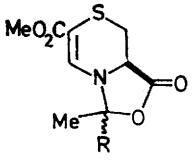
Studies Related to Dihydro-1,4-thiazines. Part VIII.[1] β-Elimination Reactions of 7-Oxo-8-oxa-4-thia-1-azabicyclo[4.3.0]non-2-ene-3-carboxylates [2]

By **Anthony G. W. Baxter** and **Richard J. Stoodley,*** Department of Organic Chemistry, The University, Newcastle upon Tyne NE1 7RU

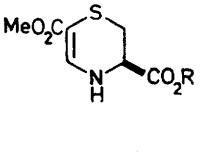
The (6*R*)-9,9-dimethyl derivative of methyl 7-oxo-8-oxa-4-thia-1-azabicyclo[4.3.0]non-2-ene-3-carboxylate (1) is converted into potassium α-(5-methoxycarbonyl-2,2-dimethyl-Δ^4-thiazolin-3-yl)acrylate (11) by potassium t-butoxide. When the reaction is conducted in the presence of iodomethane, methyl (*Z*)-β-(2,2-dimethyl-4-methylene-5-oxo-oxazolidin-3-yl)-α-methylthioacrylate (20) is formed, suggesting that the rearrangement is triggered by a β-elimination process.

A corresponding reorganization, leading to the ββ-dimethylacrylate (17), occurs with the (6*S*)-5,5,9,9-tetramethyl derivative (14). The (6*S*,9*S*)-[or (6*S*,9*R*)-]5,5,9-trimethyl compound (15) affords optically active potassium α-(5-methoxycarbonyl-2-methyl-Δ^4-thiazolin-3-yl)-ββ-dimethylacrylate (30), implying that the new C–S bond is formed by an S_N2-like pathway.

As part of a programme aimed at developing new methods of heterocyclic synthesis, we have examined some β-elimination reactions of dihydro-1,4-thiazines. The thiazino–oxazolidinone (1),[3] which is readily prepared from the thiazinecarboxylic acid (3) and 2,2-dimethoxypropane, was selected for a preliminary study. Although it was expected that this compound would initially isomerize to the mercaptoacrylate (5) under basic



(1) R = Me
(2) R = H

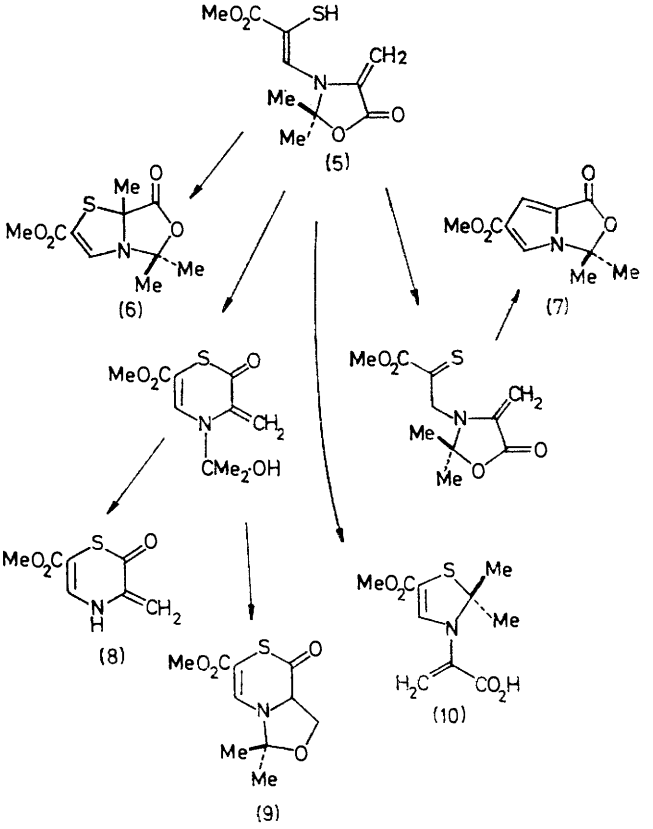


(3) R = H
(4) R = Me

conditions, the final outcome of the reaction was uncertain. Thus there appeared to be at least five plausible products; their structures (6)—(10) and possible modes of formation are summarised in the Scheme.

Treatment of the thiazino-oxazolidinone (1) with potassium t-butoxide in [$^2H_6$]dimethyl sulphoxide caused the rapid formation of one new compound. The need for 1 mol. equiv. of the base to complete the reaction suggested that the product was a potassium salt and n.m.r. spectroscopy was in accord with the thiazolinylacrylate structure (11). Repetition of the reaction in dimethyl sulphoxide, *NN*-dimethylformamide, or tetrahydrofuran followed by acidification yielded the thiazolinylacrylic acid (10) as an unstable oil; the acid decomposed, particularly in the presence of silica gel, to give the thiazolinecarboxylate (13). Attempts to form a crystalline salt of the acid or to convert it into the methyl ester (12) with diazomethane or methanolic hydrogen chloride were unsuccessful. However, when the potassium salt (11), preferably prepared in *NN*-dimethylformamide, was treated with iodomethane and the product purified by silica-gel chromatography, the thiazolinylacrylate (12) was obtained.

Under similar conditions the thiazino-oxazolidinone (14) [4] rearranged to the salt (17), which was converted



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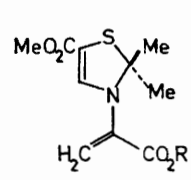
into the methyl ester (18) by iodomethane. Acidification of the salt yielded the thiazolinylacrylic acid (16) as an oil; the acid afforded a crystalline potassium salt when treated with potassium 2-ethylhexanoate in ether and decomposed to the thiazolinecarboxylate (13) in the presence of silica gel. Efforts to convert the acid into the methyl ester (18) with diazomethane or methanolic

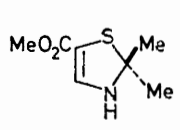
[1] Part VII, R. J. Stoodley and R. B. Wilkins, *J.C.S. Perkin I*, 1975, 716.
[2] Preliminary communication, A. G. W. Baxter and R. J. Stoodley, *J.C.S. Chem. Comm.*, 1975, 251.
[3] A. R. Dunn, I. McMillan, and R. J. Stoodley, *Tetrahedron*, 1968, **24**, 2895.
[4] J. Kitchin and R. J. Stoodley, *J.C.S. Perkin I*, 1973, 22.

hydrogen chloride were unsuccessful; a complex mixture of products was formed in each case.

It seems probable that the foregoing reorganizations involve the intermediacy of the enethiolates (19) and (23), formed from the thiazino–oxazolidinones (1) and (14) by β-elimination. In an attempt to corroborate



(11) R = K
(12) R = Me



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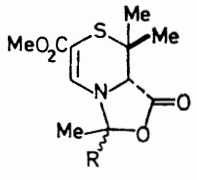
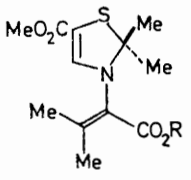
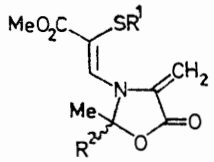


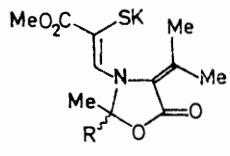
(14) R = Me
(15) R = H



(16) R = H
(17) R = K
(18) R = Me



(19) R^1 = K, R^2 = Me
(20) R^1 = R^2 = Me
(21) R^1 = Me, R^2 = H
(22) R^1 = K, R^2 = H



(23) R = Me
(24) R = H

this pathway, the thiazino–oxazolidinones (1) and (14) were treated with potassium t-butoxide in the presence of iodomethane. The former compound afforded the expected methylthioacrylate (20) but the latter yielded the thiazolinylacrylate (18). Evidently the species (23) undergoes rearrangement faster than alkylation.

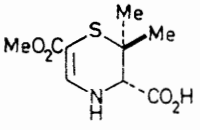
The conversion of the enethiolates (19) and (23) into the thiazolinylacrylates (11) and (17) must involve a C–O bond cleavage and the formation of a C–S bond. In principle, these processes may be coupled (S_N2-like) or bond rupture may precede bond formation (S_N1-like). To distinguish between these mechanisms, a thiazino–oxazolidinone possessing a chiral tertiary centre at position 9 was required. Attempts to condense the thiazinecarboxylic acids (3) [3] and (25) [5] with unsymmetrical ketones in the presence of acidic catalysts were, however, unrewarding.

Having failed to prepare the desired compound, we turned attention to the synthesis of a thiazino–oxazolidinone bearing a chiral secondary centre at position 9. When the acid (3) was treated with freshly distilled acetaldehyde in deuteriochloroform * containing magnesium sulphate, the thiazino-oxazolidinone (2) was obtained as a crystalline 3 : 2 mixture of isomers. Attempts to alter the isomer ratio by recrystallisation were unsuccessful. Treatment of the mixture with potassium t-butoxide in *NN*-dimethylformamide followed by the addition of iodomethane and fractionation of the product by silica-gel chromatography yielded only the methylthioacrylate (21); there was no evidence for the presence of the desired thiazolinylacrylate (26). Efforts to obtain compound (26) by varying the base and the solvent were unproductive.

The thiazino–oxazolidinone (15) was prepared as a crystalline single isomer from the acid (25) in a manner analogous to that employed for the synthesis of the derivative (2). It was converted into the thiazolinylacrylate (27) when treated with potassium t-butoxide followed by iodomethane. Although the derivative (27) was unstable, a pure syrupy sample could be obtained after silica-gel chromatography; it possessed $[\alpha]_D$ +38° ($CHCl_3$). The t-butylamine salt (29), which was a stable crystalline solid, showed $[\alpha]_D$ +9° ($CHCl_3$); its o.r.d. spectrum (see Experimental) confirmed that the compound was optically active.

Although it is not possible to define the stereochemistry at position 9 of the starting thiazino-oxazolidinone (15) and neither the absolute stereochemistry nor the optical purity of the derived thiazolinylacrylate (29), it is clear that chirality is maintained during the reorganization. This result implicates an S_N2-like process in the conversion of the enethiolate (24) into the thiazolinylacrylate (30).

The difference in the reactivity of the thiazino–oxazolidinones (2) and (15) towards potassium t-butoxide–iodomethane is striking. Conceivably, the failure of the former derivatives to afford the thiazolinylacrylate (26)



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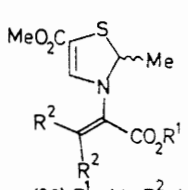
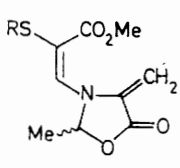
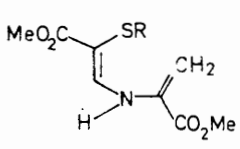


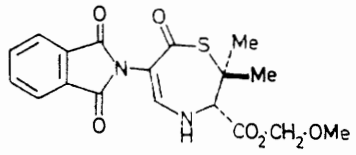
(26) R^1 = Me, R^2 = H
(27) R^1 = R^2 = Me
(28) R^1 = H, R^2 = Me
(29) R^1 = H, NH_2Bu^t, R^2 = Me
(30) R^1 = K, R^2 = Me



(31) R = K
(32) R = Me



(33) R = Me
(34) R = K



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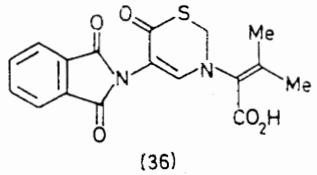

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may be due to a rapid conversion of the initially formed (*Z*)-enethiolate (22) into the (*E*)-isomer (31), which is incapable of undergoing the intramolecular reaction.

* The reaction failed when the deuteriochloroform was replaced by dichloromethane or freshly prepared ethanol-free chloroform.

[5] I. McMillan and R. J. Stoodley, *Tetrahedron Letters*, 1966, 1205; *J. Chem. Soc.* (*C*), 1968, 2533.

According to this postulate the derived methylthioacrylate should possess the *E*-configuration (**32**), opposite to

C=O), 1 690br (vinylogous urethane C=O), and 1 590 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 208 (ε 6 300), 222sh (5 000), 285 (2 200), 334 (5 000), and 345sh nm (4 800), δ (CDCl$_3$) 1.68 (6 H, s

t-Butoxide and Iodomethane.—(*a*) The thiazino–oxazolidinone (14) (1.00 g, 3.69 mmol) was treated with potassium t-butoxide followed by iodomethane as for compound (1) [procedure (*a*)]. The mixture was worked up as before and the product fractionated by silica-gel chromatography [C_6H_6–Et_2O (5 : 1) as eluant]. The first-eluted compound (0.125 g, 13%) was identical (t.l.c. and n.m.r. spectroscopy) with the starting material. The second-eluted compound (0.795 g, 71%), isolated as a chromatograhically homogeneous syrup, was *methyl* α-(*5-methoxycarbonyl-2,2-dimethyl-*Δ^4*-thiazolin-3-yl*)-ββ-*dimethylacrylate* (18), $[\alpha]_D$ 0° (0.65% in $CHCl_3$), $\nu_{max.}$ (film) 1 720 (unsat. ester C=O), 1 690 (vinylogous urethane C=O), and 1 590 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 217 (ε 12,500), 285sh (5 600), 319 (7 400), and 337 nm (7 400), δ ($CDCl_3$) 1.48 (6 H, s, *gem*-Me_2), 1.90 and 2.02 (each 3 H, s, vinylic *gem*-Me_2), 3.63 and 3.66 (each 3 H, s, 2 CO_2Me), and 6.67 (1 H, s, vinylic H), *m/e* (base peak) 270 (*M* − Me) (Found: M^+, 285.1026. $C_{13}H_{19}NO_4S$ requires *M*, 285.1035).

(*b*) The thiazino–oxazolidinone (14) (0.135 g, 0.5 mmol) was treated with potassium t-butoxide in the presence of iodomethane as for compound (1) [procedure (*b*)]. Work-up and purification by silica-gel chromatography [C_6H_6–Et_2O (7 : 1) as eluant] yielded a syrup (0.128 g, 90%) identical (i.r. and n.m.r. spectroscopy) with the dimethylacrylate (18).

Methyl 2,2-*Dimethyl-*Δ^4*-thiazoline-5-carboxylate* (13).—(*a*) The crude acid (10) (0.158 g) was chromatographed on silica gel ($CHCl_3$ as eluant) to yield the *thiazolinecarboxylate* (13) (0.044 g, 26%) as a chromatographically homogeneous syrup, $[\alpha]_D$ 0° (0.5% in $CHCl_3$), $\nu_{max.}$ (film) 3 340 (NH), 1 680br (vinylogous urethane C=O), and 1 590 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 211 (ε 6 700), 292 (2 400), and 335 nm (5 700), δ ($CDCl_3$) 1.66 (6 H, s, *gem*-Me_2), 3.67 (3 H, s, CO_2Me), 4.7br (1 H, d, NH), 6.96 (1 H, d, *J* 3.6 Hz, vinylic H) (addition of D_2O caused the signal at δ 4.7 to disappear and that at 6.96 to collapse to a singlet), *m/e* (base peak) 157 (*M* − CH_4) (Found: M^+, 173.0513. $C_7H_{11}NO_2S$ requires *M*, 173.0511).

(*b*) The crude acid (16) (0.086 g) was chromatographed on silica gel ($CHCl_3$ as eluant) to yield a syrup (0.021 g, 38%) identical (i.r. and n.m.r. spectroscopy) with the thiazoline-carboxylate (13).

Reaction of the Thiazinecarboxylic Acid (3) *with Acetaldehyde.*—The acid (3) [3] (0.500 g, 2.46 mmol), dried magnesium sulphate (0.250 g), redistilled acetaldehyde (0.4 cm^3), and deuteriochloroform (1.5 cm^3) were sealed in a glass ampoule and the mixture was shaken for 40 h. Evaporation of the filtered solution left a residue which was recrystallised from dichloromethane–ether to give *methyl* (6R)-9-*methyl-7-oxo-8-oxa-4-thia-1-azabicyclo*[4.3.0]*non-2-ene-3-carboxylate* (2) (0.350 g, 62%) as a 3 : 2 mixture of isomers, m.p. 133—135° (decomp.), $[\alpha]_D$ −42° (2.32% in $CHCl_3$), $\nu_{max.}$ (KBr) 1 785 (oxazolidinone C=O), 1 690 (vinylogous urethane C=O), and 1 595 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 215 (ε 6 400), 261 (3 100), and 312 nm (10 600), δ ($CDCl_3$) (major isomer) 1.60 (3 H, d, *J* 5.5 Hz, CH*Me*), 2.39 (1 H, dd, *J* 12.4 and 10.0 Hz, S·CH_β), and 3.23 (1 H, dd, *J* 12.4 and 3.7 Hz, S·CHα), 3.69 (3 H, s, CO_2Me), 4.10 (1 H, dd, *J* 10 and 3.7 Hz, CH·CO), 4.45 (1 H, q, *J* 5.5 Hz, C*H*Me), and 7.43 (1 H, s, vinylic H); minor isomer as for the major except 1.64 (3 H, d, *J* 5.5 Hz, CH*Me*), 2.57 (1 H, dd, *J* 12.4 and 10.0 Hz, S·CH_β), 3.31 (1 H, dd, *J* 12.4 and 3.7 Hz, S·CH_α), 4.63 (1 H, q, *J* 5.5 Hz, C*H*Me), and 7.47 (1 H, s, vinylic H), *m/e* (base peak) 157 (*M* − CO_2·CHMe) (Found: C, 47.5; H, 4.7; N, 6.1%; M^+, 229. $C_9H_{11}NO_4S$ requires C, 47.2; H, 4.8; N, 6.1%; *M*, 229).

Reaction of the Thiazino–oxazolidinone (2) *with Potassium t-Butoxide and Iodomethane.*—The thiazino–oxazolidinone (2) (0.115 g, 0.5 mmol) was treated with potassium t-butoxide followed by iodomethane as for compound (1) [procedure (*a*)]. After 5 min the mixture was diluted with ether and washed (twice) with water. Evaporation of the dried ($MgSO_4$) ether layer and purification by silica-gel chromatography [C_6H_6–Et_2O (5 : 1) as eluant] yielded *methyl* (Z)-α-(*2-methyl-4-methylene-5-oxo-oxazolidin-3-yl*)-β-*methylthioacrylate* (20) (0.038 g, 31%) as a chromatographically homogeneous syrup, $[\alpha]_D$ −22° (0.28% in $CHCl_3$), $\nu_{max.}$ (film) 1 790 (oxazolidinone C=O), 1 700 (vinylogous urethane C=O), and 1 600 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 208 (ε 3 200), 223sh (2 900), 291 (4 700), and 331sh nm (3 000), δ ($CDCl_3$) 1.54 (3 H, d, *J* 5 Hz, CH*Me*), 2.20 (3 H, s, SMe), 3.75 (3 H, s, CO_2Me), 4.72 and 5.24 (each 1 H, d, *J* 2.8 Hz, vinylic H_2), 6.60 (1 H, q, *J* 5 Hz, C*H*Me), and 7.70 (1 H, s, vinylic H), *m/e* (base peaks) 243 (*M*), 171 (*M* − CO_2·CHMe), and 156 (Found: M^+, 243.0578. $C_{10}H_{13}NO_4S$ requires *M*, 243.0565).

Reaction of the Thiazinecarboxylic Acid (25) *with Acetaldehyde* (with R. B. Wilkins).—The acid (25) [5] (2.08 g, 0.9 mmol), dried magnesium sulphate (1.04 g), freshly distilled acetaldehyde (3 cm^3) and deuteriochloroform (6 cm^3) were sealed in a glass ampoule. The mixture was shaken for 17 h, filtered, and evaporated to give *methyl* (6S,9S)-[or (6S,9R)-] 5,5,9-*trimethyl-7-oxo-8-oxa-4-thia-1-azabicyclo*-[4.3.0]*non-2-ene-3-carboxylate* (15) (2.01 g, 86%) as a single isomer, m.p. 50—52° (from $CHCl_3$–Et_2O), $[\alpha]_D$ +276° (1.14% in $CHCl_3$), $\nu_{max.}$ (KBr) 1 800 (oxazolidinone C=O), 1 695 (vinylogous urethane C=O), and 1 590 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 216 (ε 6 900), 265 (2 600), 277sh (4 500), and 318 nm (8 800), δ ($CDCl_3$) 1.19 and 1.67 (each 3 H, s, *gem*-Me_2), 1.64 (3 H, d, *J* 5.2 Hz, CH*Me*), 3.67 (3 H, s, CO_2Me), 3.93 (1 H, s, CH·CO), 5.54 (1 H, q, *J* 5.2 Hz, C*H*Me), and 7.75 (1 H, s, vinylic H), *m/e* (base peak) 170 (Found: C, 51.3; H, 5.8; N, 5.4%: M^+, 257. $C_{11}H_{15}NO_4S$ requires C, 51.4; H, 5.8; N, 5.5%; *M*, 257).

Reaction of the Thiazino–oxazolidinone (15) *with Potassium t-Butoxide.*—(*a*) The thiazino–oxazolidinone (15) (0.128 g, 0.5 mmol) was treated with potassium t-butoxide as for the compound (14) [procedure (*a*)]. Work-up as before afforded α-(*5-methoxycarbonyl-2-methyl-*Δ^4*-thiazolin-3-yl*)-ββ-*dimethylacrylic acid* (28) (0.073 g, 56%) as a syrup, $[\alpha]_D$ +6° (1.5% in $CHCl_3$), $\nu_{max.}$ (film) 3 350 (OH), 1 685 (unsat. carboxy and vinylogous urethane C=O), and 1 585 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 214 (ε 8 900), 298 (2 800), and 351 nm (5 500), δ ($CDCl_3$) 1.51 (3 H, d, *J* 6 Hz, CH*Me*), 2.09 and 2.24 (each 3 H, s, vinylic *gem*-Me_2), 3.71 (3 H, s, CO_2Me), 5.58 (1 H, q, *J* 6 Hz, C*H*Me), 6.84 (1 H, s, vinylic H), and 10.6br (1 H, s, CO_2H) (addition of D_2O caused the signal at δ 10.6 to disappear), *m/e* (base peak) 242 (*M* − Me) (Found: M^+, 257.0696. $C_{11}H_{15}NO_4S$ requires *M*, 257.0722).

(*b*) The thiazino-oxazolidinone (15) (0.256 g, 1 mmol) was treated with potassium t-butoxide as in procedure (*a*). The product was worked up as before and the ether layer was dried ($MgSO_4$), cooled to −15°, and treated with t-butylamine (0.3 cm^3). Addition of light petroleum induced crystallisation of *t-butylammonium* α-(*5-methoxycarbonyl-2-methyl-*Δ^4*-thiazolin-3-yl*)-ββ-*dimethylacrylate* (29) (0.112 g, 33%), m.p. 130—132° (from Et_2O–light petroleum), $[\alpha]_D$ +9° (2.25% in $CHCl_3$), $[\phi]$ (EtOH) +13,800° (252), −160° (290), +4 800° (333), and −4 600° (382 nm), $\nu_{max.}$ (KBr) 3 000 (NH), 1 690 (vinylogous urethane C=O), 1 640, 1 630, 1 590 (C=C), 1 550 (unsat. carboxylate C=O), and 1 530 cm^{-1}, $\lambda_{max.}$ (EtOH) 210 (11,400), 302sh (2 600), and 353 nm

(11,400), δ ($CDCl_3$) 1.29 (9 H, s, CMe_3), 1.48 (3 H, d, *J* 6 Hz CH*Me*), 1.89 and 2.15 (each 3 H, s, *gem*-Me_2), 3.69 (3 H, s, CO_2Me), 5.59 (1 H, q, *J* 6 Hz, C*H*Me), 6.84 (1 H, s, vinylic H), and 7.4br (3 H, s, $^+NH_3$) (addition of D_2O caused the signal at δ 7.4 to disappear) (Found: C, 53.3; H, 7.7; N, 8.1. $C_{15}H_{26}N_2O_4S$ requires C, 53.0; H, 7.7; N, 8.2%).

Reaction of the Thiazino–oxazolidinone (15) *with Potassium t-Butoxide and Iodomethane.*—The thiazino–oxazolidinone (15) (0.063 g, 0.25 mmol) was treated with potassium t-butoxide followed by iodomethane as for compound (1). After 15 min the mixture was diluted with ether and washed (twice) with water. Evaporation of the dried ($MgSO_4$) ethereal layer and purification by silica-gel chromatography [C_6H_6–Et_2O (9 : 1) as eluant] gave *methyl α-(5-methoxycarbonyl-2-methyl-Δ⁴-thiazolin-3-yl)-ββ-dimethylacrylate* (27) (0.053 g, 78%) as a chromatographically homogeneous syrup, $[\alpha]_D$ +38° (0.6% in $CHCl_3$), $\nu_{max.}$ (film) 1 720 (unsat. ester C=O), 1 690 (vinylogous urethane C=O), and 1 590 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 219 (ε 15,800), 286 (4 100), 311sh (7 900), and 346 nm (8 800), δ ($CDCl_3$) 1.43 (3 H, d, *J* 6 Hz, CH*Me*), 1.96 and 2.13 (each 3 H, s, *gem*-Me_2), 3.63 and 3.70 (each 3 H, s, 2 CO_2Me), 5.35 (1 H, q, *J* 6 Hz, C*H*Me), and 6.62 (1 H, s, vinylic H), *m/e* (base peak) 256 (*M* − Me) (Found: M^+, 271.0862. $C_{12}H_{17}NO_4S$ requires *M*, 271.0878).

Methyl (Z)-β-[1-(*Methoxycarbonyl*)*vinylamino*]-α-*methylthioacrylate* (33).—(a) *From the thiazinecarboxylate* (4). The thiazinecarboxylate (4) [3] (0.217 g, 1 mmol) was treated with potassium t-butoxide followed by iodomethane as for the derivative (1) [procedure (*a*)]. Work-up as before afforded a 1 : 1 mixture (n.m.r. spectroscopy) of the starting material and a new substance. Silica-gel chromatography [C_6H_6–Et_2O (5 : 1) as eluant] yielded the *methylthioacrylate* (33) (0.103 g, 45%) as a chromatographically homogeneous syrup, $[\alpha]_D$ 0° (0.9% in $CHCl_3$), $\nu_{max.}$ (film) 3 400br (NH), 1 720 (unsat. ester C=O), 1 690 (vinylogous urethane C=O), and 1 610 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 207 (ε 5 000), 284 (5 500), and 319sh nm (3 600), δ ($CDCl_3$) 2.18 (3 H, s, SMe), 3.77 and 3.85 (each 3 H, s, 2 CO_2Me), 5.14 and 5.48 (each 1 H, d, *J* 2.2 Hz, vinylic H_2), and 8.0br (2 H, s, NH and vinylic H), *m/e* (base peak) 231 (Found: M^+, 231.0565. $C_9H_{13}NO_4S$ requires *M*, 231.0565).

(b) *From the thiazolinylacrylate* (20). The thiazolinylacrylate (20) (0.105 g, 0.41 mmol) was treated with methanolic 0.9M-sodium methoxide (5 cm^3) at 0 °C. After 5 min the mixture was diluted with ether and washed with M-hydrochloric acid. Evaporation of the dried ($MgSO_4$) organic layer left a residue which was purified by silica-gel chromatography [C_6H_6–Et_2O (1 : 1) as eluant]. The derived material (0.041 g, 44%) was identical (t.l.c.; i.r. and n.m.r. spectroscopy) with the methylthioacrylate (33).

(c) *From the thiazolinylacrylate* (21). The thiazolinylacrylate (21) (0.037 g, 0.15 mmol) was treated with sodium methoxide as in procedure (*b*). Work-up as before gave a syrup (0.034 g, 90%) identical (t.l.c.; i.r. and n.m.r spectroscopy) with the methylthioacrylate (33).

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