The chemistry of 5-oxodihydroisoxazoles. Part 22.[1] The synthesis of 1,3-oxazin-6-ones from *N*-thioacylisoxazol-5(2*H*)-ones

David S. Millan and Rolf H. Prager *

Department of Chemistry, Flinders University of South Australia, GPO Box 2100, Adelaide, Australia 5001

Received (in Cambridge) 15th June 1998, Accepted 4th August 1998

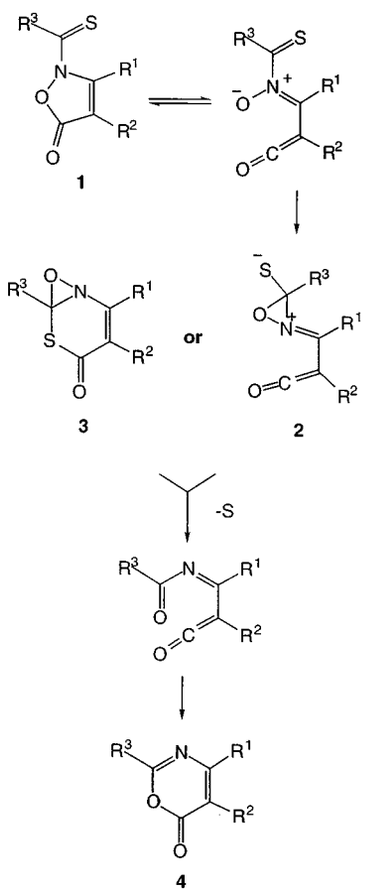
N-Thioacylisoxazol-5(2*H*)-ones, prepared by the reaction of thiocarbonyl chlorides with isoxazol-5(2*H*)-ones in the presence of base, are reduced by triphenylphosphine to afford 1,3-oxazin-6-ones and triphenylphosphine sulfide. If the thioacylation is carried out with phenyl chlorodithioformate, the thermal rearrangement of the intermediate, to again form the oxazin-6-one and sulfur, is so rapid that the use of the phosphine is not required. The presence of an ethoxycarbonyl group at C-3, or of a bromine atom at C-4 of the isoxazolone results in the formation of thiazoles.

Introduction

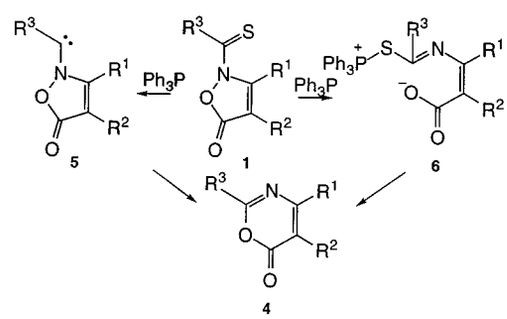
Over the last few years isoxazol-5(2*H*)-ones have been used to develop new syntheses of a variety of heterocyclic systems including pyrimidines,[2] pyrroles, furans, thiophenes, and their benzo analogues,[3] and more recently oxazoles[4] and thiazoles.[5] Several reports[6–13] have shown that these compounds may be used as starting materials for simple and high yielding syntheses of 1,3-oxazin-6-ones, but by totally different pathways to those described herein. Alkynes and other dienophiles[14] add smoothly to 1,3-oxazin-6-ones in cycloaddition reactions and hence 1,3-oxazin-6-ones are useful intermediates in the synthesis of several heterocyclic systems[15–21]—it would therefore be useful to find a general procedure for their synthesis. During the synthesis of some *N*-thioacylisoxazol-5-ones[5] **1** we noted that several 1,3-oxazin-6-ones **4** were produced concomitantly in moderate to high yields. It was suggested[5] that thermal loss of sulfur occurred through either of the intermediates **2** or **3** (Scheme 1).

In our earlier report[5] we were unable to predict the substitution patterns in *N*-thioacylisoxazolones **1** which would lead to 1,3-oxazin-6-ones **4** cleanly, and hence this paper has two aims. The first is to determine the range of 1,3-oxazin-6-ones **4** formed thermally from the *N*-thioacylisoxazolones **1** and secondly to find a general procedure that converts the thermally stable isoxazolones to 1,3-oxazin-6-ones.

Koketsu[22] reported the reduction of several thioketones with triphenylphosphine, and Davis[23] reported that reaction of ethylene sulfide with triphenylphosphine resulted in the elimination of sulfur and formation of olefins. More relevant is the Corey–Winter reaction,[24] in which a cyclic thionocarbonate, derived from a vicinal diol, is converted to the alkene and carbon dioxide in the presence of a phosphite. To the best of our knowledge the reaction of phosphines with thiocarbamates has not been reported, but extrapolation of the above observations suggested a phosphine might desulfurise *N*-thioacylisoxazolones **1**, leading to 1,3-oxazin-6-ones **4**, involving either an intermediate carbene **5**[24] or a zwitterionic intermediate **6** (Scheme 2). We herein report that *N*-thioacylisoxazolones generally react with triphenylphosphine at room temperature or in boiling benzene to give 1,3-oxazin-6-ones.



Scheme 1

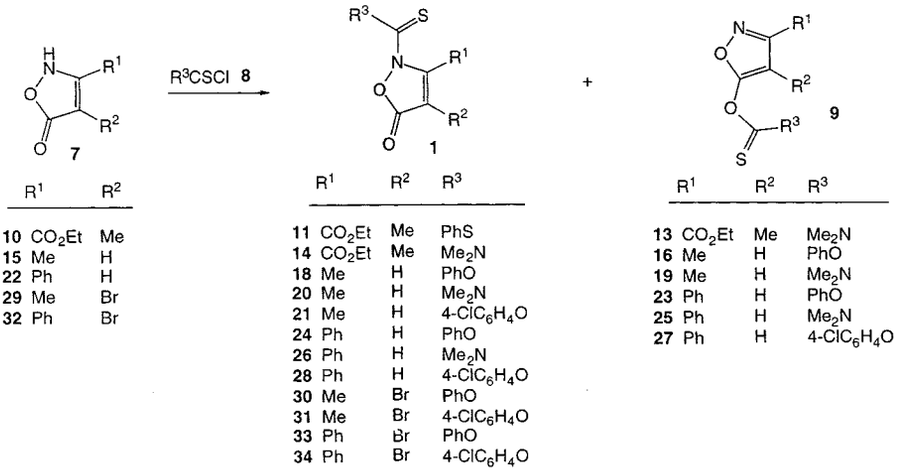


Scheme 2

Results and discussion

Further synthesis of *N*-thioacylisoxazol-5-ones, 1

We have reported[5] that isoxazol-5(2*H*)-ones **7** react with thiocarbonyl chlorides **8** in the presence of amines, such as pyridine,



Scheme 3

Table 1 Thioacylation of isoxazol-5-ones

Isoxazolone	Thiocarbonyl chloride	Amine base	*O*-Acylation Yield (%)	*N*-Acylation Yield (%)
10	PhSCSCl	Pyridine	(0)	**11** (16); **12** (82)
	Me_2NCSCl	Pyridine	**13** (17)	**14** (60)
15	PhOCSCl	Triethylamine	**16** (27)[a]; **17** (5)	**18** (65)[a] (72)[b]
	PhOCSCl	*N*,*N*-Diisopropylethylamine	(0)	**18** (97)
	Me_2NCSCl	Triethylamine	**19** (9)	**20** (45)
	4-ClPhOCSCl	*N*,*N*-Diisopropylethylamine	(0)	**21** (99)
22	PhOCSCl	Triethylamine	**23** (67)	**24** (27)
	PhOCSCl	*N*,*N*-Diisopropylethylamine	**23** (29)	**24** (43)
	Me_2NCSCl	Triethylamine	**25** (16)	**26** (42)
	4-ClPhOCSCl	*N*,*N*-Diisopropylethylamine	**27** (15)	**28** (52)
29	PhOCSCl	Pyridine	(0)	**30** (95)
	4-ClPhOCSCl	Pyridine	(0)	**31** (82)
32	PhOCSCl	Pyridine	(0)	**33** (100)
	4-ClPhOSCCl	Pyridine	(0)	**34** (88)

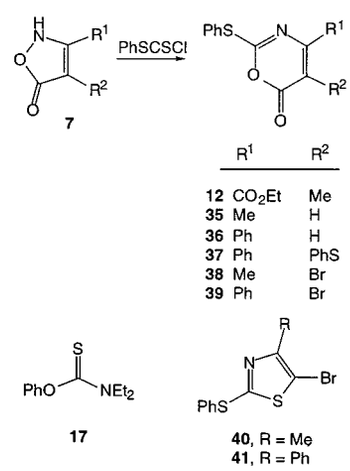
[a] Yield obtained prior to isomerisation. [b] Yield obtained after isomerisation.

to give the *N*-thioacylated derivatives **1** in moderate to good yields with little competing formation of the *O*-thioacylated isomer **9**. This procedure has now been extended by the synthesis of several new *N*-thioacylisoxazol-5-ones (Scheme 3, Table 1).

When the thioacylation of 3-methylisoxazol-5-one **15** was carried out in the presence of triethylamine,[25] the *N*- and *O*-thioacylated products **18** and **16** were obtained, contaminated with a little **17**. However, **16** was isomerised totally to the *N*-acylated isoxazolone **18** in deuterochloroform overnight. The thiocarbamate **17** arises by dealkylation of triethylamine by phenyl chlorothionoformate,[26–28] and hence *N*,*N*-diisopropylethylamine was used instead, giving the *N*-acylated material **18** essentially quantitatively.

N-Thioacylation of the more hindered 3-phenylisoxazolone **22** also proved difficult,[25] as shown in Table 1, and only 27% of the *N*-thioacylated isoxazolone **24** was obtained when triethylamine was used as the base. None of the thiocarbamate **17** was isolated from the reaction, presumably because thioacylation of the isoxazolone **22** occurred faster than dealkylation of the tertiary amine. However, when *N*,*N*-diisopropylethylamine was employed, the ratio of *N* to *O*-thioacylation increased to yield 43% of *N*-thioacylisoxazolone **24**. *O* to *N*-acyl group transfer could not be induced. As hoped, thioacylation on nitrogen of the brominated isoxazolones **29** and **32** proceeded smoothly without *O*-thioacylation, affording excellent yields of *N*-thioacylated isoxazolones (Table 1).

While the thiocarbonyl chlorides generally reacted with the isoxazolones **7** to give mixtures of *N* and *O*-thioacylated products initially, as reported above, the reaction at room temperature of phenyl chlorodithioformate with all of the isoxazolones



Scheme 4

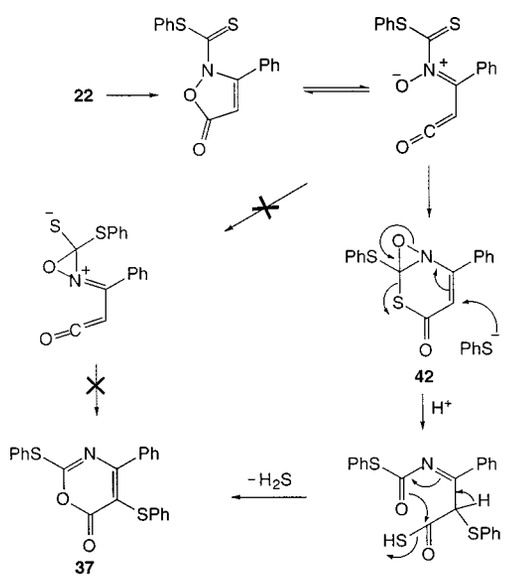
7, used herein, led to the formation of the corresponding 1,3-oxazin-6-ones in varying yields (Scheme 4 and Table 2). The yields of oxazines **36** and **37** were unexpectedly low, and it is probable that the remaining material had undergone thioacylation at C-4, followed by decomposition during chromatographic work-up. Reaction of phenyl chlorodithioformate with the brominated isoxazolones **29** and **32** gave oxazines **38** (13%) and **39** (36%), respectively, but also yielded the thiazoles **40** (14%) and **41** (36%),[29] presumably by thermal extrusion of carbon dioxide. This result is unprecedented as thiazoles had previously been obtained only after photolysis of *N*-thioacylisoxazolones.[5] It is possible that the bromine atom lowers the

Table 2 Reaction of phenyl chlorodithioformate with isoxazol-5(2*H*)-ones **7**

Isoxazolone	Amine base	Product Yield (%)
10	Pyridine	**12** (94)
15	Triethylamine	**35** (32)
22	Triethylamine	**36** (29); **37** (7)
29	Pyridine	**38** (13); **40** (14)
32	Pyridine	**39** (36); **41** (36)

activation energy required for thermal extrusion of carbon dioxide; the corresponding oxazole formation from 2-acylisoxazolones requires flash vacuum pyrolysis at 500 °C.[4]

We previously[5] reported the synthesis of ethyl 5-methyl-6-oxo-2-phenylsulfanyl-6*H*-1,3-oxazine-4-carboxylate **12** after reaction of isoxazolone **10** with phenyl chlorodithioformate at 80 °C, but when this reaction was repeated it was noted that the 1,3-oxazin-6-one **12** could be isolated in 94% yield, even when the reaction was carried out at room temperature. However, at 0 °C the presumed intermediate *N*-thioacylated isoxazolone **11** (16%), and 1,3-oxazin-6-one **12** (82%) were formed, but isoxazolone **11** was totally converted to oxazine **12** at room temperature over 2 h. This suggests that the oxazine **12**, reported from the photolysis of isoxazolone **11**,[5] arose not from a photochemical process, but thermally. The reaction of isoxazolone **22** with phenyl chlorodithioformate gave the oxazines **36** and **37**. While the formation of oxazine **37** is unprecedented, it appears to be consistent only with the pathway for oxazine synthesis through the epoxythiazine intermediate **42**, shown in Scheme 5.

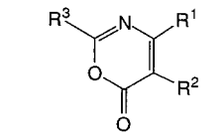


Scheme 5

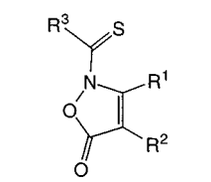
Synthesis of 1,3-oxazin-6-ones 4 with triphenylphosphine

The conversion of most *N*-thioacylisoxazolones **1** to 1,3-oxazin-6-ones **4** proceeded smoothly by stirring the isoxazolone with triphenylphosphine for 16 h at room temperature. The results and conditions necessary are compiled in Table 3, and a number of anomalies are discussed below.

In the reaction of **14** with triphenylphosphine, two compounds were obtained: the basic thiazole **46** (25%), and the neutral oxazine **45** (11%). This is the only time that a thiazole has been produced from its corresponding *N*-thioacylisoxazolone on reaction with triphenylphosphine. Since this reaction appears to require both the amino and the ethoxycarbonyl groups, it is unlikely to involve carbenoid intermediates, and we suggest the pathway shown in Scheme 6, which is clearly dependent on the presence of the ethoxycarbonyl group.



	R^1	R^2	R^3
44	CO_2Et	Me	PhO
45	CO_2Et	Me	Me_2N
48	CO_2Et	Me	4-ClC_6H_4O
49	Me	H	PhO
50	Me	H	Me_2N
51	Me	H	4-ClC_6H_4O
53	Ph	H	PhO
54	Ph	H	Me_2N
55	Ph	H	4-ClC_6H_4O
56	Ph	Br	PhO
57	Ph	Br	4-ClC_6H_4O



	R^1	R^2	R^3
43	CO_2Et	Me	PhO
47	CO_2Et	Me	4-ClC_6H_4O
58	H	CO_2Et	PhO
61	H	CO_2Et	PhS

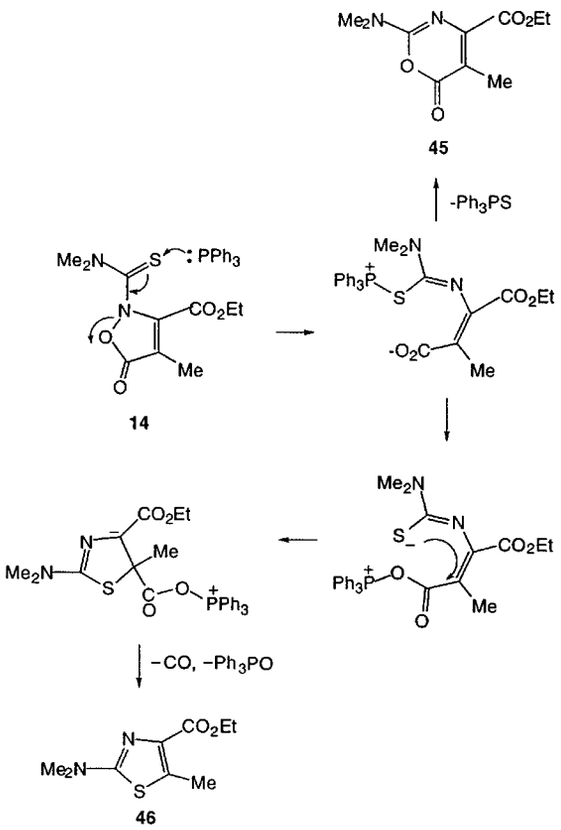
Table 3 Synthesis of 1,3-oxazin-6-ones **4**

Isoxazolone	Conditions	Product[a] Yield (%)
43	16 h, r.t.	**44** (73)
14	48 h, 110 °C, toluene	**45** (11); **46** (25)
47	16 h, r.t.	**48** (85)
18	16 h, r.t.	**49** (73)
20	48 h, 110 °C, toluene	**50** (46)
21	16 h, r.t.	**51** (20) [82];[b] **52** (18)
24	16 h, r.t.	**53** (11) [66][b]
26	48 h, 110 °C, toluene	**54** (56)
28	16 h, r.t.	**55** (11) [43][b]
30	16 h, r.t.	Decomposition
31	16 h, r.t.	Decomposition
33	16 h, r.t.	**56** (0) [71][b]
34	16 h, r.t.	**57** (25)
58	16 h, r.t.	**59** (28); **60** (6)
61	16 h, r.t.	**62** (7); **63** (22); **64** (30)

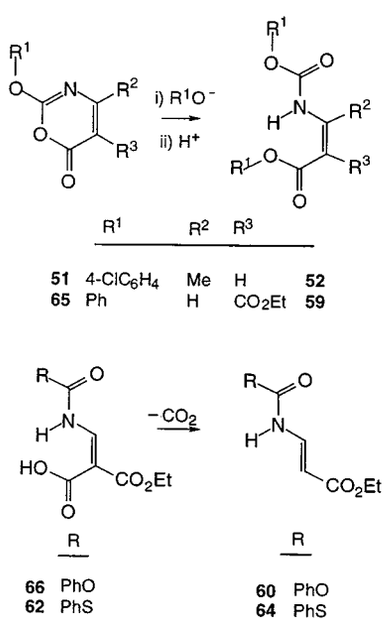
[a] Isolated yield. [b] Decomposed on work-up; yield of crude material in square brackets.

The oxazines **53**, **55** and **56** were contaminated by triphenylphosphine sulfide, even after chromatography. Since trifluoroacetic anhydride (TFAA) converts triphenylphosphine sulfide to the more polar oxide,[30] these mixtures were stirred with TFAA which allowed removal of the phosphine oxide by chromatography, but also led to decomposition of oxazine **56**, while oxazines **53** and **55** were isolated in low yield, due to some decomposition. Subsequent reactions of the oxazines could frequently be carried out in the presence of the phosphine sulfide.

It was noted that oxazine **51** was partially converted to the butenoate **52** during work-up (Scheme 7). The origin of the required *p*-chlorophenoxide is unclear but probably arises by decomposition of the excess thiocarbonyl chloride. When isoxazolone **58** was reacted with triphenylphosphine no oxazine product **65** could be detected. Instead two ring-opened compounds **59** and **60** were isolated. The propenoate **60** probably arises by attack of water on the intermediate oxazine **65** to give



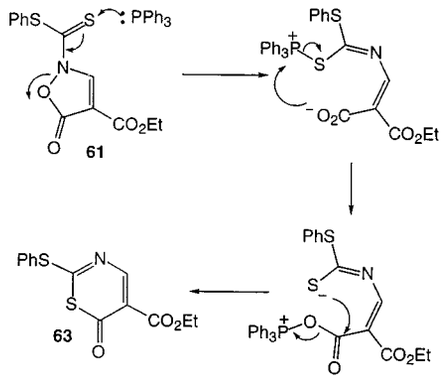
Scheme 6



Scheme 7

the malonate derivative **66** which spontaneously decarboxylates to give the propenoate **60**. The ready hydrolysis of the oxazine-5-carboxylate **65** suggests that these compounds are particularly labile at C-6.

The reaction of isoxazolone **61** with triphenylphosphine gave three products, two of which were the malonate **62** and the propenoate **64**. The third product was the unprecedented 1,3-thiazin-6-one **63**, which is thought to have originated by the pathway shown in Scheme 8. The structure for **63** was confirmed by ^{1}H NMR analysis and more specifically by observation of the H-4 proton resonating at 8.66 ppm which is consistent with literature values.[31] Carbon-13 atoms resonating at δ_C 112.0, 157.6, 176.5 and 189.7 are consistent with literature values[31] for C5, C4, C2 and C6, respectively. Stretching frequencies of ν_{max} 1602 and 1456 cm^{-1} were also consistent with known[31] 1,3-thiazin-6-ones.



Scheme 8

The mechanism postulated in Scheme 2 for the phosphine reaction has been suggested to involve either a carbene intermediate **5** or the zwitterionic intermediate **6**. Since all isoxazolones **1** probably follow a single pathway, the above observations support the pathway involving intermediate **6**. The conversion of the electron rich isoxazolones **20** and **26** to their corresponding oxazines **50** and **54** required elevated temperatures, suggesting that the initial step in the synthesis of the 1,3-oxazin-6-ones **4** is nucleophilic attack of phosphorous on the sulfur of the *N*-thioacylisoxazolone **1**, as has been assumed in Schemes 6 and 8.

Finally, spectral data obtained for the oxazine **45** was different to that reported in our previous paper[5] and it is now thought that the product isolated from the photolysis reaction was actually the unreacted *O*-thioacylated isoxazole **13**. Hence it is clear that oxazines arise by a thermal, and not a photochemical process.

In conclusion, the reaction of isoxazol-5(2*H*)-ones with thiocarbonyl chlorides gives *N*-acylisoxazolones **1** which afford 1,3-oxazin-6-ones **4** in fair to good yields on treatment with triphenylphosphine. The use of phenyl chlorodithioformate leads to the formation of 1,3-oxazin-6-ones directly by thermal loss of elemental sulfur.

Experimental

General Experimental procedures have been described previously.[4] All commercially available thiocarbonyl chlorides were purchased either from the Sigma/Aldrich Chemical Company or Merck Chemicals. Ether refers to diethyl ether, and light petroleum refers to the fraction boiling in the range 40–60 °C.

Typical thioacylation: 2-phenoxythiocarbonyl-3-methylisoxazol-5(2*H*)-one 18

Phenyl chlorothionoformate (0.383 g; 0.31 mL; 2.22 mmol) and triethylamine (0.22 g; 0.31 mL; 2.22 mmol) were added to a solution of 3-methylisoxazol-5(2*H*)-one **15**[32] (0.2 g; 2.02 mmol) in benzene (10 mL) and the solution stirred at room temperature for 16 h. The solvent was removed and the residue diluted with dichloromethane–ether (1:4) (10 mL) and washed with water (5 mL), dried and evaporated. The residue was subjected to radial chromatography (dichloromethane–light petroleum, 1:4) on silica. The first fraction, obtained as a cream solid, was a mixture of *3-methyl-5-phenoxythiocarbonyloxyisoxazole* **16** (27%) and *O*-phenyl *N*,*N*-diethylthiocarbamate **17**[26] (0.125 g, 5%).

Isoxazole **16**: (Found: M$^+$, 235.0304. $C_{11}H_9NO_3S$ requires *M*, 235.0303). Spectral data is given in Table 5.

When the mixture was allowed to stand in chloroform overnight at room temperature, the isoxazole **16** isomerised totally to the isoxazolone **18**.

Table 4 2-Thioacylisoxazol-5(2*H*)-ones,[a] **1**

Compound	R^1	R^2	R^3	Mp (°C)	Yield (%)	δ_H	δ_C	ν_{max}/cm^{-1} (CO)
11	CO_2Et	Me	PhS	Oil	11	1.31 (3H, t, *J* 7.0), 1.98 (3H, s), 4.32 (2H, q, *J* 7.0), 7.40–7.63 (5H, m)	6.9, 13.5, 63.5, 110.4, 128.0, 129.8, 131.2, 136.6, 145.9, 158.8, 165.9, 190.7	NA
14	CO_2Et	Me	Me_2N	Oil	60	1.36 (3H, t, *J* 7.2), 2.13 (3H, s), 3.48 (3H, br s), 4.37 (2H, q, *J* 7.2)	7.8, 13.4, 43.0, 62.2, 114.4, 151.2, 158.3, 169.7, 180.7	1766, 1739
18	Me	H	PhO	92–94	97	2.72 (3H, d, *J* 1.2), 5.50 (1H, q, *J* 0.9), 7.09–7.12 (2H, m), 7.30–7.35 (1H, m), 7.40–7.48 (2H, m)	17.7, 97.6, 122.0, 127.0, 129,7, 151.9, 158.7, 164.6, 176.6	1794
20	Me	H	Me_2N	66–68	45	2.45 (3H, s), 3.43 (6H, s), 5.36 (1H, s)	16.1, 43.1, 96.2, 165.0, 168.5, 177.0	1744
21	Me	H	4-ClPhO	98–100	99	2.74 (3H, s), 5.53 (1H, d, *J* 0.9), 7.04–7.09 (2H, m), 7.39–7.44 (2H, m)	17.8, 98.0, 123.6, 129.8, 132.7, 150.3, 158.9, 164.4, 176.2	1773
24	Ph	H	PhO	141–143	43	5.71 (1H, s), 6.92–7.00 (2H, m), 7.22–7.64 (8H, m)	98.7, 121.6, 126.9, 128.1, 128.5, 128.6, 129.6, 131.2, 152.0, 160.8, 165.3, 178.3	1771
26	Ph	H	Me_2N	148–150	42	3.39 (3H, s), 3.62 (3H, s), 5.80 (1H, s), 7.41–7.52 (5H, m)	42.3, 43.6, 96.5, 127.2, 129.0, 129.3, 131.5, 168.2, 169.1, 180.3	1745
28	Ph	H	4-ClPhO	146–148	52	5.73 (1H, s), 6.84–6.92 (2H, m), 7.24–7.36 (2H, m), 7.38–7.58 (5H, m)	99.0, 123.2, 128.1, 128.6, 129.8, 131.3, 132.6, 150.4, 160.8, 165.2, 177.8	1774
30	Me	Br	PhO	124–126	95	2.83 (3H, s), 7.09–7.16 (2H, m), 7.32–7.42 (1H, m), 7.43–7.51 (2H, m)	17.6, 90.9, 122.1, 127.4, 129.9, 152.0, 155.5, 161.7, 176.4	1780
31	Me	Br	4-ClPhO	154–156	82	2.83 (3H, s), 7.03–7.11 (2H, m), 7.39–7.47 (2H, m)	17.7, 91.2, 123.5, 130.0, 133.0, 150.3, 155.5, 161.5, 175.8	1780
33	Ph	Br	PhO	154–156	99	6.86–6.94 (2H, m), 7.22–7.30 (1H, m), 7.30–7.40 (2H, m), 7.48–7.62 (5H, m)	91.9, 121.6, 127.2, 127.9, 128.6, 128.8, 129.7, 131.5, 152.1, 156.3, 162.8, 177.6	1776
34	Ph	Br	4-ClPhO	Oil	88	6.8–6.9 (2H, m), 7.24–7.34 (2H, m), 7.44–7.60 (5H, m)	92.0, 123.0, 128.5, 128.5, 128.7, 129.8, 131.5, 132.6, 150.2, 154.3, 162.0, 177.4	1774

[a] All compounds gave satisfactory CHN analyses (solids) or high resolution mass spectral data (liquids).

Table 5 Thiocarbonyloxyisoxazoles, **9**[a]

Compound	R^1	R^2	R^3	Mp (°C)	Yield (%)	δ_H	δ_C
13	CO_2Et	Me	Me_2N	Oil	17	1.42 (3H, t, *J* 7.2), 2.07 (3H, s), 3.39 (3H), 3.44 (3H, s), 4.44 (2H, q, *J* 7.2)	6.3, 13.7, 39.0, 43.5, 61.6, 102.2, 156.3, 159.9, 165.1, 182.1
16	Me	H	PhO	Oil	27	2.31 (3H, s), 5.94 (1H, s), 7.15–7.20 (2H, m), 7.30–7.36 (1H, m), 7.42–7.48 (2H, m)	12.4, 90.8, 121.3, 127.3, 129.9, 153.3, 162.3, 165.7, 188.9
19	Me	H	Me_2N	Oil	9	2.30 (3H, s), 3.34 (3H, s), 3.43 (3H, s), 5.80 (1H, s)	12.4, 39.2, 43.6, 91.4, 162.2, 166.8, 182.7
23	Ph	H	PhO	Oil	67	6.41 (1H, s), 7.16–7.22 (2H, m), 7.28–7.36 (1H, m), 7.40–7.48 (5H, m), 7.78–7.84 (2H, m)	88.5, 121.2, 126.5, 127.3, 128.7, 128.9, 129.9, 130.5, 153.3, 164.3, 166.2, 188.7
25	Ph	H	Me_2N	91–92	16	3.53 (3H, s), 3.44 (3H, s), 6.29 (1H, s), 7.42–7.48 (3H, m), 7.76–7.84 (2H, m)	39.3, 43.6, 89.1, 126.5, 128.9, 129.2, 130.3, 164.1, 167.3, 182.6
27	Ph	H	4-ClPhO	97–98	27	6.42 (1H, s), 7.12–7.20 (2H, m), 7.40–7.52 (5H, m), 7.78–7.84 (2H, m)	88.5, 122.9, 126.6, 128.7, 129.0, 130.1, 130.6, 133.1, 151.7, 164.4, 166.1, 188.5

[a] All compounds gave satisfactory CHN analyses (solids) or high resolution mass spectral data (liquids).

The second fraction was recrystallised from dichloromethane–ether–light petroleum as tan cubic crystals, identified as the *title compound* **18** (0.31 g, 72%), mp 92–94 °C (Found: C, 56.4; H, 4.0; N, 6.1%; M^+, 235.0304. $C_{11}H_9NO_3S$ requires C, 56.2; H, 3.8; N, 6.0%; *M*, 235.0303); *m*/*z* 235 (M, <1%), 203 (5), 191 (23), 137 (40), 118 (25), 110 (100), 109 (22), 94 (25), 77 (64). The spectral data is given in Table 4.

When the reaction was repeated using *N*,*N*-diisopropylethylamine (0.29 g; 0.357 mL; 2.22 mmol) in place of triethylamine, the title compound **18** was obtained as tan cubic crystals (0.46 g; 97%).

Further examples are given in Tables 4 and 5, and the relevant base used may be seen from Table 1.

Reaction of 3-methylisoxazol-5(2*H*)-one 15 with phenyl chlorodithioformate

The major fraction, identified as *4-methyl-2-phenylsulfanyl-6H-1,3-oxazin-6-one* **35**, was obtained as a yellow solid which was recrystallised from ether–light petroleum as yellow cubic crystals (0.14 g; 32%), mp 89–90 °C (Found: C, 60.1; H, 3.9; N, 6.4. $C_{11}H_9NO_2S$ requires C, 60.3; H, 4.1; N, 6.4%); *m*/*z* 219

Table 6 1,3-Oxazin-6-ones, **4**[a]

Compound	R^1	R^2	R^3	Mp (°C)	Yield (%)	δ_H	δ_C	ν_{max}/cm^{-1} (CO)
12	CO_2Et	Me	PhS	61–63	94	1.33 (3H, t, *J* 6.9), 2.18 (3H, s), 4.32 (2H, q, *J* 6.9), 7.40–7.52 (3H, m), 7.58–7.66 (2H, m)	11.8, 13.9, 62.2, 117.8, 125.4, 129.6, 130.5, 135.4, 148.5, 160.4, 163.8, 167.4	1751
38	Me	Br	PhS	140–144	13	2.26 (3H, s), 2.29 (3H, s), 7.39–7.52 (3H, m), 7.53–7.63 (2H, m)	21.6, 24.2, 102.4, 125.3, 129.7, 130.8, 135.4, 155.4, 155.4, 161.5, 164.0, 167.0, 168.1	1766
39	Ph	Br	PhS	Oil	36	7.31–7.52 (6H, m), 7.57–7.65 (2H, m), 7.69–7.81 (2H, m)	100.6, 110.8, 125.4, 125.5, 128.0, 128.2, 129.6, 129.7, 129.7, 130.7, 131.2, 131.3, 133.8, 135.2, 135.4, 135.5, 156.5, 156.8, 157.1, 160.2, 166.6, 167.9	1759
35	Me	H	PhS	89–90	32	2.12 (3H, d, *J* 1.2), 5.78 (1H, q, *J* 0.9), 7.41–7.53 (3H, m), 7.58–7.61 (2H, m)	23.4, 102.9, 125.5, 129.6, 130.5, 135.5, 158.5, 166.5, 170.3	1762
36	Ph	H	PhS	117–118	29	6.35 (1H, s), 7.34–7.56 (6H, m), 7.62–7.78 (4H, m)	98.5, 126.0, 127.4, 128.9, 129.6, 130.5, 132.0, 133.9, 135.7, 159.4, 161.5, 170.9	1745
37	Ph	PhS	PhS	172–174	7	6.64–6.70 (2H, m), 7.00–7.07 (2H, m), 7.12–7.42 (11H, m)	112.6, 128.3, 128.4, 128.5, 129.3, 129.4, 129.5, 129.8, 129.9, 130.5, 132.2, 134.1, 161.3, 167.9, 174.9	1743
44	CO_2Et	Me	PhO	90–92	73	1.32 (3H, t, *J* 6.9), 2.19 (3H, s), 4.31 (2H, q, *J* 7.2), 7.25–7.42 (5H, m)	11.6, 13.8, 62.2, 115.1, 120.9, 126.7, 129.7, 150.6, 151.0, 156.8, 160.4, 164.0	1759, 1724
45	CO_2Et	Me	Me_2N	39–40	11	1.39 (3H, t, *J* 7.2), 2.02 (3H, s), 3.14 (6H, br s), 4.38 (2H, q, *J* 7.2)	10.8, 13.9, 36.1, 37.1, 61.8, 103.8, 154.5, 157.9, 161.4, 165.5	1743, 1722
48	CO_2Et	Me	4-ClPhO	88–90	85	1.34 (3H, t, *J* 6.9), 2.19 (3H, s), 4.33 (2H, q, *J* 6.9), 7.20–7.26 (2H, m), 7.34–7.42 (2H, m)	11.7, 13.9, 62.3, 115.5, 122.4, 129.8, 132.2, 149.5, 150.3, 156.6, 160.2, 163.9	1772, 1721
49	Me	H	PhO	190–192	73	2.11 (3H, d, *J* 0.9), 5.83 (1H, q, *J* 0.9), 7.20–7.26 (2H, m), 7.27–7.33 (1H, m), 7.40–7.48 (2H, m)	23.6, 100.9, 121.1, 126.7, 129.8, 151.1, 158.7, 159.0, 169.4	1705
50	Me	H	Me_2N	82–86	46	2.07 (3H, d, *J* 0.6), 3.11 (6H, br s), 5.33 (1H, q, *J* 0.6)	24.1, 35.9, 37.8, 92.8, 159.2, 160.1, 170.9	1749
51	Me	H	4-ClPhO	Oil	20 (82)[b]	2.12 (3H, d, *J* 0.9), 5.84 (1H, q, *J* 0.9), 7.15–7.22 (2H, m), 7.38–7.43 (2H, m)	23.7, 101.2, 122.7, 129.9, 132.3, 149.5, 158.5, 158.8, 169.2	1778
53	Ph	H	PhO	72–76	11 (66)[b]	6.43 (1H, s), 7.24–7.58 (8H, m), 7.76–7.86 (2H, m)	97.0, 121.2, 126.7, 127.4, 128.9, 129.8, 132.2, 134.1, 151.3, 159.5, 159.5, 164.4	1762
54	Ph	H	Me_2N	114–118	56	3.19 (3H, s), 3.28 (3H, s), 5.98 (1H, s), 7.40–7.52 (3H, m), 7.92–7.82 (2H, m)	36.1, 37.3, 89.6, 127.2, 128.6, 131.3, 136.1, 159.3, 161.0, 166.3	1740
55	Ph	H	4-ClPhO	120–124	11 (43)[b]	6.44 (1H, s), 7.24–7.32 (2H, m), 7.38–7.58 (6H, m), 7.76–7.82 (2H, m)	97.2, 122.7, 127.3, 129.0, 129.9, 132.2, 132.4, 133.9, 149.7, 159.0, 159.2, 164.2	1770
56	Ph	Br	PhO	NA	0 (71)[b]	7.24–7.31 (2H, m), 7.33–7.52 (8H, m)	97.9, 120.8, 126.8, 128.0, 129.4, 129.8, 131.2, 135.3, 151.1, 156.4, 156.9, 162.2	
57	Ph	Br	4-ClPhO	140–141	25	7.21–7.29 (2H, m), 7.38–7.53 (5H, m), 7.78–7.84 (2H, m)	109.2, 122.4, 128.3, 129.6, 130.0, 131.5, 132.4, 133.9, 149.6, 155.6, 156.4, 159.0	1777

[a] All compounds gave satisfactory CHN analyses (solids) or high resolution mass spectral data (liquids). [b] Yields of crude material in parentheses.

(M, 5%), 110 (100), 70 (13). Further spectral data is given in Table 6.

The remaining material could not be identified.

Typical reaction of 2-thiocarbonylisoxazolones with triphenylphosphine: ethyl 5-methyl-6-oxo-2-phenoxy-6*H*-1,3-oxazine-4-carboxylate 44

Triphenylphosphine (0.094 g; 0.36 mmol) was added to a solution of isoxazolone **43**[5] (0.1 g; 0.33 mmol) in benzene (10 mL) and the mixture was stirred in the dark under an atmosphere of nitrogen for 16 h. The solvent was evaporated under reduced pressure. The residue was subjected to radial chromatography (dichloromethane–ether–light petroleum, 1:3:6) on silica, giving the *title compound* **44** as white needles (0.065 g; 73%), mp 90–92 °C (ether–light petroleum) (Found: C, 61.3; H, 4.8; N, 5.0%; M^+, 275.0797. $C_{14}H_{13}NO_5$ requires C, 61.0; H, 4.7; N, 5.0%; *M*, 275.0794); *m/z* 275 (M^+, 19%), 182 (100), 154 (32), 94 (21), 83 (11), 82 (30), 77 (28). Further spectral data is given in Table 6.

The compounds described in Table 6 were prepared by the above method.

Ethyl 2-dimethylamino-5-methyl-6-oxo-6*H*-1,3-oxazine-4-carboxylate 45

Triphenylphosphine (0.20 g; 0.77 mmol) was added to the mixture of thioacylated compounds **13** and **14** (0.18 g; 0.70 mmol) in toluene (5 mL) and the solution was refluxed under nitrogen in the dark. After 48 h the solvent was evaporated and the oil was subjected to radial chromatography on silica (ether–dichloromethane–light petroleum, 1:1:8) to give a major frac-

tion (0.07 g), which still contained two compounds. The oil was redissolved in ether (10 mL) and washed with 2 M HCl (5 mL), and the ethereal layer dried and the solvent evaporated. The pale green solid was recrystallised from ether–light petroleum as white needles (0.038 g; 11%), mp 39–40 °C, identified as the *title compound* **45** (Found: C, 53.1; H, 6.0; N, 12.3%; M^+, 226.0953. $C_{10}H_{14}N_2O_4$ requires C, 53.1; H, 6.2; N, 12.4%; *M* 226.0955). Further spectral data is collected in Table 6.

The aqueous layer was basified ($NaHCO_3$) and extracted with ether (2 × 10 mL) and the extract dried and evaporated affording a colourless oil identified as ethyl 2-dimethylamino-5-methylthiazole-4-carboxylate **46** (0.036 g; 25%) by direct comparison with an authentic sample.[5] (Found: M^+, 214.0777. Calc. for $C_9H_{14}N_2O_2$: *M*, 214.0776).

Reaction of isoxazolone 21 with triphenylphosphine

Isoxazolone **21** (0.1 g; 0.37 mmol) and triphenylphosphine (0.11 g; 0.41 mmol) were reacted in the usual way. Radial chromatography (dichloromethane–light petroleum, 1:4) on silica gave two fractions: the first was *4-chlorophenyl (Z)-3-[(4-chlorophenoxy)carbonylamino]but-2-enoate* **52** as white needles (0.024 g; 18%), mp 141–142 °C (ether–light petroleum) (Found: $M^+ - C_6H_4ClO$, 238.0262. $C_{11}H_9{}^{35}ClNO_3$ requires *M*, 238.0271); δ_H 2.12 (3H, d, *J* 0.9), 5.35 (1H, s), 7.06–7.16 (2H, m), 7.30–7.40 (2H, m), 11.27 (1H, br s); δ_C 21.3, 95.6, 122.9, 123.2, 129.6, 131.4, 131.5, 148.79, 148.9, 150.8, 157.1, 167.5; ν_{max}/cm^{-1} 3320, 1762, 1698, 1490, 1269, 1198, 1152; *m*/*z* 238 ($M - C_6H_4ClO$, 11%), 139 (14), 128 (54), 116 (13), 110 (100), 100 (32), 88 (21).

The second fraction was a colourless oil, identified as *2-(4-chlorophenoxy)-4-methyl-6H-1,3-oxazin-6-one* **51** (0.018 g; 20%) (Found: M^+, 237.0191. $C_{11}H_8{}^{35}ClNO_3$ requires *M*, 237.0193); *m*/*z* 237 (M, 3%), 128 (23), 110 (100). Further spectral data is given in Table 6.

2-Phenoxy-4-phenyl-6*H*-1,3-oxazin-6-one 53

Isoxazolone **24** (0.1 g; 0.34 mmol) was reacted with triphenylphosphine (0.097 g; 0.37 mmol) in the usual way. Trifluoroacetic anhydride (2 mL) was added to the solid residue (0.2 g) in dichloromethane (10 mL) and the solution stirred for 6 h. The solvent was evaporated under reduced pressure and the oil was subjected to radial chromatography (dichloromethane–light petroleum, 1:4) on silica. The *title compound* was isolated as a pale green oil which later solidified (10 mg, 11%), mp 72–76 °C (Found: M^+, 265.0742. $C_{16}H_{11}NO_3$ requires *M*, 265.0739); *m*/*z* 265 (M, 2%), 204 (10), 172 (52), 146 (46), 105 (39), 94 (100). Further spectral data is collected in Table 6.

Reaction of 4-bromo-3-methylisoxazol-5(2*H*)-one 29 with phenyl chlorodithioformate

Phenyl chlorodithioformate (0.21 g; 0.16 mL; 1.12 mmol) and pyridine (0.089 g; 0.091 mL; 1.12 mmol) were added to a solution of isoxazolone **29**[25] (0.2 g; 1.12 mmol) in benzene (10 mL) and the solution was stirred in the dark under nitrogen. After 16 h at room temperature the residue was subjected to radial chromatography, on silica, (dichloromethane–light petroleum, 1:4). The first fraction was a yellow oil (45 mg; 14%) identified as *5-bromo-4-methyl-2-phenylsulfanyl-1,3-thiazole* **40** (Found: M^+, 284.9281. $C_{10}H_8{}^{79}BrNS_2$ requires *M*, 284.9282); δ_H 2.34 (3H, s), 2.35 (3H, s), 7.38–7.48 (3H, m), 7.58–7.66 (2H, m); δ_C 14.4, 15.6, 104.1, 130.0, 130.0, 131.1, 131.3, 134.0, 134.1, 150.0, 152.7, 162.3, 165.3; ν_{max}/cm^{-1} 1476, 1440, 1409, 1374, 748, 691; *m*/*z* 287, 285 (M^+, 72, 74%), 241 (75), 206 (60), 121 (36), 109 (51), 77 (43), 69 (100).

The second fraction, a light brown solid (42 mg; 13%), mp 140–144 °C was *5-bromo-4-methyl-2-phenylsulfanyl-6H-1,3-oxazin-6-one* **38** (Found: M^+, 296.9473, 298.9431; $C_{11}H_8{}^{79}BrNO_2S$, $C_{11}H_8{}^{81}BrNO_2S$ requires *M*, 296.9460, 298.9440); *m*/*z* 299, 297 (M^+, 2, 3%), 218 (90), 190 (35), 188 (30), 144 (25), 110 (85), 109 (100). Other spectral data is collected in Table 6.

Reaction of 4-bromo-3-phenylisoxazol-5(2*H*)-one 32 with phenyl chlorodithioformate

Phenyl chlorodithioformate (0.16 g; 0.12 mL; 0.83 mmol) and pyridine (0.066 g; 0.067 mL; 0.83 mmol) were added to a solution of isoxazolone **32**[33] (0.2 g; 0.83 mmol) in benzene (10 mL) and the solution was stirred in the dark under nitrogen. After 16 h at room temperature the residue was subjected to radial chromatography, on silica (dichloromethane–light petroleum, 1:4). The first fraction was *5-bromo-4-phenyl-2-phenylsulfanyl-1,3-thiazole* **41**, white needles (105 mg; 36%), mp 72–75 °C (ether–light petroleum) (Found: M^+, 346.9437. $C_{15}H_{10}{}^{81}BrNS_2$ requires *M*, 346.9439); δ_H 7.80–7.48 (6H, m), 7.60–7.70 (2H, m), 7.84–7.96 (2H, m); δ_C 103.0, 128.3, 128.4, 128.4, 128.6, 128.6, 128.7, 130.1, 130.1, 130.2, 130.3, 130.6, 130.7, 132.5, 133.0, 134.5, 134.6, 150.5, 153.2, 163.6, 166.7; ν_{max}/cm^{-1} 1560, 1424, 1150; *m*/*z* 348, 346 (M^+, 21, 19%), 305 (45), 304 (33), 303 (100), 302 (44), 268 (12), 218 (20), 168 (47), 132 (91), 121 (17), 110 (25), 109 (56), 89 (52). The ^{13}C NMR spectrum at 40 °C ($CDCl_3$) reduced the six resonances seen at 22 °C *i.e.* 128.3, 128.4, 128.4, 128.6, 128.6, 128.7 ppm to four resonances at 128.4, 128.5, 128.7, 128.8 ppm. In addition, the remaining resonances approached coalescence at 40 °C.

The structure was confirmed by single crystal X-ray analysis.

The second fraction was *5-bromo-4-phenyl-2-phenylsulfanyl-6H-1,3-oxazin-6-one* **39** (107 mg; 36%), obtained as a thick yellow–green oil (Found: M^+, 358.9615, 360.9563; $C_{16}H_{10}{}^{79}BrNO_2S$, $C_{16}H_{10}{}^{81}BrNO_2S$ require *M*, 358.9616, 360.9596); *m*/*z* 361, 359 (M^+, 1, 1%), 252 (7), 250 (10), 218 (27), 206 (13), 110 (77), 109 (34), 105 (100). Additional spectral data is found in Table 6.

Reaction of ethyl 5-oxo-2-phenoxythiocarbonyl-2,5-dihydroisoxazole-4-carboxylate 58 with triphenylphosphine

Isoxazolone **58**[5] (0.1 g; 0.34 mmol) was reacted with triphenylphosphine (0.098 g; 0.38 mmol) in the usual way. The product was subjected to radial chromatography (dichloromethane–light petroleum, 1:9), on silica. The first fraction *was ethyl phenyl (Z)-2-(phenoxycarbonylaminomethylene)malonate* **59** (0.034 g, 28%), mp 110–112 °C (dichloromethane–light petroleum) (Found: $M^+ - PhO$, 262.0717. $C_{13}H_{12}NO_5$ requires *M*, 262.0715); δ_H 1.39 (3H, t, *J* 7.2), 4.37 (2H, q, *J* 7.2), 7.13–7.35 (3H, m), 7.35–7.50 (2H, m), 8.70 (1H, d, *J* 12.3), 10.80 (1H, d, *J* 12.3); δ_C 14.0, 61.6, 101.5, 121.1, 121.9, 125.9, 126.6, 129.5, 129.8, 149.7, 150.2, 150.2, 151.1, 162.7, 167.3; ν_{max}/cm^{-1} 3350, 1769, 1741, 1725, 1683, 1609, 1458, 1377, 1243, 1179; *m*/*z* 355 (M^+, 1%), 262 (31), 168 (51), 142 (11), 140 (10), 96 (13), 94 (100).

The second fraction was *ethyl (E)-3-(phenoxycarbonylamino)prop-2-enoate* **60**, white needles (5 mg; 6%), mp 136–138 °C (dichloromethane–light petroleum) (Found: M^+, 235.0844. $C_{12}H_{13}NO_4$ requires, *M* 235.0845); δ_H 1.31 (3H, t, *J* 7.2), 4.28 (2H, q, *J* 7.2), 6.13 (1H, br s), 7.08–7.28 (3H, m), 7.32–7.42 (2H, m), 8.27 (1H, dd, *J* 8.7, 8.7), 8.86 (1H, br s); δ_C 14.2, 60.1, 91.3, 122.2, 125.4, 129.4, 151.2, 159.0, 164.6, 168.8; ν_{max}/cm^{-1} 3373, 3287, 3229, 1699, 1670, 1513, 1338, 1284; *m*/*z* 235 (M^+, 2%), 190 (5), 142 (100), 114 (21), 98 (11), 94 (44).

Reaction of ethyl 5-oxo-2-phenylsulfanylthiocarbonyl-2,5-dihydroisoxazole-4-carboxylate 61 with triphenylphosphine

Isoxazolone **61**[5] (0.1 g) was reacted with triphenylphosphine (0.093 g) in the usual way. The product was subjected to radial chromatography (dichloromethane–ether–light petroleum, 1:3:7), on silica. The first fraction was *ethyl hydrogen (E)-2-(phenylsulfanylcarbonylaminomethylene)malonate* **62**, white needles (0.007 g; 7%), mp 90–92 °C (ether–light petroleum)

(Found: $M^+ - Ph$, 218.0123. $C_7H_8NO_5S$ requires *M*, 218.0125); δ_H 1.38 (3H, t, *J* 7.2), 4.37 (2H, q, *J* 7.2), 7.48–7.62 (5H, m), 9.07 (1H, d, J 11.7), 11.66 (1H, d, J 11.7); δ_C 14.0, 62.5, 96.7, 125.2, 130.1, 131.1, 135.5, 147.6, 167.9, 167.9, 170.0; ν_{max}/cm^{-1} 3210, 1719, 1693, 1594, 1459, 1377, 1264; *m*/*z* 218 ($M^+ - Ph$, 30%), 168 (10), 142 (19), 141 (12), 110 (100), 109 (70), 96 (11).

The second fraction was a yellow oil (0.021 g; 22%), *ethyl 2-phenylsulfanyl-6-oxo-6H-1,3-thiazine-5-carboxylate* **63** (Found: $M^+ - EtO$, 247.9847. $C_{11}H_6NO_2S_2$ requires *M*, 247.9840); δ_H 1.34 (3H, t, *J* 7.2), 4.33 (2H, q, *J* 7.2), 7.50–7.66 (5H, m), 8.66 (1H, s); δ_C 14.1, 61.8, 112.0, 124.5, 130.5, 132.0, 136.5, 157.6, 163.5, 176.5, 189.7; ν_{max}/cm^{-1} 1735, 1713, 1684, 1602, 1456, 1275, 1111, 983; *m*/*z* 293 (M^+, 3%), 248 (5), 218 (12), 184 (100), 110 (99).

The third fraction was a white solid (0.024 g; 30%), identified as *ethyl (E)-3-(phenylsulfanylcarbonylamino)prop-2-enoate* **64**, mp 94–96 °C (ether–light petroleum) (Found: M^+, 251.0610. $C_{12}H_{13}NO_3S$ requires *M*, 251.0616); δ_H 1.43 (3H, t, *J* 7.2), 4.36 (2H, q, *J* 7.2), 7.26–7.50 (5H, m), 8.13 (1H, dd, *J* 8.4, 8.4), 9.40 (1H, br s); δ_C 14.4, 60.1, 99.9, 129.0, 129.2, 129.9, 135.8, 156.6, 166.5, 190.7; ν_{max}/cm^{-1} 3372, 3235, 1664, 1616, 1500, 1379, 1325, 1287, 1151, 923; *m*/*z* 251 (M^+, 4%), 206 (4), 142 (100), 114 (34), 110 (40), 109 (30), 98 (14).

Acknowledgements

The authors are grateful for support from the Australian Research Council. D. S. M. acknowledges an Australian Post-graduate Award. The authors are also grateful for the single crystal X-ray analysis carried out by Dr M. R. Taylor and Shona-Marie Norman.

References

1 Part 21, M. M. Baradarani, A. Clark and R. H. Prager, *Aust. J. Chem.*, 1998, **51**, 491.
2 R. H. Prager and Y. Singh, *Aust. J. Chem.*, 1994, **47**, 1263.
3 R. H. Prager and C. M. Williams, *Aust. J. Chem.*, 1996, **49**, 1315.
4 K. H. Ang, R. H. Prager, J. A. Smith, B. Weber and C. M. Williams, *Tetrahedron Lett.*, 1996, **37**, 675; R. H. Prager, J. A. Smith, B. Weber and C. M. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1997, 2665.
5 R. H. Prager, M. R. Taylor and C. M. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1997, 2673.
6 N. Almirante, M. L. Gelmi and C. Scarpellini, *Heterocycles*, 1991, **32**, 1181.
7 E. M. Beccalli, T. Benincori and A. Marchesini, *Synthesis*, 1988, **8**, 630.
8 E. M. Beccalli and A. Marchesini, *J. Org. Chem.*, 1987, **52**, 3426.
9 E. M. Beccalli, M. L. Gelmi, T. Pilati and A. Marchesini, *J. Org. Chem.*, 1987, **52**, 1666.
10 E. M. Beccalli, A. Marchesini and H. Molinari, *Tetrahedron Lett.*, 1986, **27**, 3426.
11 E. M. Beccalli, C. La Rosa and A. Marchesini, *J. Org. Chem.*, 1984, **49**, 4287.
12 E. M. Beccalli, B. Gioia and A. Marchesini, *J. Heterocycl. Chem.*, 1980, **17**, 763.
13 F. Caruso, F. Foti, G. Grassi, G. Lo Vecchio and F. Risitano, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1522.
14 E. Buschmann, E. Jeschke and W. Steglich, *Gazz. Chim. Ital.*, 1986, **116**, 361.
15 T. Aoyama, T. Shioiri and K. Takaoka, *Tetrahedron Lett.*, 1996, **37**, 4973.
16 P. Meffert, R. Neidlein and Z. Sui, *Synthesis*, 1992, **6**, 443.
17 R. Neidlein and Z. Sui, *Synthesis*, 1991, **8**, 658.
18 D. L. Boger and R. J. Wysocki, Jr., *J. Org. Chem.*, 1989, **54**, 714.
19 E. Buschmann and W. Steglich, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 484.
20 E. Buschmann, O. Hollitzer and W. Steglich, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 533.
21 G. Hofle, O. Hollitzer and W. Steglich, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 720.
22 M. Tamano and J. Koketsu, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 2577.
23 R. R. Davis, *J. Org. Chem.*, 1958, **23**, 1767.
24 E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, 1963, **85**, 2677; E. J. Corey, F. A. Carey and R. A. E. Winter, *J. Am. Chem. Soc.*, 1965, **87**, 934.
25 R. H. Prager, J. A. Smith, B. Weber and C. M. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1997, 2659.
26 D. S. Millan and R. H. Prager, *Tetrahedron Lett.*, 1998, **39**, 4387.
27 J. D. Hobson and J. G. McCluskey, *J. Chem. Soc.* (*C*), 1967, 2015.
28 P. Pfaffli and H. Hauth, *Helv. Chim. Acta*, 1973, **56**, 347.
29 The connectivity of the molecule **41** was confirmed by a single crystal X-ray analysis, but the accuracy of the atomic coordinates does not justify their publication.
30 J. Helinski, Z. Skrzypczynski, J. Wasiak and J. Michalski, *Tetrahedron Lett.*, 1990, **28**, 4081.
31 H. Quiniou and O. Guilloton, *Adv. Heterocycl. Chem.*, 1990, **50**, 85.
32 R. Jacquier, C. Petrus, F. Petrus and J. Verducci, *Bull. Soc. Chim. Fr.*, 1970, **7**, 2685.
33 T. Posner, *Ber. Dtsch. Chem. Ges.*, 1906, **39**, 3515.

Paper 8/04527E