The Structures of 4- and 5-Substituted Δ^4-Thiazolin-2-ones

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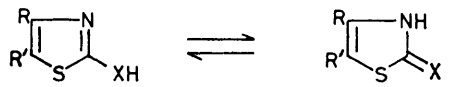
In order to establish the structures of compounds described as Δ^4-thiazolin-2-ones ten sets of heterocycles (each comprising a 4- or 5-substituted Δ^4-thiazolin-2-one, the *N*-methyl derivative, and the corresponding 2-methoxythiazole) have been examined by i.r., u.v., and ^{1}H and ^{13}C n.m.r. spectrometry. The i.r. results established that in solution the parent compounds exist entirely or predominantly as the 2-oxo-forms. This conclusion is supported by the ^{1}H n.m.r. evidence, but the u.v. and ^{13}C n.m.r. data do not give a clear distinction between the possible 2-oxo- and 2-hydroxy-structures.

THE numerous investigations into the structures of 2-substituted thiazoles of general type (I) have been reviewed,[1,2] and it is now broadly accepted that the amines exist predominantly in the amino-form (IA; X = NH) whereas the formal alcohols and thiols adopt the oxo- and thioxo-forms (IB; X = O,S). However, the literature shows that the rigour with which these conclusions have been established varies between the series. With the amines, examinations by u.v., i.r., and ^{1}H n.m.r.[3] spectrometry do not reveal the presence of the imino-forms (IB; X = NH); evidence for these, in concentrations of *ca.* 5×10^{-5}M, is restricted to pK_a measurements.[4] Similar measurements[5] of thiones indicate traces (*ca.* 10^{-6}M) of the mercapto-forms (IA; X = S) and while some i.r. work[6] suggests appreciable amounts of these forms, the spectra can be interpreted in terms of the thione forms only[7] (as can the u.v. and ^{1}H n.m.r. spectra). The Δ^4-thiazolin-2-ones have been much less



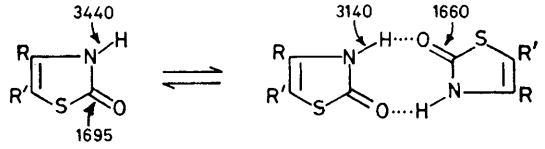
(IA) (IB)

actively studied than the others during the last two decades. Early work which suggested the predominance of the oxo-forms was based mainly on the presence of strong i.r. C=O bonds[2] (even though these are at unexpectedly low values, *ca.* 1 650 cm^{-1}), but the evidence from u.v. spectrometry is less clear-cut.[2,8] The conclusions from recent studies are difficult to reconcile; pK_a measurements[9] indicate only a trace (*ca.* 1.2×10^{-4}M) of the hydroxy-form in an aqueous solution of Δ^4-thiazolin-2-one (and, in agreement, the ^{1}H n.m.r. signals of this compound and the 4-methyl derivative in dimethyl sulphoxide solutions are satisfactorily assigned to the oxo-forms[10]), but dipole-moment measurements[11] of the 4-phenylthiazolinone in benzene indicate a preference for the hydroxy-form.† Several 2-thiones[12] and a few 2-amines[13] have been studied by ^{13}C n.m.r. spectrometry, but this technique has not been used with the thiazolinones.

† The phenylthiazolinone (cited in ref. 2, p. 389) for which the ^{1}H n.m.r. evidence favours the hydroxy-form is 2-phenyl-Δ^2-thiazolin-4-one not 4-phenyl-Δ^4-thiazolin-2-one (S. Gronowitz, B. Mathiasson, R. Dahlbom, B. Holmberg, and K. A. Jensen, *Acta Chem. Scand.*, 1965, **19**, 1215).

Before continuing an investigation into compounds (*e.g.* the trifluoroacetyl derivatives) obtained from the three types of 2-substituted thiazoles it was considered advisable to remove any uncertainties about the structures of the thiazolinone starting materials (Table 1). The surprising feature, which is probably connected with the paucity of thiazolinone studies, was that so few of the appropriate methylated models (2-methoxythiazoles and 3-methylthiazolinones) representing the alternative structural possibilities had been prepared. In the present work the thiazolinones and the *N*-methyl compounds were obtained by the Hantzsch reaction. Repeated treatment of the thiazolinones with portions of diazomethane slowly generated mixtures (*ca.* 1 : 1) of the *O*- and *N*-methyl derivatives which were separated cleanly by preparative-layer chromatography. (Since the preparative work was repetitive only one set, the 4-t-butyl compounds, is described fully; for the others the characterisation of new compounds is recorded in Table 2 of the Experimental section.) A summary of the results obtained by comparing the u.v., i.r., and ^{1}H and ^{13}C n.m.r. spectra of the thiazolinones with those of their methyl derivatives is shown in Table 1, absorptions from the 4- and 5-substituents having been excluded since they do not bear directly on the main problem.

Of the techniques used here, i.r. spectrometry (see Scheme 1) gives the clearest evidence about the structures of the thiazolinones. Variable-concentration ex-



SCHEME 1 NH and CO bands (cm^{-1}) of Δ^4-thiazolin-2-ones in CCl_4

periments show that there is a marked tendency for intermolecular association and although the present results do not reveal the nature of the associated forms they are represented, for simplicity, as the cyclic dimers by analogy with the established behaviour of Δ^4-thiazoline-2-thiones.[14] The tendency for association is solvent-dependent and decreases in the sequence carbon tetrachloride, benzene, and acetonitrile. In the last solvent Δ^4-thiazolin-2-one (1a) is in the free form (probably

TABLE 1

Comparison between Δ^4-thiazolin-2-ones and their *N*-and *O*-methyl derivatives

The approximate molar concentrations of the solutions were generally: u.v., 10^{-4}; i.r., 10^{-2}; ^{1}H n.m.r., 4×10^{-2}; and ^{13}C n.m.r., 8×10^{-2}M. Some solutions used for i.r. spectra had markedly different concentrations; for these the approximate concentrations are given, in parentheses, after the specified solvent. The positions of u.v. maxima, $\lambda_{max.}$ (nm), and those of some i.r. bands, $\nu_{max.}$ (cm^{-1}), are followed, in parentheses, by $\epsilon_{max.}$ values. The ^{1}H n.m.r. signals (τ values) were recorded at 90 MHz; the multiplicity and the coupling constant(s) (in Hz) of those which are not singlets or unresolved multiplets (m) are given, in parentheses, beneath or after the position of the signals. The ^{13}C n.m.r. signals (δ values) were recorded at 22.62 MHz with broad-band proton irradiation.

Compound [a]	U.v.		I.r.		^{1}H and ^{13}C n.m.r.				
						5-H	4-H	5-C	2-C
(1a)	EtOH	219 (5 650), 240 (5 850)	CCl_4(4 × 10^{-2})	3 442 (35), 3 141 (130),	$(CD_3)_2SO$	3.74	3.26	102.5	173.4
	MeCN [b]	241 (5 050)		1 701 (175), 1 693 (195), 1 661 (1 070)		(4; 5.6	(4; 5.6		
			CCl_4(4 × 10^{-4})	3 442 (95), 3 141 (75),		and 1.2)	and 2.6)		
				1 701 (465), 1 693 (510), 1 661 (660)					
			C_6H_6(3 × 10^{-2})	1 689 (450), 1 658 (895)					
			C_6H_6(4 × 10^{-3})	1 689 (905), 1 658 (295)					
			MeCN	1 679 (1 250)					
(2a)	EtOH	226 (5 400), 240 (5 350)	CCl_4	1 676 (1 015)	$(CD_3)_2SO$	3.67	3.08	100.2	171.2
	MeCN	243 (4 150)	C_6H_6	1 669 (1 325)		(2; 5.8)	(2; 5.8)		
			MeCN	1 661 (1 205)					
(3a)	EtOH	237 (5 500)	CCl_4	1 740 (*ca.* 10)	$(CD_3)_2SO$	3.08	2.87	111.9	174.7
	MeCN	236 (4 300)	MeCN	1 738 (*ca.* 10)		(2; 4.0)	(2; 4.0)		
(1b)	EtOH	221 (5 850), 243 (5 950)	CCl_4(2 × 10^{-2})	3 441 (15), 3 140 (160),	$(CD_3)_2SO$	4.19		96.1	173.0
				1 692 (120), 1660 (1 205)		(5; 1.3)			
					$CDCl_3$	4.35			
						(5; 1.3)			
			C_6H_6(2 × 10^{-2})	1 687 (510), 1 656 (640)					
(2b)	EtOH	225 (5 800), 242 (5 650)	CCl_4	1 677 (1 150)	$(CD_3)_2SO$	3.91		94.2	171.3
						(4; 1.3)			
					$CDCl_3$	4.25			
						(4; 1.3)			
(3b)	EtOH	239 (5 600)	CCl_4		$(CD_3)_2SO$	3.51		105.7	173.6
						(4; 1.2)			
					$CDCl_3$	3.80			
						(4; 1.2)			
(1c) *	EtOH	220 (6 235), 242 (6 450)	CCl_4(4 × 10^{-3})	3 440 (40), 3 140 (110),	$CDCl_3$	4.35		94.4	177.2
						(2; 1.8) [c]			
	$CHCl_3$ [d]	242 (5 900)		1 691 (210), 1 660 (995)					
			$CHCl_3$(3 × 10^{-2})	1 684 (310), 1 653 (890)					
			C_6H_6(2 × 10^{-2})	1 687 (540), 1 655 (605)					
(2c) *	EtOH	226 (5 600), 241 (5 550)	CCl_4	1 685 (240), 1 670 (1 045)	$CDCl_3$	4.22		93.5	173.4
	$CHCl_3$	240 (5 350)							
(3c) *	EtOH	237 (5 800)	CCl_4		$CDCl_3$	3.79		101.7	174.0
	$CHCl_3$	236 (5 500)							
(1d) *	EtOH	215 (3 400), 246 (6 050)	CCl_4(2 × 10^{-2})	3 440 (25), 3 155 (155),	$(CD_3)_2SO$		3.55	114.0	173.0
				1 695 (185), 1 662 (1 150)			(5; 1.3) [d]		
			CCl_4(2 × 10^{-3})	3 442 (60), 3 156 (115),	$CDCl_3$		3.72 (m)		
				1 695 (405), 1 662 (850)					
			C_6H_6(3 × 10^{-2})	1 691 (530), 1 657 (790)					
(2d) *		225 (2 900), 246 (4 200)	CCl_4	1 678 (1 020)	$(CD_3)_2SO$		3.44	111.7	170.5
							(4; 1.3)		
					$CDCl_3$		3.78		
							(4; 1.4)		
(3d) *		234 (5 300)			$(CD_3)_2SO$		3.15	125.3	172.5
							(4; 1.6)		
					$CDCl_3$		3.25		
							(4; 1.3)		
(1e) *	EtOH	215 (3 300), 246 (5 950)	CCl_4(2 × 10^{-3})	3 441 (60), 3 160 (110),	$(CD_3)_2SO$		3.55	113.2	172.8
				1 693 (420), 1 661 (840)			(4; 1.4)		
(2e) *		226 (2 850), 245 (4 200)	CCl_4	1 679 (995)	$(CD_3)_2SO$		3.46	111.1	170.3
							(3; 1.4)		
(3e) *		233 (5 400)			$(CD_3)_2SO$		3.14	124.6	172.4
							(3; 1.6)		
(1f)	EtOH	224 (12 600), 284 (10 900)	CCl_4(3 × 10^{-2})	3 438 (50), 3 142 (120),	$(CD_3)_2SO$	3.29		98.1	173.0
				1 698 (320), 1 661 (970)		(2; 1.8)			
			C_6H_6(3 × 10^{-3})	1 694 (425), 1 694 (930)					
(2f)	EtOH	215 (10 400), 269 (6 100)	CCl_4	1 677 (1 040)	$(CD_3)_2SO$ [e]	3.60		98.1	171.3
(3f) *	EtOH	219 (19 500), 271 (11 700)	CCl_4		$(CD_3)_2SO$	2.54		106.1	173.9
(1g)	EtOH	227 (14 400), 282 (13 300)	CCl_4(4 × 10^{-3})	3 435 (40), 3 140 (120),	$(CD_3)_2SO$	3.30		97.2	173.4
				1 695 (205), 1 660 (1 050)		(2; 1.8)			
(2g) *	EtOH	222 (12 150), 261 (6 900)	CCl_4	1 673 (1 080)	$(CD_3)_2SO$ [e]	3.63		97.7	171.3
(3g) *	EtOH	223 (21 200), 272 (14 000)	CCl_4		$(CD_3)_2SO$	2.69		105.0	173.9
(1h)	MeCN	238 (11 400), 282 (14 300)	CCl_4(5 × 10^{-3})	1 694 (145), 1 659 (1 210)	$(CD_3)_2SO$	3.45		96.8	173.0
						(2; 1.9)			
(2h) *	MeCN	233 (14 300), 270 (9 050)	CCl_4	1 672 (1 150)	$(CD_3)_2SO$	3.69		97.2	171.2
(3h) *	MeCN	235 (12 200), 275 (17 100)	CCl_4		$(CD_3)_2SO$	2.75		104.0	173.8
(1i)	EtOH	232 (9 600), 291 (8 700)	CCl_4(5 × 10^{-4})	3 436 (90), 3 140 (80),	$(CD_3)_2SO$ [e]	3.20		99.1	172.8
				1 697 (505), 1 662 (705)		(2; 2.0)			
(2i)	EtOH	230 (16 650), 279 (7 900)	CCl_4	1 675 (1 090)	$(CD_3)_2SO$	3.56		98.8	171.2
(3i) *	EtOH	236 (17 600), 276 (17 000)	CCl_4		$(CD_3)_2SO$	2.58		107.1	174.1
(1j)	MeCN	238 (8 700), 355 (7 800)	(Nujol)	1 648	$(CD_3)_2SO$	2.85		102.4	172.5
						(2; 1.9)			
(2j) *	MeCN	236 (12 100),[f] (343 6 500)	(Nujol)	1 660	$(CD_3)_2SO$	3.32		101.4	171.0
(3j) *	MeCN	232 (11 100),[f] 338 (13 750)	(Nujol)		$(CD_3)_2SO$	2.20		109.9	174.4

[a] New compounds marked with an asterisk; the Tables in ref. 2 (p. 505 *et seq.*) give references for the other compounds. [b] Lower wavelength limit 220 nm for solutions in MeCN and $CHCl_3$. [c] The coupling removed on irradiation of the broad NH signal at τ *ca.* −1. [d] One coupling removed on irradiating the broad NH signal at *ca.* −1. [e] The benzenoid proton resonances appear as singlets; they give two broad signals (relative intensities 2 : 3) in compounds (1f) and (3f), and A_2B_2 patterns in the other 4-aryl compounds. [f] Inflexions on stronger bands at lower wavelength.

stabilised by solute–solvent interaction) and gives a very strong band at 1 679 cm^{-1} with an intensity similar to that of the C=O bond at 1 661 cm^{-1} in the *N*-methyl analogue (2a). Since 2-methoxythiazole (3a) is devoid of such an absorption and a decrease in wavenumber would be expected to accompany *N*-methylation, the 1 679 cm^{-1} band of Δ^4-thiazolin-2-one (1a) must be attributed to the C=O vibration of a compound which is entirely or predominantly in the oxo-form. Although the intensity data of the solutions in carbon tetrachloride and benzene cannot be treated so precisely it appears very likely that sufficiently dilute solutions of the Δ^4-thiazolin-2-ones (1) would contain free forms with intensities comparable with those of the *N*-methyl compounds (2), and that the adoption of the oxo-form is general for Δ^4-thiazolin-2-ones irrespective of solvent.

In carbon tetrachloride the free oxo-forms are characterised by NH and CO bands at *ca.* 3 440 and 1 695 cm^{-1}, and the associated forms by bands near 3 140 and 1 660 cm^{-1}. [The free form of the unsubstituted compound (1a) is exceptional in having a second strong band, whose origin is obscure, in the carbonyl region.] Literature values [2] of *ca.* 1 650 cm^{-1} for some thiazolinones under various conditions must refer to associated species. The present conclusion about the structure of 4-phenyl-Δ^4-thiazolin-2-one (1f) differs from that of the earlier work,[11] which is based, in part, on a calculated rather than a measured value for the dipole moment of 2-methoxy-4-phenylthiazole (3f).

The u.v. spectra do not give clear evidence about the hydroxy–oxo-problem. While in the parent and 4- and 5-alkyl substituted systems the spectra of the thiazolinones resemble more closely those of the *N*-methyl compounds (2) than those of the 2-methoxythiazoles (3) the differences within the sets are too small for convincing application of this technique. With some systems containing phenyl and substituted phenyl groups at position 4 the standard interpretative approach would appear to favour the hydroxy-structures. Thus in set f, for example, the thiazolone (1f) differs more markedly from the *N*-methyl analogue (2f) than from 2-methoxy-4-phenylthiazole (3f). This confusing situation probably stems from an increase in the dihedral angle between the two rings caused by introducing an *N*-methyl group (as suggested previously for Δ^4-thiazoline-2-thione systems [15]); reduced conjugation in the reference compounds (2) would then reduce the otherwise expected similarity between their spectra and those of the thiazolinones.

The n.m.r. characteristics of the thiazolinones, particularly their proton spectra, will be influenced not only by their structures (hydroxy or oxo), but also by a number of additional features such as the position of the equilibrium and rate of interconversion between free and associated forms, and the rate of proton transfer between the associated forms. It may also be noted that when association occurs by hydrogen bonding, as here, the distinction between hydroxy- and oxo-forms becomes blurred. From the i.r. results it is very likely that in the deuteriochloroform solutions used for ^1H n.m.r. work the thiazolinones are largely associated, but solutions in hexadeuteriodimethyl sulphoxide (by analogy with those in acetonitrile) may contain appreciable amounts of the free forms; further, a marked difference between the rate of proton transfer in the two solvents may be expected. The observed ^1H resonances (Table 1) do not provide evidence for the presence of more than one type of molecule in any of the thiazolines. In view of the possible complexities, however, the spectra should be regarded as representing weighted averages of forms which are rapidly interconverting rather than particular molecular species, and it is unrealistic to seek a quantitative answer to the hydroxy–oxo problem from ^1H n.m.r. spectrometry.

In line with previous studies of thiazole systems with nitrogen-[3] and sulphur-containing [6] substituents at position 2 the 5-H resonance of the aromatic 4-substituted 2-methoxythiazoles (3) are at lower field than those of the corresponding *N*-methyl compounds (2), and a similar relation holds for the 4-H signals of 5-substituted systems. All the thiazolinones resemble more closely the *N*-methyl compounds (2) than the 2-methoxythiazoles (3), thus confirming the general preference for the oxo-structure. The precise relationship of a thiazolinone to the two models varies between sets and, for a given set, between solvents, but interpretation in terms of hydroxy–oxo equilibria would not be justified.

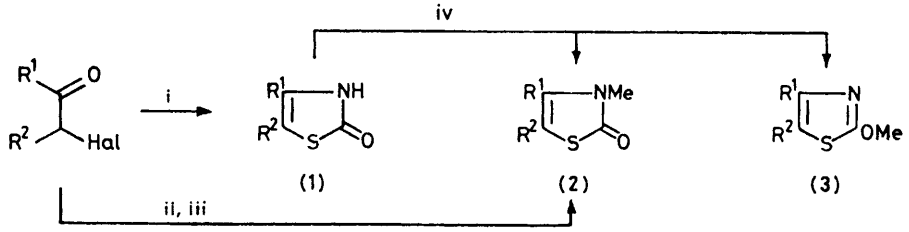
Previous ^{13}C n.m.r. work [12] has shown that the 2-C signals of Δ^4-thiazoline-2-thione and the 3-methyl derivative are at similar positions, and are appreciably displaced from the signal of 2-methylthiothiazole. In the 2-oxygenated series (Table 1) there is a consistent, but much smaller difference, between the signals of pairs of model compounds (2) and (3). The unexpected feature with regard to signal position is that in each of the sets the thiazolinone is closer to the 2-methoxythiazole than the *N*-methyl compound. With the 5-C signals a contrasting situation is found; the model systems (2) and (3) resonate at appreciably different positions (*ca.* 10 p.p.m.) and the thiazolinones resemble the *N*-methyl derivatives. Consideration of either the 2-C or the 5-C resonances only would, then, lead to opposite conclusions about the structures of the thiazolinones, and since there is no reason for attaching greater significance to one centre rather than the other the method is not well suited to the present problem.

EXPERIMENTAL

4-t-Butyl-Δ^4-thiazolin-2-one (1c).—1-Bromo-3,3-dimethylbutan-2-one (6.4 ml) was added in drops during 20 min to a vigorously stirred solution of ammonium thiocarbamate (freshly prepared; 5 g) in H_2O (15 ml)–EtOH (15 ml) at 0 °C. The mixture was stirred for 1 h at 0 °C and then for 12 h at 20 °C (Scheme 2). The precipitate was collected and crystallised from EtOH–H_2O to give the *thiazolinone* (1c) (4.9 g), characterised by the data shown in Table 2.

4-t-Butyl-3-methyl-Δ^4-thiazolin-2-one (2c).—1-Bromo-3,3-dimethylbutan-2-one (6.8 ml) was added in drops during 20 min to a vigorously stirred solution of methylammonium *N*-methylthiocarbamate (6.71 g) in EtOH (20 ml)–H_2O (20 ml) at 0 °C. The mixture was stirred for 12 h at 20 °C, and then poured into ice–water (100 ml). The precipitate was collected, washed with cold H_2O, and dried to give 4-t-butyl-4-hydroxy-3-methylthiazolidin-2-one (4.75 g); τ(CDCl_3) 5.62 (1 H, br, OH), 6.36 and 6.86 (2 H, AB, 5-H_2), 7.04 (3 H, s, Me), and 8.9 (9 H, s, Bu^t). This material was dissolved in 3M HCl (50 ml)–MeOH (50 ml) and the solution kept at 20 °C for 12 h (Scheme 2). Basification with saturated aqueous $NaHCO_3$, extraction with EtOAc, and distillation of the product at 0.1 mmHg gave the *3-methylthiazolinone* (2c) (3.9 g).

With sets f—j, containing aromatic substituents at position 4, the thiazolidinone intermediates (*ca.* 3 g) were dissolved in 48% aqueous HBr (10 ml)–MeOH (50 ml) and the solutions were boiled under reflux for 2 h. The crystal-



	R^1	R^2		R^1	R^2
a;	H	H	f;	Ph	H
b;	Me	H	g;	C_6H_4Me-*p*	H
c;	Bu^t	H	h;	C_6H_4OMe-*p*	H
d;	H	Me	i;	C_6H_4Br-*p*	H
e;	H	Et	j;	$C_6H_4NO_2$-*p*	H

Hal = halogen

SCHEME 2 *Reagents:* i, $[NH_4]^+[S{\cdot}CO{\cdot}NH_2]^-$; ii, $[MeNH_3]^+[S{\cdot}CO{\cdot}NHMe]^-$; iii, H^+–MeOH; iv, CH_2N_2

TABLE 2

Characterisation of new compounds

Compound	M.p. (°C)	B.p. (°C) bath temp/ mmHg	Analyses (%) found C	H	N	Molecular formula	Required C	H	N
(1c)	135—136		53.3	7.0	8.7	$C_7H_{11}NOS$	53.5	7.05	8.9
(2c)		86—88/0.2	56.1	7.7	8.0	$C_8H_{13}NOS$	56.1	7.65	8.2
(3c)		60—62/0.2	56.3	7.6	8.0	$C_8H_{13}NOS$	56.1	7.65	8.2
(1d)	144—145		41.7	4.5	12.3	C_4H_5NOS	41.7	4.4	12.2
(2d)		47—49/0.1	46.8	5.8	10.7	C_5H_7NOS	46.5	5.5	10.85
(3d)		90—92/15	46.7	5.5	10.8	C_5H_7NOS	46.5	5.5	10.85
(1e)	130—131		46.2	5.5	10.7	C_5H_7NOS	46.5	5.5	10.85
(2e)		56—58/0.1	50.2	6.4	9.9	C_6H_9NOS	50.3	6.3	9.8
(3e)		33—35/0.2	50.0	6.2	9.8	C_6H_9NOS	50.3	6.3	9.8
(3f) [a]	29—30	62.64/0.01	62.7	4.8	7.2	$C_{10}H_9NOS$	62.8	4.7	7.3
(2g)	82—83		64.5	5.4	6.9	$C_{11}H_{11}NOS$	64.4	5.4	6.8
(3g)	61—63	80—82/0.02	64.1	5.2	6.7	$C_{11}H_{11}NOS$	64.4	5.4	6.8
(2h)	74—75		59.7	4.9	6.6	$C_{11}H_{11}NO_2S$	59.7	5.0	6.3
(3h)	73—74		59.8	5.1	6.5	$C_{11}H_{11}NO_2S$	59.7	5.0	6.3
(3i)	117—118		44.5	3.3	5.2	$C_{10}H_8BrNOS$	44.5	3.0	5.2
(2j)	152—154		50.8	3.1	11.7	$C_{10}H_8N_2O_3S$	50.8	3.4	11.9
(3j)	148—150		51.0	3.1	11.9	$C_{10}H_8N_2O_3S$	50.8	3.4	11.9

[a] A product formulated as 2-methoxy-4-phenyl-Δ^4-thiazolin-2-one is reported to have m.p. 139 °C (H. Beyer and G. Ruhlig, *Chem. Ber.*, 1956, **89**, 107).

line 3-*methylthiazolinones* (3f)—(3j) were collected after cooling.

4-*t-Butyl*-2-*methoxythiazole* (3c).—A cold solution of CH_2N_2 (*ca.* 1.2 g) in Et_2O (20 ml) was added to a stirred solution of 4-t-butyl-Δ^4-thiazolin-2-one (1.6 g) in EtOH (50 ml) at 0 °C (Scheme 2). The solution was stirred for 2 h at 0 °C, kept at 20 °C for 12 h, and then evaporated behind a safety screen. The product, which was shown by ^1H n.m.r. examination to contain *ca.* 15% of starting material, was subjected to a further treatment with CH_2N_2. (With some sets four treatments were needed to reduce the amount of starting material to below 3%.) Preparative layer chromatography [2-m plates, developed with light petroleum–Et_2O (1 : 1)] afforded the 3-*methylthiazoline* (2c) (0.79 g, lower R_F) and another material (0.71 g, higher R_F) which was distilled under reduced pressure to give 4-*t-butyl*-2-*methoxythiazole* (3c) as a colourless oil (0.58 g).

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