCHEME 10

ring opening in methanolic solution affording β-aminoacrylates.[9] The aminoacrylates (11a and b) are formed in good yields from the mesoions (6f and g), respectively, on photolysis in the presence of phosphines (Scheme 8).

Our results strongly suggest the formation of a four-membered, bicyclic, ring-contraction product of type (15) on photolysis of mesoionic thiazol-4-ones of type (6). Thiirans of type (15) rearrange to thiazolin-2-ones of type (14), lose sulphur affording β-aminoacrylates of type (11), or are trapped by methanol yielding β-lactams of types (12) and (13).



SCHEME 11

The photolytically induced ring contraction of mesoionic thiazolones, producing methoxy-substituted β-lactams, suggests a synthesis of 6-alkoxycephalosporins. However the inaccessibility of 5-amino-substituted mesoions, the slowness of the photolysis of the bicyclic

[8] P. O. Cowan and R. L. E. Drisho, *J. Amer. Chem. Soc.*, 1970, **92**, 6281.

[9] G. Kretschmer, and R. N. Warrener, *Tetrahedron Letters*, 1975, 1335.

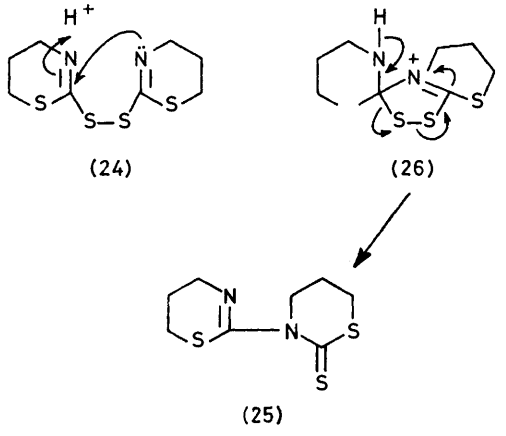
chromophore of type (6), and the fact that the yields of isolated β-lactams are low make this process not especially promising as a route to penicillins, cephalosporins, or their nuclear analogues.

In connection with our investigation of the photochemistry of mesoionic thiazolones we tried to prepare mesoionic oxazolones (17) and imidazolones (18).

Alkylation of the ozazolones (19), which were prepared by standard procedures, did not afford any mesoions of type (17) (Scheme 9).

The mesoionic imidazolone (18a) was obtained from *NN'S*-trimethylisothiourea (20) and chloroacetyl chloride (Scheme 10). Alkylation of 1-methyl-2-thiohydantoin (21) with 1,3-dibromopropane gave the *S*-alkyl derivative (22) as a major product, which was transformed into the amino-acid (23) and subsequently into the mesoions (18b and c) (Scheme 11). Photolysis of the mesoionic imidazolones (18) gave no β-lactam.

From the reaction of the dithiocarbamate (7) with diethyl bromomalonate (8) a product was isolated with the properties expected for the disulphide (24) (see discussion above). In chloroform in the presence of a trace of trifluoroacetic acid this product underwent an interesting rearrangement with sulphur elimination to give the derivative (25). This reaction may well proceed through an intermediate of type (26) (Scheme 12). The disulphide (24) was synthesised by oxidation of the dithiocarbamate (7) with iodine. Treatment in chloroform with a trace of acid gave (25) in 61% yield.



(24) (26) (25)

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were recorded for solutions in chloroform with a Perkin-Elmer 257 spectrophotometer. U.v. spectra were determined for solutions in ethanol with a Unicam SP 800 spectrophotometer. ^{1}H N.m.r. spectra were taken for solutions in $CDCl_3$ (unless stated otherwise) (Me_4Si as internal standard) with a Varian T60 spectrometer. Mass spectra were obtained with an A.E.I. MS9 spectrometer operating at 70 eV. T.l.c. and p.l.c. were carried out on Merck Kieselgel GF_{254} plates (0.2 mm and 1 mm layers, respectively). Anhydrous sodium sulphate was used for drying solutions. Photolysis was carried out with a 125 W high-pressure mercury lamp in a water-cooled Pyrex vessel. Light petroleum refers to the fraction of b.p. 40—60 °C.

Ethyl 3-Methyl-4-oxo-2-thioxothiazolidine-5-carboxylate (5c).—Methylammonium *N*-methyldithiocarbamate (27.6 g) in dry dimethylformamide (50 ml) was added to a cooled solution of ethyl chloromalonate (38.8 g) in the same solvent (100 ml). After 15 h water (400 ml) was added and the product extracted with ether. The solution was washed with water and repeatedly with saturated aqueous sodium hydrogen carbonate. After acidification of the hydrogen carbonate extract the precipitate was dissolved in ether (100 ml) and the solution dried, evaporated, and distilled, affording the *rhodanine* (5c) (12 g, 47%) as a yellow oil, $\nu_{max.}$ 1 733 cm^{-1}, $\lambda_{max.}$ 256 (ε 10 500), 292 (8 100), and 360 nm (5 800), δ 1.30 (3 H, t, *J* 8 Hz, $CH_2{\cdot}CH_3$), 3.19 (3 H, s, NCH_3), 4.26 (2 H, q, *J* 8 Hz, $CH_2{\cdot}CH_3$), and 4.87 (1 H, s, CHS), *m/e* 219 (M^+) and 74 (100%) (Found: C, 38.2; H, 4.2; N, 6.4; S, 29.3. $C_7H_9NO_3S_2$ requires C, 38.4; H, 4.1; N, 6.4; S, 29.2%).

Ethyl 5-Ethoxycarbonyl-4-oxo-2-thioxothiazolidin-3-ylacetate (5e).—To ethyl aminoacetate hydrochloride (14 g) in ethanol (250 ml) were added *N*-ethyldi-isopropylamine (26 g) and carbon disulphide (7.6 g). After 30 min stirring, diethyl chloromalonate (19.4 g) was added. After 15 h, work-up as above gave the *rhodanine* (5e) (5.1 g, 18%) as a yellow oil, $\nu_{max.}$ 1 733 cm^{-1}, $\lambda_{max.}$ 254 (ε 10 130), 291 (7 410) and 362 nm (7 170), δ 1.27 (3 H, t, *J* 8 Hz, CH_3), 1.30 (3 H, t, *J* 8 Hz, CH_3), 4.17 (2 H, q, *J* 8 Hz, OCH_2), 4.26 (2 H, q, *J* 8 Hz, OCH_2), 4.65 (2 H, s, NCH_2), and 4.92 (1 H, s, CHS), *m/e* 291 (M^+) and 145 (100%) (Found: C, 41.0; H, 4.5; N, 4.8; S, 22.0. $C_{10}H_{13}NO_5S_2$ requires C, 41.2; H, 4.5; N, 4.8; S, 22.0%).

3-(2,2-Dimethoxyethyl)-2-thioxothiazolidin-4-one (5g).—To 2,2-dimethoxyethylamine (2.1 g) in methanol (20 ml) were added carbon disulphide (1.2 ml) and triethylamine (2.02 g). After 30 min, methyl bromoacetate (3.2 g) was added. The solution was heated to reflux for 5 min and evaporated. Addition of ice and water to the residue precipitated a yellow oil (4.27 g, 35%) which was distilled (120 °C; high vacuum) to give the *rhodanine* (5g) as prisms, m.p. 44—46 °C, $\nu_{max.}$ 1 740 cm^{-1}, $\lambda_{max.}$ 258 (ε 11 340) and 294 nm (13 340), δ 3.33 (6 H, s, OCH_3), 4.00 (2 H, s, SCH_2), 4.05 (2 H, d, *J* 5 Hz, NCH_2), and 4.80 (1 H, t, *J* 5 Hz, CHO_2), *m/e* 221 (M^+) and 190 (100%) (Found: C, 38.0; H, 4.8; N, 6.2. $C_7H_{11}NO_3S_2$ requires C, 38.0; H, 5.0; N, 6.3%).

5-Phenylacetyl-2-thioxothiazolidin-4-one (5h).—To a stirred solution of the rhodanine (5a) (6.65 g, 50 mmol) in dry 1,2-dimethoxyethane (70 ml) under nitrogen at 0 °C was added sodium hydride (1.44 g, 50 mmol; 80% dispersion in oil) in small portions over 30 min. Phenylacetyl chloride (7.23 g, 50 mmol), was added to the slurry over 15 min and the mixture stirred under nitrogen for 30 min at 0 °C. Addition of sodium hydride (50 mmol) and phenylacetyl chloride was repeated twice. The mixture was stirred at 0 °C under nitrogen for 12 h and carefully added to sodium ethoxide (1.02 g, 0.15 mmol) in ethanol (100 ml) at 0 °C. After 30 min the mixture was diluted with water (200 ml), acidified with 6N-hydrochloric acid, and extracted with chloroform (3 × 150 ml). The extract was washed with water (2 × 70 ml), dried, and evaporated *in vacuo*. Crystallisation of the residue from chloroform–benzene gave crude starting material (3.66 g). Chromatography of the mother liquor on silica (200 g) gave starting material (eluant ethyl acetate–benzene, 1 : 10) and *5-phenylacetylrhodanine* (5h) (eluant

ethyl acetate–benzene, 1 : 2) (3.12 g, 25%), m.p. 127—128° (from chloroform), $\nu_{max.}$ (Nujol) 3 140, 2 500—3 300br, 1 670, and 1 595 cm^{-1}, $\lambda_{max.}$ 265 (ε 11 100) and 357 nm (30 500), δ 3.70 (2 H, s, CH_2), 7.37br (5 H, Ph), 10.2br (1 H, NH), and 11.0br (1 H, OH), *m/e* 251 (M^+) and 91 (100%)(Found: C, 52.5; H, 3.6; N, 5.5. $C_{11}H_9NO_2S_2$ requires C, 52.6; H, 3.6; N, 5.6%).

Ethyl 3-*Allyl*-4-*oxo*-2-*thioxothiazolidin*-5-*ylglyoxylate* (5i). —To the rhodanine (5f) (3.46 g) in anhydrous dichloromethane (20 ml) were added pyridine (2.37 g), 4-dimethylaminopyridine (122 mg), and ethoxalyl chloride (3.47 ml). After 30 h more solvent (20 ml) was added. The solution was dried and evaporated, and the residue taken up with ether. After 15 h a small amount of solid was filtered off. The solution was extracted repeatedly with saturated aqueous sodium hydrogen carbonate. After acidification with 10N-hydrochloric acid the precipitate was removed and dissolved in chloroform, and the solution dried and evaporated. Trituration with ether–light petroleum and crystallization from ether–light petroleum gave the *rhodanine* (5i) (450 mg, 8%) as yellow needles, m.p. 91—92°, $\nu_{max.}$ 1 740, 1 710, 1 665, and 1 600 cm^{-1}, $\lambda_{max.}$ 273 (ε 12 800) and 372 nm (21 400), δ 1.40 (3 H, t, *J* 7 Hz, O·CH_2·CH_3), 4.45 (2 H, q, *J* 7 Hz, OCH_2), 4.66 (2 H, d, *J* 6 Hz, CH_2N), and 4.90—6.10 (3 H, m, CH=CH_2), *m/e* 273 (M^+) and 131 (100%) (Found: C, 44.2; H, 3.9; N, 5.1. $C_{10}H_{11}NO_4S_2$ requires C, 43.9; H, 4.1; N, 5.1%).

Ethyl 3-(2,2-*Dimethoxyethyl*)-4-*oxo*-2-*thioxothiazolidin*-5-*ylglyoxylate* (5k).—A solution of the rhodanine (5 g) (4.21 g), pyridine (3.16 g), 4-dimethylaminopyridine (122 mg), and ethoxalyl chloride (4.7 ml) in anhydrous dichloromethane (50 ml) was heated to reflux for 3 h. After addition of more solvent (50 ml) the solution was repeatedly washed with water, dried, and evaporated and the residue taken up with ether. After 15 h a small amount of solid was filtered off. After addition of saturated aqueous potassium hydrogen carbonate the precipitated rhodanine salt was filtered off, washed with ether, and with a small amount of hydrogen carbonate solution. The crude salt (5.5 g, 78%) was suspended in water and acidified with citric acid (10 g). A solution of the precipitate in chloroform was dried and evaporated. Trituration with light petroleum and crystallisation from ether–light petroleum gave the *rhodanine* (5k) (4.11 g, 64%) as yellow needles, m.p. 80—81°, $\nu_{max.}$ 1 745, 1 670, and 1 605 cm^{-1}, $\lambda_{max.}$ 274 (ε 7 430) and 380 nm (17 990), δ 1.40 (3 H, t, *J* 7 Hz, OCH_2·CH_3), 3.40 (6 H, s, OCH_3), 4.20 (2 H, d, *J* 5 Hz, NCH_2), 4.42 (2 H, q, *J* 7 Hz, OCH_2), and 4.88 (1 H, t, *J* 5 Hz, CHO_2), *m/e* 321 (M^+) and 216 (100%) (Found: C, 40.9; H, 4.8; N, 4.4. $C_{11}H_{15}NO_6S_2$ requires C, 41.1; H, 4.7; N, 4.4%).

General Procedure for the Alkylation of N-*Substituted Rhodanines* (5c—g) *yielding Mesoions* (6a—e).—The rhodanine (5) (10 mmol) was dissolved in cold absolute ethanol (20 ml) containing sodium ethoxide (from 80% sodium hydride in oil) (600 mg). The alkylating reagent (1 equiv.) was added and the solution set aside for 15 h at room temperature. After evaporation, chloroform (20 ml) was added, and the solution washed with water, dried, and evaporated. Trituration with diethyl ether and crystallization from chloroform–ether gave the mesoion (6).

(a) 5-*Ethoxycarbonyl*-3-*methyl*-2-*methylthiothiazolium*-4-*olate* (6b) (73%) was obtained as yellow needles, m.p. 162—163°, $\nu_{max.}$ 1 720 and 1 650 cm^{-1}, $\lambda_{max.}$ 237 (ε 13 150), 253sh (10 420), and 365 nm (11 450), δ 1.33 (3 H, t, *J* 8 Hz, O·CH_2·CH_3), 2.77 (3 H, s, SCH_3), 3.48 (3 H, s, NCH_3), and 4.28 (2 H, q, *J* 8 Hz, O·CH_2·CH_3), *m/e* 233 (M^+) and 87 (100%) (Found: C, 41.4; H, 4.7; N, 5.9; S, 27.5. $C_8H_{11}NO_3S_2$ requires C, 41.2; H, 4.8; N, 6.0; S, 27.4%).

(b) 5-*Ethoxycarbonyl*-3-*ethoxycarbonylmethyl*-2-*ethoxycarbonylmethylthiothiazolium*-4-*olate* (6c) (44%) was obtained as yellow needles, m.p. 115°, $\nu_{max.}$ 1 745, 1 723, and 1 660 cm^{-1}, $\lambda_{max.}$ 238 (ε 10 100), 255sh (8 600), and 366 nm (8 160), δ 1.28 (3 H, t, *J* 8 Hz, O·CH_2·CH_3), 1.30 (6 H, t, *J* 8 Hz, O·CH_2·CH_3), 4.07 (2 H, s, CH_2S), 4.21 (2 H, q, *J* 8 Hz, O·CH_2·CH_3), 4.27 (4 H, q, *J* 8 Hz, O·CH_2·CH_3), and 4.85 (2 H, s, NCH_2), *m/e* 377 (M^+) and 345 (100%) (Found: C, 44.4; H, 5.1; N, 3.9; S, 17.3. $C_{14}H_{19}NO_7S_2$ requires C, 44.5; H, 5.1; N, 3.7; S, 17.0%).

(c) 3-*Allyl*-5-*ethoxalyl*-2-*methylthiothiazolium*-4-*olate* (6d) (58%) was obtained as yellow plates, m.p. 111°, $\nu_{max.}$ 1 745 and 1 695 cm^{-1}, $\lambda_{max.}$ 258 (ε 10 400) and 385 nm (13 360), δ 1.35 (3 H, t, *J* 7 Hz, CH_2·CH_3), 2.83 (3 H, s, SCH_3), 4.40 (2 H, q, *J* 7 Hz, O·CH_2·CH_3), 4.62 (2 H, d, *J* 6 Hz, NCH_2), and 5.10—6.20 (3 H, m, CH·CH_2), *m/e* 287 (M^+) and 214 (100%) (Found: C, 46.0; H, 4.6; N, 4.9. $C_{11}H_{13}NO_4S_2$ requires C, 46.0; H, 4.6; N, 4.9%).

(d) 3-(2,2-*Dimethoxyethyl*)-5-*ethoxalyl*-2-*methylthiothiazolium*-4-*olate* (6e) (54%) was obtained as yellow rhombs, m.p. 93—95°, $\nu_{max.}$ 1 735 and 1 685 cm^{-1}, $\lambda_{max.}$ 262 (ε 10 800) and 385 nm (14 000), δ 1.3 (3 H, t, *J* 7 Hz, CH_2·CH_3), 2.78 (3 H, s, SCH_3), 3.42 (6 H, s, OCH_3), 4.05 (2 H, d, *J* 6 Hz, NCH_2), 4.38 (2 H, q, *J* 7 Hz, CH_2·CH_3), and 4.70 (1 H, t, *J* 6 Hz, CHO_2), *m/e* 335 (M^+) and 262 (100%) (Found: C, 43.2; H, 5.0; N, 4.0. $C_{12}H_{17}NO_6S_2$ requires C, 43.0; H, 5.1; N, 4.2%).

Mesoions (6b *and* 6f—h) *from the Rhodanines* (5b *and* h).—To the rhodanines (5b or h) (10 mmol) in chloroform (50 ml) were added the alkylating reagent (11 mmol) [22 mmol in the case of (6b)] and *N*-ethyldi-isopropylamine (22 mmol) under nitrogen. After 24 h at room temperature the mixture was heated to reflux for 45 min. The solution was washed with water, dried, and evaporated. Chromatography on silica gave the mesoion (6) (eluant ethanol–chloroform, 1 : 3).

(a) 5-*Ethoxycarbonyl*-3-*methyl*-2-*methylthiothiazolium*-4-*olate* (6b) (65%) was identical with the mesoion prepared *via* methylation of the rhodanine (5c).

(b) 2-*Ethoxycarbonyl*-6,7-*dihydro*-5H-*thiazolo*[2,3-b][1,3]-*thiazinylium*-3-*olate* (6f) (65%) was obtained as yellow needles, m.p. 198—199°, $\nu_{max.}$ 1 725 and 1 665 cm^{-1}, $\lambda_{max.}$ 244 (ε 9 600), 252 (5 100), and 372 nm (10 500), δ 1.74 (3 H, t, *J* 7 Hz, O·CH_2·CH_3), 2.43 (2 H, quint, *J* 5 Hz, CH_2·CH_2·CH_2), 3.40 (2 H, t, *J* 5 Hz, SCH_2), 4.07 (2 H, t, *J* 5 Hz, NCH_2), and 4.34 (2 H, q, *J* 7 Hz, OCH_2), *m/e* 245 (M^+) and 173 (100%) (Found: C, 44.4; H, 4.7; N, 5.5; S, 26.3. $C_9H_{11}NO_3S_2$ requires C, 44.1; H, 4.5; N, 5.7; S, 26.1%).

(c) 6,7-*Dihydro*-2-*phenylacetyl*-5H-*thiazolo*[2,3-b][1,3]*thiazinylium*-3-*olate* (6g) (79%) was obtained as yellow plates, m.p. 155—160°, $\nu_{max.}$ 1 610 and 1 665 cm^{-1}, $\lambda_{max.}$ 252 (ε 11 375), 267sh (8 500), and 382 nm (13 500), δ 2.28 (2 H, m, CH_2·CH_2·CH_2), 3.20 (2 H, t, *J* 6 Hz, SCH_2), 3.94 (2 H, t, *J* 5 Hz, NCH_2), 4.27 (2 H, s, CH_2·CO), and 7.1—8.6 (5 H, m, Ph), *m/e* 291 (M^+) and 200 (100%) (Found: C, 57.8; H, 4.6; N, 4.8; S, 22.0. $C_{14}H_{13}NO_2S_2$ requires C, 57.7; H, 4.5; N, 4.8; S, 22.0%).

(d) *Ethoxycarbonyl*-5,6,7,8-*tetrahydrothiazolo*[2,3-b][1,3]*thiazepinylium*-3-*olate* (6h) (69%) was obtained as yellow needles, m.p. 175—176°, $\nu_{max.}$ 1 715 and 1 650 cm^{-1}, $\lambda_{max.}$ 229 (ε 7 190), 248 (4 690), and 385 nm (8 470), δ 1.30 (3 H, t, *J* 8 Hz, O·CH_2·CH_3), 1.60—2.46 (4 H, m, CH_2·CH_2),

2.88—3.13 (2 H, m, SCH_2), 4.23 (2 H, q, *J* 8 Hz, O·C*H*$_2$·CH_3), and 4.08—4.50 (2 H, m, NCH_2), *m/e* 259 (M^+) and 114 (100%) (Found: C, 46.3; H, 5.0; N, 5.3; S, 24.4. $C_{10}H_{13}NO_3S_2$ requires C, 46.3; H, 5.1; N, 5.4; S, 24.7%).

2-*Ethoxycarbonyl*-6,7-*dihydro*-5H-*thiazolo*[2,3-b][1,3]*thiazinylium*-3-*olate* (6f).—Diethyl bromomalonate (960 mg) was added to tetrahydro-1,3-thiazine-2-thione (7) (530 mg) in chloroform (40 ml) at room temperature. After 4 h *N*-ethyldi-isopropylamine (260 mg) was added, the mixture cooled to 0 °C (12 h), and trifluoroacetic acid (50 mg) added. After 12 h at 0 °C evaporation and chromatography on silica gave (eluant chloroform–methanol, 3 : 1) the mesoion (6f) (780 mg, 80%), identical with the mesoion prepared *via* 5-ethoxycarbonylrhodanine (5b).

5-*Ethoxycarbonyl*-2-*ethylthio*-3-*methylthiazolium*-4-*olate* (6i).—Diethyl bromomalonate (12 g) was added to ethyl *N*-methyldithiocarbamate (6.7 g) in chloroform (50 ml) at room temperature. After 15 h the solution was washed with water and evaporated, and the residue chromatographed over silica to give (eluant chloroform) the *mesoion* (6i) (46 g, 38%) as yellow prisms, m.p. 160—161° (from chloroform–ether), $\nu_{max.}$ 1 710 and 1 645 cm^{-1}, $\lambda_{max.}$ 238 (ε 9 320), 253 (7 790), and 368 nm (8 170), δ 1.33 (3 H, t, *J* 8 Hz, CH_2·C*H*$_3$), 1.56 (3 H, t, *J* 8 Hz, CH_2·C*H*$_3$), 3.27 (2 H, q, *J* 8 Hz, S·C*H*$_2$·CH_3), 3.50 (3 H, s, NCH_3), and 4.30 (2 H, q, *J* 8 Hz, O·C*H*$_2$·CH_3), *m/e* 247 (M^+) and 102 (100%) (Found: C, 43.7; H, 5.2; N, 5.7; S, 26.0. $C_9H_{13}NO_3S_2$ requires C, 43.7; H, 5.3; N, 5.7; S, 25.9%).

5-*Ethoxycarbonyl*-3-*ethoxycarbonylmethyl*-2-*methylthiothiazolium*-4-*olate* (6k).—Diethyl bromomalonate (7.2 g) was added to a cooled solution of methyl *N*-ethoxycarbonylmethyldithiocarbamate (5.8 g) and *N*-ethyldi-isopropylamine (3.9 g) in chloroform (50 ml). After 15 h at room temperature trifluoroacetic acid (0.5 ml) was added. After 15 h the solution was washed with water and evaporated and the residue chromatographed over silica to give (eluant chloroform) the *mesoion* (6k) (2 g, 22%), as yellow prisms, m.p. 177—179° (from chloroform–ether), $\nu_{max.}$ 1 750, 1 720, and 1 655 cm^{-1}, $\lambda_{max.}$ 239 (ε 11 300), 255sh (9 100), and 370 nm (10 100), δ 1.30 (3 H, t, SCH_3), 1.35 (3 H, t, *J* 7 Hz, O·CH_2*Me*), 2.80 (3 H, s, SMe), 4.23 (2 H, q, *J* 7 Hz, OCH_2), 4.30 (2 H, q, *J* 7 Hz, OCH_2), and 4.78 (2 H, s, NCH_2), *m/e* 305 (M^+) and 233 (100%) (Found: C, 43.4; H, 4.9; N, 4.5; S, 20.7. $C_{11}H_{15}NO_5S_2$ requires C, 43.3; H, 4.9; N, 4.6; S, 21.0%).

Diethyl (*Tetrahydro*-1,3-*thiazin*-2-*ylidene*)*malonate* (11a).—A solution of tetrahydro-1,3-thiazine (0.67 g), triethylamine (0.55 g), and diethyl chloromalonate (1.06 g) in anhydrous dichloromethane (15 ml) was heated to reflux for 15 h. The solution was washed with water, dried, and evaporated and the residue separated by p.l.c. (PhH–EtOAc, 3 : 2) to give (R_F 0.3) starting material (150 mg) and (R_F 0.43) *compound* (11a) (350 mg, 35%) as needles, m.p. 64° (from light petroleum), $\nu_{max.}$ (Nujol) 1 668, 1 630, and 1 570 cm^{-1}, $\lambda_{max.}$ 233 (ε 11 800) and 297 nm (21 500), δ 1.34 (6 H, t, *J* 8 Hz, O·CH_2·C*H*$_3$), 2.20 (2 H, quint, *J* 6 Hz, CH_2C*H*$_2$·CH_2), 3.00 (2 H, t, *J* 6 Hz, SCH_2), 3.57 (2 H, dt, *J* 2 and 6 Hz, NCH_2), 4.17 (4 H, q, *J* 8 Hz, OCH_2), and 8.54 (1 H, s, NH), *m/e* 259 (M^+) and 115 (100%) (Found: C, 51.2; H, 6.7; N, 5.5; S, 12.3. $C_{11}H_{17}NO_4S$ requires C, 51.0; H, 6.6; N, 5.4; S, 12.4%).

3-*Allyl*-2-*butylthio*-5-*ethoxalylthiazolium*-4-*olate* (6l).—A solution of the mesoion (6d) (145 mg) and butane-1-thiol (100 mg) in ethanol (4 ml) was heated to reflux for 40 min, then evaporated. The residue was separated by p.l.c. (EtOH–$CHCl_3$, 1 : 9) to give (R_F 0.6) the *mesoion* (6l) (70 mg, 43%) as a yellow oil, $\nu_{max.}$ 1 735 and 1 690 cm^{-1}, $\lambda_{max.}$ 259 (ε 10 710) and 388 nm (8 560), δ (CCl_4) 0.70—2.10 (7 H, m, C_3H_7), 1.38 (3 H, t, *J* 7 Hz, O·CH_2·C*H*$_3$), 3.30 (2 H, m, SCH_2), 4.28 (2 H, q, *J* 7 Hz, OCH_2), 4.50 (2 H, d, *J* 6 Hz, NCH_2), and 4.90—6.20 (3 H, m, CH=CH_2), *m/e* 329 (M^+) and 256 (100%) (Found: C, 50.9; H, 5.8; N, 4.2. $C_{14}H_{19}NO_4S_2$ requires C, 51.0; H, 5.8; N, 4.3%).

2-*Butylthio*-5-*ethoxycarbonyl*-3-*ethoxycarbonylmethylthiazolium*-4-*olate* (6m).—A solution of the mesoion (6k) (210 mg) and butane-1-thiol (1 ml) in ethanol (5 ml) was heated to reflux for 60 min, then evaporated. Ether (5 ml) was added, precipitating starting material (20 mg). Chromatography on silica (EtOH–EtOAc, 1 : 4) gave the *mesoion* (6m) (60 mg, 26%) as yellow needles, m.p. 45—47° (from ether–light petroleum), $\nu_{max.}$ 1 750, 1 715, and 1 650 cm^{-1}, $\lambda_{max.}$ 240 (ε 10 500), 255sh (8 950), and 372 nm (9 210), δ 1.25 (3 H, t, *J* 7 Hz, O·CH_2·C*H*$_3$), 1.30 (3 H, t, *J* 7 Hz, O·C*H*$_2$C*H*$_3$), 0.90—2.20 (7 H, m, C_3H_7), 3.22 (2 H, m, SCH_2), 4.18 (2 H, q, *J* 7 Hz, OCH_2), 4.25 (2 H, q, *J* 7 Hz, OCH_2), and 4.68 (2 H, s, NCH_2), *m/e* 347 (M^+) and 72 (100%) (Found: C, 48.6; H, 6.3; N, 3.9; S, 18.7. $C_{14}H_{21}NO_5S_2$ requires C, 48.4; H, 6.1; N, 4.0; S, 18.5%).

5-*Ethoxycarbonyl*-2-(2-*hydroxyethylthio*)-3-*methylthiazolium*-4-*olate* (6n).—To a suspension of the mesoion (6b) in anhydrous ethanol (11 ml) were added acetic anhydride (two drops) and 2-mercaptoethanol (0.39 ml). After heating to reflux for 3 h while nitrogen was passed through the mixture, the solvent was removed under vacuum and anhydrous ether added (40 ml). The precipitated crude product (0.75 g) contained about 16% (n.m.r.) of the starting mesoion (6b). Recrystallisation from chloroform–ether and then chloroform gave the *mesoion* (6n) (0.49 g, 30%), m.p. 151—153° (pale yellow needles), $\nu_{max.}$ 1 650br and 1 715 cm^{-1}, δ [$(CD_3)_2$SO] 1.18 (3 H, t, *J* 7 Hz, CH_2·C*H*$_3$), 3.17 (3 H, s, NCH_3), 3.20 (2 H, t, *J* 5 Hz, SCH_2), 3.78 (2 H, dt, *J* 5.5 Hz, OCH_2), 4.10 (2 H, q, *J* 7 Hz), and 5.68 (1 H, t, *J* 5 Hz, SH), *m/e* 263 (M^+), 130 (100%) (Found: C, 41.2; H, 5.1; N, 5.3. $C_9H_{13}NO_4S_2$ requires C, 41.1; H, 5.0; N, 5.3%).

4-*Methoxy*-1-*methyl*-4-*methylthio*-3-*phenylazetidin*-2-*one* (12a).—The mesoion (6a) (1 g) in methanol (200 ml) was irradiated for 5 h at 50 °C under argon. Evaporation gave a yellow gum (1.01 g). This photolysate (560 mg) in tetrahydrofuran (5 ml), followed by sodium borohydride (1 g) in water (10 ml) (dropwise), was added to nickel(II) chloride hexahydrate (2 g) and boric acid (8 g) in ethanol (100 ml) and tetrahydrofuran (35 ml) under nitrogen. The black mixture was stirred for 15 min, filtered through Celite, and evaporated, and the residue was partitioned between chloroform and water. The organic phase was filtered through Celite and evaporated to give a gum (304 mg). P.l.c. (EtOAc–PhH, 1 : 10) gave the β-*lactam* (12a) (both diastereoisomers, 73 : 27) as an oil (125 mg, 22%), $\nu_{max.}$ 1 760 cm^{-1}, δ 1.92 and 2.30 (2.2 H and 0.8 H, 2s, SCH_3), 3.07 (3 H, s, NCH_3), 3.23 and 3.67 (0.8 H and 2.2 H, 2s, OCH_3), 4.67 (1 H, s, CH), and 7.40 (5 H, s, Ph), *m/e* 237 (M^+) and 189 (100%) (Found: C, 60.8; H, 6.3; N, 5.9; S, 13.6. $C_{12}H_{15}NO_2S$ requires C, 60.8; H, 6.3; N, 5.9; S, 13.5%).

Ethyl 6-*Methoxy*-8-*oxo*-5-*thia*-1-*azabicyclo*[4.2.0]*octane*-7-*carboxylate* (12b).—The mesoion (6f) (500 mg) in methanol (130 ml) was irradiated for 34 h at 50 °C under argon. The crude product (after evaporation) was dissolved in dry benzene (2 ml) and tributylphosphine (500 mg) in benzene (2 ml) was added. After heating to reflux (5 min) the mixture was chromatographed on silica (30 g) to give unchanged

phosphine and its sulphide (eluant light petroleum–benzene) and crude β-lactam (eluant ethyl acetate–benzene, 3 : 17). Subsequent chromatography on alumina (12 g) gave an enriched β-lactam fraction (eluant ethyl acetate–benzene, 1 : 5). P.l.c. (ethyl acetate–benzene, 1 : 3) gave (R_F 0.55) the *β-lactam* (12b) (both diastereoisomers, 82 : 18) as an oil (45 mg, 9%), $\nu_{max.}$ 1 785 and 1 735 cm^{-1}, δ 1.34 (3 H, t, *J* 7 Hz, O·CH$_2$·C*H*$_3$), 1 : 90 (2 H, m, CH$_2$·C*H*$_2$·CH$_2$), 3.60—4.00 (4 H, m, SCH$_2$ and NCH$_2$), 3.44 and 3.50 (0.53 H and 2.47 H, 2s, OCH$_3$), 4.14 (1 H, s, CH), and 4.30 (2 H, q, *J* 7 Hz, O·C*H*$_2$·CH$_3$), *m/e* 245 (M^+) and 217 (100%) (Found: C, 49.2; H, 6.0; N, 5.6; S, 13.2. $C_{10}H_{15}NO_4S$ requires C, 48.95; H, 6.2; N, 5.7; S, 13.1%).

Bis-(2-methoxy-1-methyl-2-methylthio-4-oxo-3-phenylazetidin-3-yl) Disulphide (13a).—The mesoion (6a) (0.8 g) and methyl iodide (2 g) in methanol (150 ml) were irradiated under argon for 6 h. After evaporation the residue was separated by p.l.c. (EtOAc–PhH, 1 : 19) to give (R_F 0.6) the *disulphide β-lactam* (13a) (200 mg, 25%) as an oil. Rechromatography gave a sample showing $\nu_{max.}$ 1 760 cm^{-1}, δ 2.28 (3 H, s, SCH$_3$), 2.95 (3 H, s, NCH$_3$), 3.27 (3 H, s, OCH$_3$), and 7.20—7.68 (5 H, m, Ph) (Found: C, 53.7; H, 5.3; N, 5.2; S, 22.3. $C_{12}H_{14}NO_2S_2$ requires C, 53.7; H, 5.3; N, 5.2; S, 23.9%).

Photolysis of the Mesoion (6b).—The mesoion (6b) (0.8 g) and methyl (or ethyl) iodide (2 g) in methanol (150 ml) were irradiated for 15 h under argon. After evaporation, the residue was separated by p.l.c. (EtOAc–PhH, 1 : 10) to give (R_F 0.33) the β-lactam (13b) (170 mg, 21%) and (R_F 0.1) the thiazol-2-one (14b) (110 mg, 14%). The β-lactam (13b) had $\nu_{max.}$ 1 777 and 1 730 cm^{-1}, δ 1.28 (3 H, t, *J* 8 Hz, O·CH$_2$·C*H*$_3$), 2.53 (3 H, s, SMe), 2.97 (3 H, s, NMe), 3.45 (3 H, s, OMe), and 4.26 (2 H, q, *J* 8 Hz, O·C*H*$_2$·CH$_3$). The thiazol-2-one (14b) had m.p. 107—108° (from ether–light petroleum), $\nu_{max.}$ 1 725, 1 680sh, and 1 650 cm^{-1}, $\lambda_{max.}$ 288 nm (ε 13 700), δ 1.38 (3 H, t, *J* 8 Hz, O·CH$_2$·C*H*$_3$), 2.47 (3 H, s, SCH$_3$), 3.30 (3 H, s, NCH$_3$), and 4.37 (2 H, q, *J* 8 Hz, O·C*H*$_2$·CH$_3$), *m/e* 233 (M^+) and 187 (100%) (Found: C, 41.4; H, 4.7; N, 6.1; S, 27.4. Calc. for $C_8H_{11}NO_3S_2$: C, 41.2; H, 4.8; N, 6.0; S, 27.4%).

Ethyl 3,4-Dihydro-6-oxo-2H-thiazolo[4,3-b][1,3]thiazine-8-carboxylate (14c).—The mesoion (6f) (517 mg) in anhydrous dioxan (100 ml) was irradiated at room temperature for 36 h. Evaporation and p.l.c. (EtOAc–PhH, 1 : 1) of the yellow oil gave (R_F 0.28) *compound* (14c) (98 mg, 19%) as prisms, m.p. 122—123° (from benzene–light petroleum), $\nu_{max.}$ 1 720sh and 1 680 cm^{-1}, $\lambda_{max.}$ 232 (ε 10 400), 272 (9 200), and 281sh nm (8 800), δ 1.30 (3 H, t, *J* 8 Hz, O·CH$_2$·C*H*$_3$), 2.2—2.7 (2 H, m, CH$_2$·C*H*$_2$·CH$_2$), 3.03 (2 H, t, *J* 5 Hz, S·CH$_2$), 3.70 (2 H, t, *J* 6 Hz, N·CH$_2$), and 4.24 (2 H, q, *J* 8 Hz, O·C*H*$_2$CH$_3$), *m/e* 245 (M^+, 100%) (Found: C, 44.0; H, 4.4; N, 5.7. $C_9H_{11}NO_3S_2$ requires C, 44.1; H, 4.5; N, 5.7%).

Diethyl (Tetrahydro-1,3-thiazin-2-ylidene)malonate (11a).—The mesoion (6f) (720 mg) and tributylphosphine (1.5 g) in ethanol (150 ml) were irradiated for 35 h under argon. Evaporation gave an oil which was chromatographed over silica to give (eluant PhH) unchanged phosphine and its sulphide and (eluant EtOAc–PhH, 1 : 5) compound (11a) (93 mg, 42%), identical with the β-aminoacrylate prepared from tetrahydro-1,3-thiazine-2-thione and chloromalonate (see above).

Methyl 2-(Tetrahydro-1,3-thiazin-2-ylidene)phenylacetoacetate (11b).—The mesoion (6g) (650 mg) and tributylphosphine (1.2 g) in methanol (150 ml) were irradiated for 35 h under argon. Evaporation gave an oil (1.94 g) which was chromatographed over silica (80 g) to give (eluant PhH) unchanged phosphine and its sulphide and (eluant EtOAc–PhH, 1 : 4) an enriched fraction of (11b). P.l.c. (EtOAc–PhH, 1 : 4) gave (R_F 0.45) *compound* (11b) (228 mg, 35%), m.p. 84—85° (from methanol), $\nu_{max.}$ 3 200, 1 685, and 1 570 cm^{-1}, $\lambda_{max.}$ 236 (ε 12 200) and 312 nm (ε 17 150), δ 2.15 (2 H, m, CH$_2$·C*H*$_2$·CH$_2$), 2.93 (2 H, t, *J* 5 Hz, SCH$_2$), 3.48 (2 H, t, *J* 6 Hz, NCH$_2$), 3.78 (3 H, s, OCH$_3$), 4.02 (2 H, s, CH$_2$·CO), and 7.25br (5 H, Ph), *m/e* 291 (M^+) and 200 (100%) (Found: C, 61.8; H, 5.9; N, 4.8; S, 11.2. $C_{15}H_{17}NO_3S$ requires C, 61.9; H, 5.8; N, 4.8; S, 11.0%).

3-Methyl-2-thioxo-oxazolidin-4-one (19a).—This was prepared in 52% yield following the procedure of Holmberg [10] for the preparation of the analogous 3-ethyloxazolidinedione, using methylamine instead of ethylamine. Crystallised from ether *compound* (19a) had m.p. 56°, $\nu_{max.}$ 1 770 cm^{-1}, $\lambda_{max.}$ 254 nm (ε 18 100), δ 3.25 (3 H, s, NCH$_3$) and 4.87 (2 H, s, OCH$_2$), *m/e* 131 (M^+) (Found: C, 37.0; H, 3.6; N, 10.8; S, 23.8. $C_4H_5NO_2S$ requires C, 36.7; H, 3.8; N, 10.7; S, 24.4%).

3-Methyl-5-phenyl-2-thioxo-oxazolidin-4-one (19c).—This was prepared in 28% yield following the procedure of Holmberg [10] for the preparation of 3-ethyl-2-thioxo-oxazolidin-4-one, using methylamine and mandelic acid instead of ethylamine and glycolic acid. Crystallised from ether *compound* (19c) had m.p. 68°, $\nu_{max.}$ 1 762 cm^{-1}, $\lambda_{max.}$ 256 nm (ε 19 550), δ 3.37 (3 H, s, NCH$_3$), 5.80 (1 H, s, CH), and 7.42 (5 H, s, Ph), *m/e* 207 (M^+) and 118 (100%) (Found: C, 41.9; H, 4.3; N, 8.2; S, 18.4. $C_6H_7NO_3S$ requires C, 41.6; H, 4.1; N, 8.1; S, 18.5%).

5-Acetyl-3-methyl-2-thioxo-oxazolidin-4-one (19d).—The thioxo-oxazolinone (19a) (1.95 g) was dissolved at −80 °C in absolute tetrahydrofuran (30 ml) containing lithium diisopropylamide (1 mol. equiv.). After 30 min acetyl chloride was added. After 5 h at room temperature the dark red solution was acidified with N-hydrochloric acid (50 ml), and extracted with ether. The extract was washed with N-hydrochloric acid and water, dried, and evaporated. The product was crystallised from ether affording *compound* (19d) (1.2 g, 46%) as pale yellow prisms, m.p. 115—119°, $\nu_{max.}$ 1 760 and 1 740 cm^{-1}, $\lambda_{max.}$ 242 (ε 15 900) and 320 nm (18 840), δ 2.41 (3 H, s, CH$_3$CO), 3.33 (3 H, s, NCH$_3$), and 5.50 (1 H, s, CH·CO), *m/e* 173 (M^+) and 74 (100%) (Found: C, 41.9; H, 4.3; N, 8.2; S, 18.4. $C_6H_7NO_3S$ requires C, 41.6; H, 4.1; N, 8.1; S, 18.5%).

5-Chloroacetyl-1,3-dimethyl-2-methylthioimidazolium-4-olate (18a).—Chloroacetyl chloride (1.12 g) in dry chloroform (30 ml) was added dropwise to a solution of *NN'S*-trimethylisothiourea (590 mg) and *N*-ethyldi-isopropylamine (1.84 g) in chloroform (30 ml) at 0 °C over 30 min. The mixture was heated to reflux for 1 h under nitrogen. The solution was washed, dried, and evaporated. Chromatography of the residue over silica (100 g) (eluant EtOH–CHCl$_3$, 1 : 4) gave the *mesoion* (18a) (530 mg, 45%), m.p. 155—156° (from chloroform–ether), $\nu_{max.}$ (Nujol) 1 670 and 1 620 cm^{-1}, $\lambda_{max.}$ 255 (ε 6 900) and 324 nm (21 700), δ 2.50 (3 H, s, SCH$_3$), 3.55 (3 H, s, NCH$_3$), 4.17 (3 H, s, NCH$_3$), and 4.36 (2 H, s, CH$_2$Cl), *m/e* 234 (M^+) (Found: C, 40.9; H, 4.7; N, 12.1. $C_8H_{11}ClN_2O_2S$ requires C, 41.0; H, 4.7; N, 11.9%).

2-(2-Bromoethylthio)-1-methylimidazolin-4-one (22).—To 1-methylthiohydantoin (21) (2.6 g) in acetone (200 ml) at 0 °C under nitrogen were added 1,3-dibromopropane (4.4 g) and *N*-ethyldi-isopropylamine (2.58 g). After 12 h the solvent

[10] B. Holmberg, *J. prakt. Chem.*, 1911, **84**, 682.

was evaporated off. The residue was taken up in chloroform (100 ml) and the solution washed with water, dried, and evaporated. The residue was chromatographed over silica. Elution with 1 : 5 EtOAc–PhH gave *compound* (22) (2.4 g, 48%) as an oil, $\nu_{max.}$ 1 710 cm^{-1}, δ 2.10 (2 H, m, CH_2·CH_2·CH_2), 2.54 (2 H, t, *J* 6 Hz, SCH_2), 3.20 (3 H, s, NCH_3), 4.04 (2 H, t, *J* 6 Hz, CH_2Br), and 4.10 (2 H, s, NCH_2).

N-(5,6-*Dihydro*-4H-*thiazin*-2-*yl*)-N-*methylglycine* (23).—To a stirred solution of compound (22) (1.25 g) in dimethylacetamide (15 ml) under nitrogen at 0 °C was added sodium hydride (0.35 g; 80% dispersion in oil) in small portions over 20 min. The mixture was evaporated *in vacuo* at 40 °C and the residue was distributed between chloroform (100 ml) and water (50 ml). The aqueous solution (pH *ca.* 5.5) was freeze-dried to give compound (23) as a light brown foam, which was not further characterized.

2-*Formyl*-6,7-*dihydro*-1-*methyl*-5H-*imidazolo*[2,3-b][1,3]-*thiazinylium*-3-*olate* (18b).—A solution of the amino-acid (23) (0.65 g), oxalyl chloride (1.26 g), and *N*-ethyldi-isopropylamine (0.64 g) in dimethylformamide (10 ml) was heated under nitrogen at 65 °C for 1 h. The solvent was removed *in vacuo*. Chromatography over silica (50 g) (eluant EtOH–$CHCl_3$, 1 : 3) gave the *mesoion* (18b) (334 mg, 34%), m.p. 248—250° (decomp.) (from chloroform–ether), $\nu_{max.}$ 1 680 and 1 610 cm^{-1}, $\lambda_{max.}$ 268 (ε 3 900) and 326 nm (23 100), δ 2.38 (2 H, m, CH_2·CH_2·CH_2), 3.41 (2 H, t, *J* 6 Hz, CH_2S), 3.86 (3 H, s, NCH_3), 3.97 (2 H, t, *J* 6 Hz, NCH_2), and 9.2 (1 H, s, CHO), *m/e* 198 (M^+) (Found: C, 48.4; H, 5.1; N, 14.3. $C_8H_{10}N_2O_2S$ requires C, 48.5; H, 5.1; N, 14.1%).

2-*Acetyl*-6,7-*dihydro*-1-*methyl*-5H-*imidazolo*[2,3-b][1,3]*thiazinylium*-3-*olate* (18c).—A solution of the amino-acid (23) (0.67 g) and *N*-ethyldi-isopropylamine (0.62 g) in acetic anhydride (15 ml) was heated under nitrogen at 80 °C for 2 h. The solvent was removed *in vacuo*. Chromatography over silica (50 g) (eluant EtOH–$CHCl_3$, 1 : 3) gave the *mesoion* (18c) (464 mg, 41%), m.p. 199—200° (decomp.) (from chloroform–ether), $\nu_{max.}$ (Nujol) 1 665 and 1 605 cm^{-1}, $\lambda_{max.}$ 261 (ε 4 450) and 320 nm (23 050), δ 2.35 (2 H, m, CH_2·CH_2·CH_2), 2.50 (3 H, s, $COCH_3$), 3.36 (2 H, t, *J* 6 Hz, CH_2S), 3.85 (3 H, s, NCH_3), and 3.95 (2 H, t, *J* 6 Hz, NCH_2), *m/e* 212 (M^+) (Found: C, 50.7; H, 5.9; N, 13.2. $C_9H_{12}N_2SO_2$ requires C, 50.9; H, 5.7; N, 13.2%).

1-(5,6-*Dihydro*-4H-1,3-*thiazin*-2-*yl*)-1,3-*thiazine*-2-*thione* (25).—To a stirred solution of tetrahydro-1,3-thiazine-2-thione (7) (399 mg, 3 mmol) and triethylamine (337 mg, 3 mmol) in anhydrous chloroform (15 ml) was added dropwise a solution of iodine (385 mg, 1.5 mmol) in anhydrous chloroform (20 ml) over 30 min. The washed (H_2O) and dried (Na_2SO_4) solution was evaporated under vacuum and the residue recrystallised from chloroform–ether to give the disulphide (24) as rhombs (305 mg, 77%), m.p. 117—121°, $\nu_{max.}$ 1 605 cm^{-1}, $\lambda_{max.}$ 216 nm (ε 9 500), δ 1.70—2.20 (2 H, m, CH_2), 2.90—3.30 (2 H, m, SCH_2), and 3.65—4.00 (2 H, m, NCH_2).

The disulphide (24) (264 mg, 1 mmol) in chloroform (10 ml) and a catalytic amount of trifluoroacetic acid was set aside for 15 h. The solution was worked up by extracting with a little water and drying (Na_2SO_4). Chromatography on silica plates (benzene–ethyl acetate, 3 : 2; R_F 0.12) afforded the *rearrangement product* (25) (144 mg, 61%) as rhombs, m.p. 115—117° (from chloroform–ether), $\nu_{max.}$ 1 690 and 1 635 cm^{-1}, $\lambda_{max.}$ 245 nm (ε 11 400), δ 1.65—2.15 (2 H, m, CH_2), 2.15—2.55 (2 H, m, CH_2), 2.85—3.35 (4 H, m, SCH_2), and 3.60—4.05 (4 H, m, NCH_2), *m/e* 232 (M^+) and 100 (100%) (Found: C, 41.5; H, 5.0; N, 12.2; S, 41.5. $C_8H_{12}N_2S_3$ requires C, 41.3; H, 5.2; N, 12.1; S, 41.4%).

We thank the S.R.C. for financial support.

[6/2001 *Received*, 29*th October*, 1976]