Reinvestigation of reactions of thiazolium and benzothiazolium *N*-phenacylides with electron-deficient acetylenes

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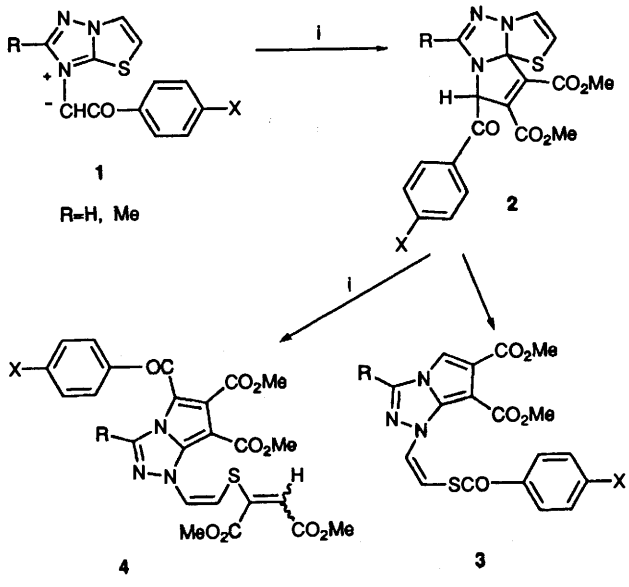
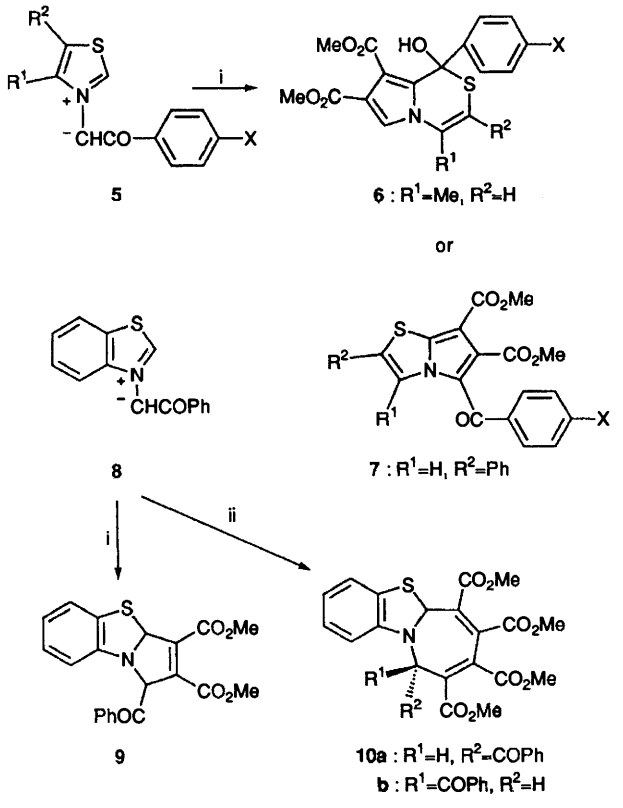
Reactions of thiazolium and benzothiazolium *N*-phenacylides with dimethyl acetylenedicarboxylate (DMAD) have been reexamined. The thiazolium *N*-phenacylides 5, generated *in situ* from 4-methyl- or 5-phenyl-3-phenacylthiazolium bromides 13 with triethylamine, reacted with DMAD in dry DMF to give the thiazole ring-opened products 15, in which two molecules of DMAD had been incorporated. The reactions when conducted in both aqueous DMF and in dry DMF in the presence of lithium perchlorate gave the hemithioacetals 6 which could be transformed into the 1:2 reaction products 15 of the ylides and DMAD. Benzothiazolium *N*-phenacylides 8 similarly reacted with DMAD to afford the 1:2 reaction products 19 or the hemithioacetals 20. The reaction mechanism is discussed.

Recently we reported that reactions of thiazolo[3,2-*b*]-[1,2,4]triazolium *N*-phenacylides **1** with dimethyl acetylenedicarboxylate (DMAD) gave 2-(1*H*-pyrrolo[2,1-*c*]-1,2,4-triazolyl)vinyl thiobenzoates **3** and 2-[2-(1*H*-pyrrolo[2,1-*c*]-1,2,4-triazolyl)vinylsulfanyl]propenoates **4**.[1] The intermediate would be a 1:1 adduct **2** of the ylide and the acetylene, and undergo intramolecular benzoyl migration or Michael-type addition to the second molecule of DMAD (Scheme 1). These results are



Scheme 1 *Reagent:* i, 1 equiv. DMAD

markedly different from those of the reactions of thiazolium[2] **5** and benzothiazolium *N*-phenacylides[3] **8** with electron-deficient acetylenes shown in Scheme 2. The thiazolium ylides **5** reacted with 1 equiv. of the acetylenes to give 1-hydroxy-1*H*-pyrrolo-[2,1-*c*][1,4]thiazines[2] **6** or pyrrolo[2,1-*b*]thiazole derivatives[3] **7**. The benzothiazolium ylides **8** reacted with 1 equiv. of the acetylenes to give the dihydropyrrolo[2,1-*b*]benzothiazoles **9** and with 2 equiv. of the acetylenes to give a mixture of two stereoisomers of dihydroazepino[2,1-*b*]benzothiazoles[3] **10**. It is known that the *N*-ylides containing a thiazole ring undergo the 1,3-dipolar cycloaddition followed by the thiazole ring-opening.[4–6] In order to clarify the differences in the results we have obtained with those of Potts and Chen, we have

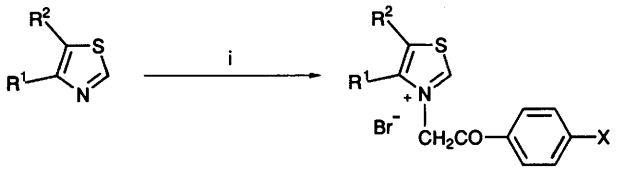


Scheme 2 *Reagents:* i, 1 equiv. DMAD; ii, 2 equiv. DMAD

reinvestigated the reactions of thiazolium and benzothiazolium *N*-phenacylides with DMAD.

Results and discussion

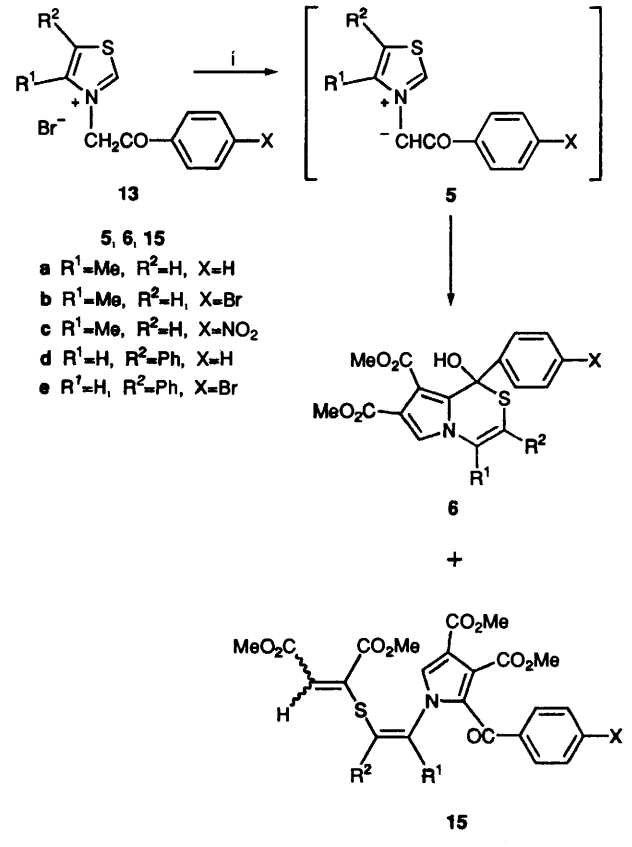
The thiazolium **13** and benzothiazolium salts **14** were prepared as colourless crystals in high yields by refluxing a mixture of 4-methyl- or 5-phenyl-thiazole **11** or benzothiazole **12** with a phenacyl bromide derivative in acetone (Scheme 3). 4-Methylthiazolium *N*-phenacylides **5a–c** were generated *in situ* at room temperature from the thiazolium salts **13a–c** and triethylamine, and allowed to react with DMAD (Scheme 4). The results are summarised in Table 1. Reaction of equimolar proportions of the thiazolium salts **13**, triethylamine and DMAD in dry DMF (entries 1–4) failed to give the



11a R^1=Me, R^2=H
11b R^1=H, R^2=Ph
12 R^1, R^2=$(CH=CH)_2$

13a R^1=Me, R^2=H, X=H
13b R^1=Me, R^2=H, X=Br
13c R^1=Me, R^2=H, X=NO_2
13d R^1=H, R^2=Ph, X=H
13e R^1=H, R^2=Ph, X=Br
14a R^1, R^2=$(CH=CH)_2$, X=H
14b R^1, R^2=$(CH=CH)_2$, X=Br

Scheme 3 *Reagents and conditions:* i, *p*-X-$C_6H_4COCH_2Br$, dry acetone, reflux



13

5, 6, 15
a R^1=Me, R^2=H, X=H
b R^1=Me, R^2=H, X=Br
c R^1=Me, R^2=H, X=NO_2
d R^1=H, R^2=Ph, X=H
e R^1=H, R^2=Ph, X=Br

5

6

15

Scheme 4 *Reagents and conditions:* i, DMAD, Et_3N, DMF

1-hydroxypyrrolo[2,1-*c*][1,4]thiazines **6**, instead the unexpected products **15** were obtained in good yields. The reaction conditions for entries 1, 2 and 4 were identical with those reported by Potts. Use of 2 equiv. of triethylamine and DMAD (entries 5–7) gave increased yields of **15** as a mixture of *E*- and *Z*- geometrical isomers. These could be separated by preparative TLC on silica gel using hexane–ethyl acetate (2:1). Analytical and mass spectral data established a molecular composition for the products **15**, in which two molecules of DMAD were incorporated (1:2-reaction product).† The ^1H NMR spectrum of compound *E*-**15a**, used here as an example, showed a doublet at δ 2.35 (*J* 1 Hz, a methyl group on a double bond), which gave rise to allylic coupling with a quartet signal at δ 6.21 (a vinyl proton) and a singlet at δ 5.78 (a terminal vinyl proton). The spectrum of *Z*-**15b** exhibited

† Such a product from the reaction of the *N*-phenacylides with DMAD has been described as a 1:2-reaction product.

Table 1 Reactions of the thiazolium ylides **5** with DMAD in dry DMF

Entry	Thiazolium salts	Molar ratios of Et_3N	Molar ratios of DMAD	Products (% yield)[a] [*E*:*Z*][b]
1	**13a**	1	1	**15a**(46.5) [3:2]
2	**13b**	1	1	**15b**(47) [3:2]
3[c]	**13c**	1	1	**15c**(36.5) [3:2]
4	**13c**	1	1	**15c**(46) [3:2]
5	**13a**	2	2	**15a**(88) [3:2]
6	**13b**	2	2	**15b**(87) [3:2]
7	**13c**	2	2	**15c**(85.5) [5:2]
8	**13d**	1	1	**6d**(44.5), **15d**(10) [1:4]
9	**13e**	1	1	**6e**(28.5), **15e**(14) [1:8]
10	**13d**	2	2	**15d**(89) [1:4]
11	**13e**	2	2	**15e**(91) [1:6]

[a] Yields were calculated based on the amount of **13**. [b] The ratio was determined by ^1H NMR spectroscopy. [c] In dry MeCN at 60 °C.

characteristic signals at δ 2.29 (doublet, *J* 1 Hz, Me), 6.29 (doublet, *J* 1 Hz, a vinyl proton) and 6.40 (singlet, a terminal vinyl proton). The vinyl proton of the dimethyl *cis*-butenedioate (maleate) moiety generally appears at higher field compared to that of the *trans*-isomer (fumarate),[1,4,6] and the *E*-isomer *E*-**15** corresponds to a maleate derivative. It is interesting that the 1:2-reaction products **15** were obtained even from the reactions of the ylides **5** with 1 equiv. of DMAD.

In contrast, 1,3-dipolar cycloaddition of 5-phenylthiazolium *N*-phenacylides **5d–e**, which were generated *in situ* from the corresponding salts **13d–e** with triethylamine in dry DMF, with 1 equiv. of DMAD provided 1-hydroxypyrrolo[2,1-*c*][1,4]thiazine derivatives **6d–e** together with thiazole ring-opened products **15d–e**. When 2 equiv. of DMAD and triethylamine were used, the 1:2-reaction products **15d–e** were obtained as the sole products. These findings were different from the results reported by Chen and his co-workers.[3] Analytical and mass spectral data showed that the products **6d–e** were the 1:1-reaction products of **5d–e** and DMAD. The IR spectrum of **6d** exhibited hydroxy absorption at 3400 cm^{-1} and ^{13}C NMR spectrum showed an sp^3 quaternary carbon at δ 80.38 instead of a benzoyl carbon. This carbon gave rise to long-range coupling with the *ortho*-protons of the benzene ring. Formation of the hemiacetals **6d–e** implies that the hemiacetals **6a–c** might be obtained from the reactions of **5a–c** with DMAD if the reaction conditions are appropriate. Experiments carried out under a variety of conditions showed that reactions of the thiazolium salts **13** with DMAD in aqueous DMF containing 7.7 equiv. of water gave the hemiacetals **6** (see Table 2).

The hemiacetals **6a–c** were obtained in good yields from the reactions of equimolar proportions of the 4-methylthiazolium salts **13a–c**, DMAD and triethylamine (entries 1–5 and 8), while the reactions of the 5-phenylthiazolium salts **13d–e** gave the hemiacetals **6d–e** together with 1:2-reaction products **15d–e** (entries 9 and 10). Although use of 2 equiv. of triethylamine did not affect the formation of the hemiacetal **6b** (entry 7), the 1:2-reaction product **15b** was produced by use of 2 equiv. of DMAD (entry 6). Since the hemiacetals **6a,b** were identical in all respects with the samples prepared by Potts and co-workers,[3] it seems likely that the DMF used in the latter work was not absolutely dry. The differences found for the reactions of thiazolium ylides **5** with DMAD carried out in aqueous DMF and in dry DMF may be explained in terms of hydrogen bonding by water, with a similar effect being expected for chelation by a metallic ion. The reactions of the ylides **5** with DMAD were conducted using lithium perchlorate and gave the hemiacetals **6** in good yields (Table 2 entries 2, 4 and 5).

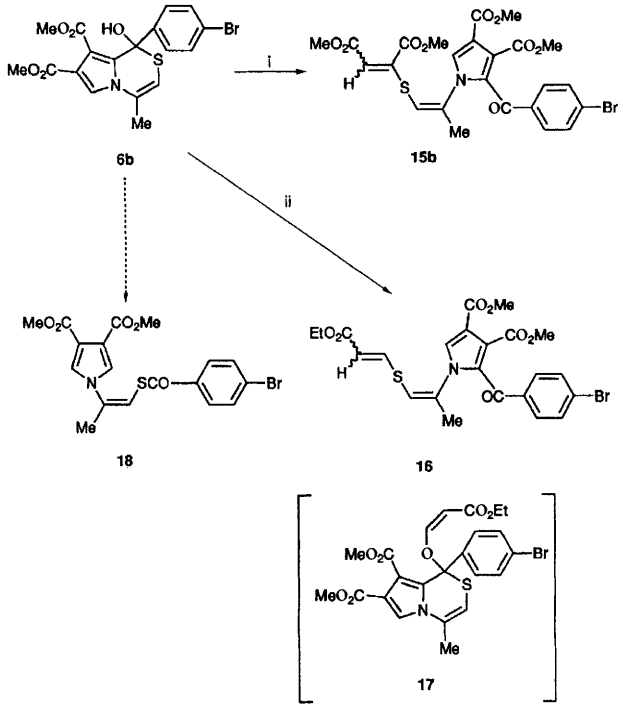
Since the use of 1 equiv. of DMAD gave the hemiacetals **6** (Table 1 entries 8–9 and Table 2 entry 3) and the use of 2 equiv gave the 1:2-reaction products **15** (Table 1 entries 10–11 and

Table 2 Reactions of the thiazolium ylides **5** with DMAD in aqueous DMF

Entry	Thiazolium salts	Molar ratios of Et_3N	Molar ratios of DMAD	Products (% yield)
1	**13a**	1	1	**6a** (70)
2[a]	**13a**	1	1	**6a** (68)
3	**13b**	1	1	**6b** (87)
4[a]	**13b**	1	1	**6b** (60.5)
5[b]	**13b**	1	1	**6b** (67)
6	**13b**	1	2	**15b** (65)[c]
7	**13b**	2	1	**6b** (60.5)
8	**13c**	1	1	**6c** (82.5)
9	**13d**	1	1	**6d** (38), **15d** (10)
10	**13e**	1	1	**6e** (23), **15e** (13)

[a] The reactions were carried out in the presence of 2 equiv. of $LiClO_4$. [b] The reaction was carried out in the presence of 3 equiv. of $LiClO_4$. [c] The $E:Z$ isomer ratio ($E:Z$ = 2:1) was determined by ^1H NMR spectroscopy.

Table 2 entry 6), the former could be intermediates for the latter. This was confirmed when reaction of the hemiacetal **6b** with DMAD gave the ring-opened product **15b** in 96% yield (Scheme 5).



Scheme 5 *Reagent and conditions:* i, 1 equiv. Et_3N, 1 equiv. DMAD, dry DMF, room temp., 4 h; ii, 1 equiv. Et_3N, 1 equiv. EP, dry DMF, room temp., 4 h

Since this finding was inconsistent with the reported result for the reaction of **6a,b** with ethyl propiolate (EP),[3] we repeated the reaction of **6b** with EP. The ring-opened product **16** was obtained rather than the Michael adduct **17**. A comparison of the melting points and the spectral data for **16** and **17**, the latter reported by Potts and his co-workers as having been isolated,[2] showed that the two compounds were identical. Product **17** with an *O*-vinyl-*O*,*S*-heteroacetal structure, would be expected to show a quaternary carbon at δ *ca.* 78 in its ^{13}C spectrum; there was no such signal in the spectrum for product **16** but, instead, a benzoyl carbon signal appears at δ 184.83. We confirmed the structure of *E*- and *Z*-**16** from correlation spectroscopy long-range couplings (COLOC) between ^1H and ^{13}C (see Fig. 1).

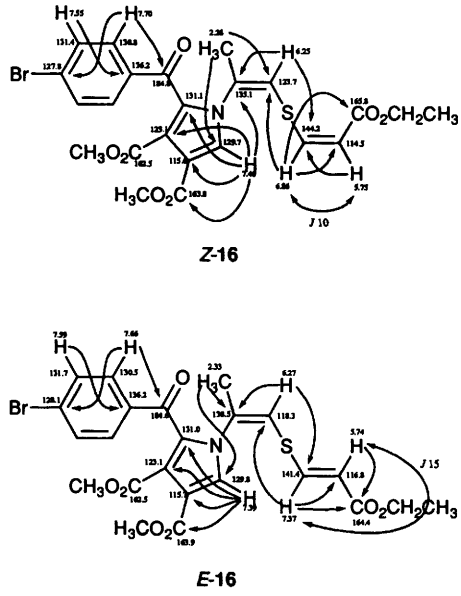
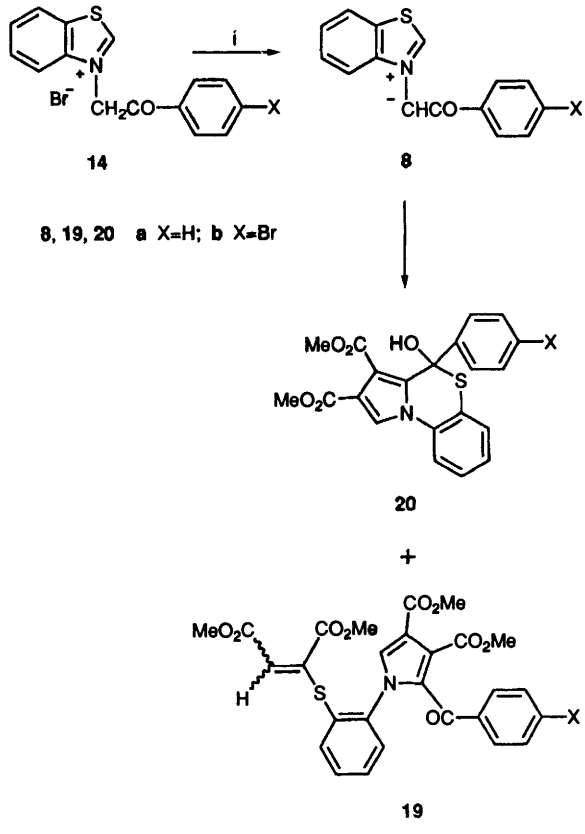


Fig. 1 ^1H and ^{13}C NMR chemical shifts (δ) and coupling constants (Hz) between the correlated protons and between the correlated protons and carbons of **16**

On the basis of the above results the structural assignment made by Potts *et al.* to their compound **17** (our compound **16**) is shown to be in error.

Since the thiol esters had been obtained from the reactions of equimolar proportions of thiazolotriazolium *N*-phenacylides and DMAD,[1] it was thought that the hemiacetal **6b** might be an intermediate for the formation of the thiol ester **18**. All attempts to transform the hemiacetal **6b** to the thiol ester **18** were, however, unsuccessful.

Next we investigated the reactions of benzothiazolium *N*-phenacylides with DMAD (Scheme 6). The results are summarised in Table 3. Equimolar proportions of the benzo-



Scheme 6 *Reagents and conditions:* i, Et_3N, DMAD, DMF

thiazolium salts **14** and DMAD reacted in the presence of triethylamine to give the 1:2-reaction products **19** in high yields (entries 1 and 2), separable into *E*- and *Z*-isomers by preparative TLC on silica gel using hexane–ethyl acetate (2:1). When aqueous DMF was used as a solvent or lithium perchlorate was added to the reaction mixture, the hemiacetals **20** were obtained in high yields (entries 5–7). Structural assignments were made for the products **19** and **20** on the basis of ^{1}H and ^{13}C NMR, IR and mass spectral data in a similar way to those for compounds **15** and **6**. Although the ^{1}H NMR and mass spectral results for *E*- and *Z*-**19** were in good agreement with those of dihydroazepinobenzothiazoles **10a** and **10b**, respectively, which had been isolated by Chen's group,[3] the structural assignment was different. If compound **19a** had a dihydroazepinobenzothiazole skeleton, the ^{13}C NMR spectra of *E*- and *Z*-**19a** should exhibit two sp^3-tertiary carbons; such signals were not, however, observed.

A mechanism for the reactions of thiazolium and benzothiazolium *N*-phenacylides with DMAD is proposed using, as an example, the reaction of 4-methylthiazolium *N*-phenacylide **5** with DMAD (see Scheme 7). Thus, the thiazolium *N*-ylide **5** reacts with DMAD to form a pair of diastereoisomeric 1:1-adducts, in which the *trans*-isomer **22** is more stable than the *cis*-isomer **21** because of steric hindrance in the latter. Further, the carbonyl group and the sulfur atom of the *trans*-form **22** are insufficiently close to interact. The *trans*-intermediate **22** would be transformed into the enol **23** in aqueous DMF or in the presence of lithium perchlorate, whilst the hemiacetal **6** would be formed by interaction between the carbonyl group and the sulfur atom of the *cis*-**21**, or the 1,5-sigmatropic rearrangement of the enol or enolate intermediate **23**. The *E*-1:1-adduct **22** or the hemiacetal **24** reacts with DMAD to give the thiazole ring-opened product **15**.

Table 3 Reactions of the benzothiazolium ylides **8** with DMAD

Entry	Benzothiazolium salts	Molar ratios of Et_3N	Molar ratios of DMAD	Products (% yield)[a] [*E*:*Z*][b]
1	**14a**	1	1	**19a** (48) [3:10]
2	**14b**	1	1	**19b** (43) [1:3]
3	**14a**	2	2	**19a** (84) [3:10]
4	**14b**	2	2	**19b** (85) [1:3]
5[c]	**14a**	1	1	**20a** (89)
6[c]	**14b**	1	1	**20b** (78.5)
7[d]	**14a**	1	1	**20a** (88.5)

[a] Yields were calculated based on the amount of **14**. [b] The ratio was determined by ^{1}H NMR spectroscopy. [c] The reactions were carried out in DMF containing 7.7 equiv. of water. [d] The reaction was carried out in the presence of 2 equiv. of $LiClO_4$.

Experimental

Mps were determined on a Yanagimoto micro-melting-point apparatus, and are uncorrected. IR spectra were recorded on a JASCO IRA-100 spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured using a JEOL GX-270 (270 MHz) and EX-400 (400 MHz) spectrometers with tetramethylsilane as an internal standard. The chemical shifts are given as δ values (ppm) with coupling constants in Hz. Mass spectra were obtained using a JEOL JMS-D300 spectrometer with a direct-insertion probe at 70 eV. All exact mass determinations were obtained on a JMA 2000 on-line system. Analytical and preparative TLC (PLC) were performed on E. Merck silica gel 60PF-254 plates.

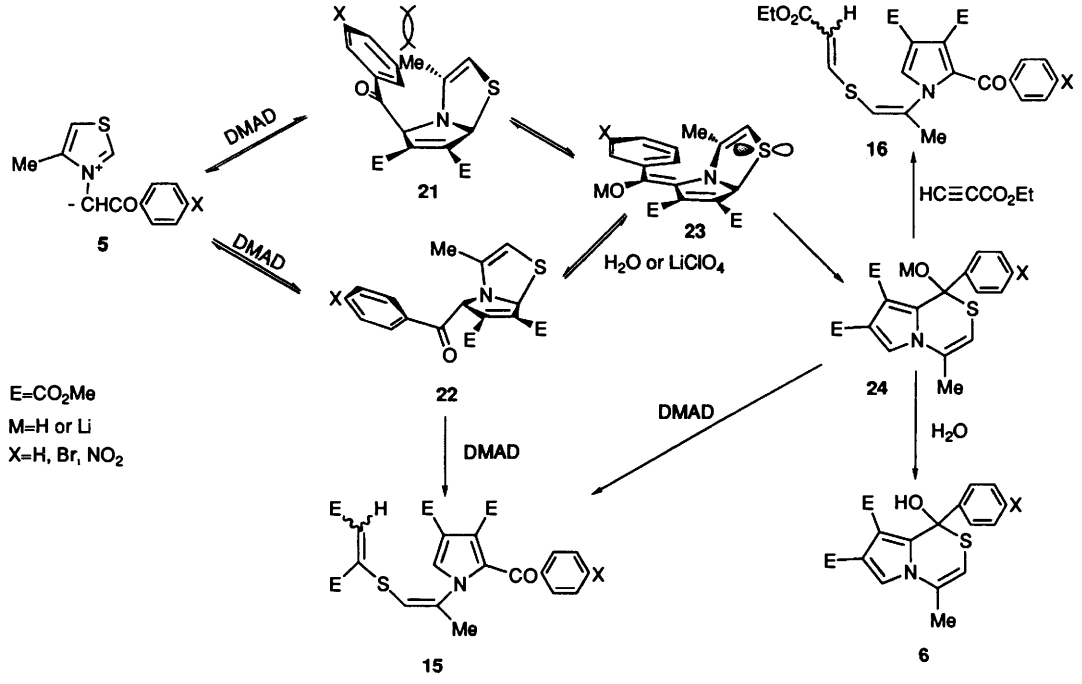
General procedure for preparation of thiazolium and benzothiazolium salts 13, 14

A mixture of the thiazole **11** or benzothiazole **12** (10 mmol) and a phenacyl bromide (15 mmol) in dry acetone (30 cm^3) was refluxed for 48 h and then cooled to room temperature. The precipitate was filtered off, dried and recrystallised from ethanol.

4-Methyl-3-phenacylthiazolium bromide 13a. Colourless needles (89%), mp 216 °C (decomp.) (lit.,[2] 210 °C); δ_C([$^2H_6$]-DMSO) 12.54 (q), 58.65 (t), 121.76 (d), 128.37 (d × 2), 129.01 (d × 2), 133.46 (s), 134.69 (d), 146.46 (s), 161.53 (d) and 190.79 (s).

3-(*p*-Bromophenacyl)-4-methylthiazolium bromide 13b. Colourless needles (94%), mp 254 °C (decomp.) (lit.,[2] 244 °C); δ_C([$^2H_6$]-DMSO) 12.61 (q), 58.64 (t), 121.84 (d), 128.87 (s), 130.33 (d × 2), 132.09 (d × 2), 132.52 (s), 146.54 (s), 161.58 (d) and 190.21 (s).

4-Methyl-3-(*p*-nitrophenacyl)thiazolium bromide 13c. Pale yellow prisms (93%), mp 262–264 °C (decomp.); ν_{max}(KBr)/cm^{-1} 1680 (CO), 1520 and 1350 (each NO_2); δ_H([$^2H_6$]-DMSO) 2.48 (3 H, s, Me), 6.50 (2 H, s, CH_2), 8.12 (1 H, d, *J* 2.5, 5-H), 8.32 and 8.47 (each 2 H, d, *J* 8.8, ArH) and 10.14 (1 H, d, *J* 2.5, 2-H);



Scheme 7

$\delta_C([^2H_6]$-DMSO) 12.60 (q), 58.85 (t), 121.69 (d), 124.01 (d × 2), 129.90 (d × 2), 138.18 (s), 146.59 (s), 150.64 (s), 161.76 (d) and 190.19 (s) (Found: C, 41.75; H, 3.25; N, 8.1. Calc. for $C_{12}H_{11}BrN_2O_3S$: C, 42.00; H, 3.23; N, 8.16%).

3-Phenacyl-5-phenylthiazolium bromide 13d. White needles (89%), $\delta_C([^2H_6]$-DMSO) 61.01 (t), 126.74 (d × 2), 127.37 (s), 128.22 (d × 2), 129.17 (d × 2), 129.76 (d × 2), 130.73 (d), 133.44 (s), 134.03 (d), 134.73 (d), 141.58 (s), 160.48 (d) and 190.35 (s).

3-(*p*-Bromophenacyl)-5-phenylthiazolium bromide 13e. Colourless needles (95%), mp 237–239 °C (decomp.); ν_{max}(KBr)/cm^{-1} 1680 (CO); $\delta_H([^2H_6]$-DMSO) 6.53 (2 H, s, CH_2), 7.58–7.82 (5 H, m, ArH), 7.89 and 8.03 (each 2 H, d, *J* 8.0, ArH), 9.09 (1 H, s, 4-H) and 10.30 (1 H, s, 2-H); $\delta_C([^2H_6]$-DMSO) 60.49 (t), 126.70 (d × 2), 127.32 (s), 128.85 (s), 129.73 (d × 2), 130.15 (d × 2), 130.70 (d), 132.25 (d × 2), 132.50 (d), 133.97 (d), 141.53 (s), 160.53 (d) and 189.78 (s) (Found: C, 46.4; H, 3.0; N, 3.3. Calc. for $C_{17}H_{13}Br_2NOS$: C, 46.49; H, 2.98; N, 3.19%).

3-Phenacylbenzothiazolium bromide 14a. White needles (78%), mp 239–240 °C (decomp.) (lit.,[3] 236–237 °C); $\delta_C([^2H_6]$-DMSO) 58.50 (t), 117.26 (d), 125.27 (d), 128.31 (s), 128.54 (d × 2), 129.02 (d × 2), 129.69 (s), 131.01 (d), 133.63 (d), 134.67 (s), 141.09 (d), 167.06 (d) and 190.54 (s).

3-(*p*-Bromophenacyl)benzothiazolium bromide 14b. Colourless needles (83%), mp 254–257 °C (decomp.); ν_{max}(KBr)/cm^{-1} 1680 (CO); $\delta_H([^2H_6]$-DMSO) 6.72 (2 H, s, CH_2), 7.61–8.61 (8 H, m, ArH) and 10.61 (1 H, s, 2-H); $\delta_C([^2H_6]$-DMSO) 58.63 (t), 117.22 (d), 125.20 (d), 128.34 (d), 128.78 (s), 129.62 (d), 130.43 (d × 2), 131.14 (s), 132.09 (d × 2), 132.71 (s), 141.05 (s), 167.06 (d) and 189.88 (s) (Found: C, 43.5; H, 2.7; N, 3.4. Calc. for $C_{15}H_{11}Br_2NOS$: C, 43.61; H, 2.68; N, 3.39%).

General procedure for reaction of thiazolium *N*-phenacylides 5 and 8 with DMAD in dry DMF

Triethylamine was added dropwise to a mixture of an appropriate thiazolium salt **13** or **14** (1 mmol) and DMAD in dry DMF (7 cm^3) with stirring. The mixture was stirred for 2 h at room temperature and then poured into ice–water and extracted with $CHCl_3$ (20 cm^3 × 4). The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by PLC on silica gel using hexane–ethyl acetate (2:1) to afford a 1:2-reaction product **15, 19**.

Dimethyl 2-benzoyl-1-[2-(1,2-bismethoxycarbonylvinyl sulfanyl)-1-methylvinyl]pyrrole-3,4-dicarboxylate 15a. *E-Isomer*.—Pale yellow powder, ν_{max}(KBr)/cm^{-1} 1720 (CO) and 1645 (CO); *m/z* (+FAB; 3-nitrobenzyl alcohol) 502 $[(M + H)]^+$; $\delta_H(CDCl_3)$ 2.35 (3 H, d, *J* 1.0, Me), 3.25, 3.65, 3.76 and 3.82 (each 3 H, s, OMe × 4), 5.78 (1 H, s, =CH), 6.21 (1 H, d, *J* 1.0, =CH) and 7.40–7.79 (6 H, m, ArH, 5-H); $\delta_C(CDCl_3)$ 24.00 (q), 51.59 (q), 51.70 (q), 51.77 (q), 52.92 (q), 115.39 (d), 115.47 (s), 116.54 (d), 123.21 (s), 128.18 (d × 2), 128.84 (d × 2), 129.59 (d), 131.29 (s), 132.82 (d), 137.40 (s), 141.87 (s), 144.83 (s), 162.42 (s), 163.36 (s), 163.78 (s), 164.52 (s) and 185.64 (s); *m/z* (+FAB; 3-nitrobenzyl alcohol) 502.1187 ($C_{24}H_{23}NO_9S$ + H requires *m/z* 502.1093).

Z-Isomer.—Pale yellow powder, ν_{max}(KBr)/cm^{-1} 1720 (CO) and 1640 (CO); *m/z* (+FAB; 3-nitrobenzyl alcohol) 502 $[(M + H)]^+$; $\delta_H(CDCl_3)$ 2.29 (3 H, d, *J* 1.0, Me), 3.24, 3.72, 3.74 and 3.82 (each 3 H, s, OMe × 4), 6.29 (1 H, d, *J* 1.0, =CH), 6.40 (1 H, s, =CH) and 7.38–7.82 (6 H, m, ArH, 5-H); $\delta_C(CDCl_3)$ 24.01 (q), 51.60 (q), 51.70 (q), 51.89 (s), 53.12 (q), 115.39 (s), 118.66 (d), 121.56 (d), 123.08 (s), 128.16 (d × 2), 129.11 (d × 2), 129.87 (d), 131.71 (s), 132.68 (d), 137.80 (s), 138.06 (s), 144.01 (s), 162.69 (s), 163.89 (s), 163.99 (s), 164.75 (s) and 185.96 (s); *m/z* (+FAB; 3-nitrobenzyl alcohol) 502.1156 ($C_{24}H_{23}NO_9S$ + H requires *m/z* 502.1093).

Dimethyl 2-(*p*-bromobenzoyl)-1-[2-(1,2-bismethoxycarbonylvinylsulfanyl)-1-methylvinyl]pyrrole-3,4-dicarboxylate 15b. E-*Isomer*.—Pale yellow powder, mp 38–41 °C; ν_{max}(KBr)/cm^{-1} 1720 (CO) and 1650 (CO); *m/z* (+FAB; 3-nitrobenzyl alcohol) 580 $[(M + H)]^+$, 582 $[(M + 2 + H)]^+$; $\delta_H(CDCl_3)$ 2.35 (3 H, d, *J* 1.0, Me), 3.35, 3.67, 3.77 and 3.83 (each 3 H, s, OMe × 4), 5.76 (1 H, s, =CH), 6.20 (1 H, d, *J* 1.0, =CH), 7.39 (1 H, s, 5-H), 7.58 and 7.66 (each 2 H, d, *J* 8.8, ArH); $\delta_C(CDCl_3)$ 24.13 (q), 51.77 (q), 51.94 (q), 52.04 (q), 53.10 (q), 115.56 (d), 115.74 (s), 116.73 (d), 123.26 (s), 128.04 (s), 129.79 (d), 130.46 (d × 2), 130.92 (s), 131.58 (d × 2), 136.16 (s), 141.80 (s), 144.67 (s), 162.43 (s), 163.43 (s), 163.83 (s), 164.54 (s) and 184.51 (s) (Found: C, 49.5; H, 3.9; N, 2.5. Calc. for $C_{24}H_{22}BrNO_9S$: C, 49.67; H, 3.82; N, 2.41%).

Z-Isomer.—Pale yellow powder, mp 33–35 °C; ν_{max}(KBr)/cm^{-1} 1710 (CO) and 1640 (CO); *m/z* (+FAB; 3-nitrobenzyl alcohol) 580 $[(M + H)]^+$ and 582 $[(M + 2 + H)]^+$; $\delta_H(CDCl_3)$ 2.30 (3 H, d, *J* 1.0, Me), 3.33, 3.73, 3.76 and 3.83 (each 3 H, s, OMe × 4), 6.30 (1 H, d, *J* 1.0, =CH), 6.39 (1 H, s, =CH), 7.57 and 7.70 (each 2 H, d, *J* 8.5, ArH); $\delta_C(CDCl_3)$ 23.99 (q), 51.66 (q), 51.90 (q), 51.92 (q), 53.17 (q), 115.51 (s), 118.75 (d), 121.46 (d), 122.97 (s), 127.77 (s), 129.90 (d), 130.67 (d × 2), 131.34 (s), 131.43 (d × 2), 136.43 (s), 137.66 (s), 143.92 (s), 162.57 (s), 163.74 (s), 163.91 (s), 164.71 (s) and 184.76 (s) (Found: C, 49.6; H, 3.9; N, 2.5. Calc. for $C_{24}H_{22}BrNO_9S$: C, 49.67; H, 3.82; N, 2.41%).

Dimethyl 1-[2-(1,2-bismethoxycarbonylvinylsulfanyl)-1-methylvinyl]-2-(*p*-nitrobenzoyl)pyrrole-3,4-dicarboxylate 15c. E-*Isomer*.—Yellow powder, mp 48–50 °C; ν_{max}(KBr)/cm^{-1} 1730 (CO), 1650 (CO), 1530, 1350 and 850 (each $ArNO_2$); *m/z* (+FAB; 3-nitrobenzyl alcohol) 547 $[(M + H)]^+$; $\delta_H(CDCl_3)$ 2.38 (3 H, d, *J* 1.0, Me), 3.33, 3.66, 3.77 and 3.84 (each 3 H, s, OMe × 4), 5.76 (1 H, s, =CH), 6.22 (1 H, d, *J* 1.0, =CH), 7.42 (1 H, s, 5-H), 7.93 and 8.28 (each 2 H, d, *J* 8.8, ArH); $\delta_C(CDCl_3)$ 24.16 (q), 51.95 (q), 52.06 (q), 52.21 (q), 53.20 (q), 115.87 (d), 116.22 (s), 117.08 (d), 123.44 (d × 2), 124.23 (s), 129.98 (d × 2), 130.23 (s), 130.47 (d), 141.74 (s), 142.37 (s), 144.41 (s), 150.04 (s), 162.30 (s), 163.43 (s), 163.76 (s), 164.50 (s) and 183.69 (s) (Found: C, 52.6; H, 4.1; N, 5.1. Calc. for $C_{24}H_{22}N_2O_{11}S$: C, 52.75; H, 4.06; N, 5.13%).

Z-Isomer.—Yellow powder, mp 37–39 °C; ν_{max}(KBr)/cm^{-1} 1730 (CO), 1650 (CO), 1530, 1350 and 850 (each $ArNO_2$); *m/z* (+FAB; 3-nitrobenzyl alcohol) 547 $[(M + H)]^+$; $\delta_H(CDCl_3)$ 2.33 (3 H, d, *J* 1.0, Me), 3.32, 3.74, 3.78 and 3.84 (each 3 H, s, OMe × 4), 6.33 (1 H, d, *J* 1.0, =CH), 6.39 (1 H, s, =CH), 7.47 (1 H, s, 5-H), 7.99 and 8.27 (each 2 H, d, *J* 8.8, ArH); $\delta_C(CDCl_3)$ 24.04 (q), 51.86 (q), 52.09 (q × 2), 53.32 (q), 116.03 (s), 119.04 (d), 121.68 (d), 123.35 (d × 2), 123.79 (s), 130.27 (d × 2), 130.48 (d), 130.89 (s), 137.42 (s), 142.63 (s), 143.81 (s), 149.96 (s), 162.49 (s), 163.72 (s), 163.85 (s), 164.83 (s) and 184.00 (s) (Found: C, 52.2; H, 4.2; N, 5.1. Calc. for $C_{24}H_{22}N_2O_{11}S\cdot 1/2H_2O$: C, 51.89; H, 4.17; N, 5.04%).

Dimethyl 2-benzoyl-1-[2-phenyl-2-(1,2-bismethoxycarbonylvinylsulfanyl)pyrrole-3,4-dicarboxylate 15d. E-*Isomer*.—Pale yellow powder, mp 49–51 °C; ν_{max}(KBr)/cm^{-1} 1740 (CO), 1720 (CO) and 1650 (CO); *m/z* (+FAB; 3-nitrobenzyl alcohol) 564 $[(M + H)]^+$; $\delta_H(CDCl_3)$ 3.26 (3 H, s, OMe), 3.57 (6 H, s, OMe × 2), 3.84 (3 H, s, OMe), 5.86 (1 H, s, =CH), 7.32–7.76 (11 H, m, ArH, 5-H) and 7.91 (1 H, s, =CH); $\delta_C(CDCl_3)$ 51.76 (q), 51.82 (q), 51.85 (q), 52.82 (q), 115.39 (s), 119.36 (d), 124.35 (s), 127.86 (d × 2), 128.28 (d × 2), 128.85 (d × 2), 128.92 (d × 2), 129.52 (s), 129.83 (d), 131.15 (d), 131.33 (s), 131.66 (d), 132.89 (d), 135.39 (s), 137.97 (s), 144.34 (s), 162.53 (s), 163.36 (s), 163.89 (s), 164.33 (s) and 186.73 (s) (Found: C, 61.7; H, 4.5; N, 2.6. Calc. for $C_{29}H_{25}NO_9S$: C, 61.80; H, 4.47; N, 2.49%).

Z-Isomer.—Yellow needles, mp 162–163 °C; ν_{max}(KBr)/cm^{-1} 1740 (CO), 1720 (CO) and 1650 (CO); *m/z* (+FAB; 3-nitrobenzyl alcohol) 564 $[(M + H)]^+$; $\delta_H(CDCl_3)$ 3.26, 3.37, 3.81 and 3.83 (each 3 H, s, OMe × 4), 6.56 (1 H, s, =CH), 7.34–7.58 (9 H, m, ArH, 5-H), 7.78 (2 H, d, *J* 7.0, ArH) and 8.08 (1 H, s, =CH); $\delta_C(CDCl_3)$ 51.65 (q), 51.80 (q), 52.09 (q), 52.95 (q), 115.11 (s), 123.98 (s), 124.90 (d), 126.30 (d), 128.26 (d × 2), 128.63 (d × 2), 128.66 (d × 2), 128.92 (d × 2), 129.63 (d),

131.48 (d), 132.78 (d), 134.75 (s), 136.11 (s), 138.27 (s), 144.03 (s), 162.73 (s), 163.70 (s), 164.09 (s), 164.89 (s) and 186.84 (s) (Found: C, 61.6; H, 4.5; N, 2.6. Calc. for $C_{29}H_{25}NO_9S$: C, 61.80; H, 4.47; N, 2.49%).

Dimethyl 2-(*p*-bromobenzoyl)-1-[2-phenyl-2-(1,2-bismethoxycarbonylvinylsulfanyl)vinyl]pyrrole-3,4-dicarboxylate 15e. E-*Isomer*.—Yellow powder, mp 45–48 °C; ν_{max}(KBr)/cm^{-1} 1720 (CO) and 1640 (CO); *m/z* (+FAB; 3-nitrobenzyl alcohol) 642 [(M + H)]$^+$ and 644 [(M + 2 + H)]$^+$; δ_H($CDCl_3$) 3.35, 3.56, 3.58 and 3.85 (each 3 H, s, OMe × 4), 5.84 (1 H, s, =CH), 7.39–7.70 (9 H, m, ArH), 7.71 (1 H, s, 5-H) and 7.89 (1 H, s, =CH); δ_C($CDCl_3$) 51.86 (q), 51.91 (q), 52.10 (q), 52.87 (q), 115.52 (s), 119.48 (d), 124.36 (s), 124.42 (d), 127.89 (d × 2), 128.01 (s), 128.92 (d × 2), 129.98 (d), 130.16 (s), 130.47 (d × 2), 130.91 (s), 131.43 (d), 131.58 (d × 2), 135.29 (s), 136.71 (s), 144.22 (s), 162.47 (s), 163.34 (s), 163.89 (s), 164.29 (s) and 185.57 (s); *m/z* (+FAB; 3-nitrobenzyl alcohol) 642.0410 ($C_{29}H_{24}BrNO_9S$ + H requires *m/z* 642.0434).

Z-*Isomer*.—Yellow powder, mp 56–58 °C; ν_{max}(KBr)/cm^{-1} 1720 (CO) and 1650 (CO); *m/z* (+FAB; 3-nitrobenzyl alcohol) 642 [(M + H)]$^+$ and 644 [(M + 2 + H)]$^+$; δ_H($CDCl_3$) 3.35, 3.37, 3.78 and 3.82 (each 3 H, s, OMe × 4), 6.55 (1 H, s, =CH), 7.32–7.35 (3 H, m, ArH), 7.40 (1 H, s, 5-H), 7.45–7.49 (2 H, m, ArH), 7.58, 7.65 (each 2 H, d, *J* 8.8, ArH) and 8.08 (1 H, s, =CH); δ_C($CDCl_3$) 51.50 (q), 51.79 (q), 51.92 (q), 52.80 (q), 115.03 (s), 123.90 (s), 124.76 (d), 126.02 (d), 127.60 (s), 128.44 (d × 2), 128.51 (d × 2), 129.54 (d), 130.25 (d × 2), 130.85 (s), 131.35 (d × 2), 131.51 (d), 134.95 (s), 135.83 (s), 136.87 (s), 143.73 (s), 162.38 (s), 163.46 (s), 163.84 (s), 164.65 (s) and 185.37 (s) (Found: C, 54.3; H, 4.0; N, 2.25. Calc. for $C_{29}H_{24}BrNO_9S$: C, 54.22; H, 3.77; N, 2.18%).

Dimethyl 2-benzoyl-1-[2-(1,2-bismethoxycarbonylvinylsulfanyl)phenyl]pyrrole-3,4-dicarboxylate 19a. E-*Isomer*.—Pale yellow powder, mp 48–49 °C; ν_{max}(KBr)/cm^{-1} 1720 (CO) and 1640 (CO); *m/z* 537 (M$^+$); δ_H($CDCl_3$) 3.26, 3.59, 3.61 and 3.83 (each 3 H, s, OMe × 4), 5.62 (1 H, s, =CH), 7.38–7.77 (10 H, m, ArH, 5-H); δ_C($CDCl_3$) 51.77 (q), 51.88 (q × 2), 52.85 (q), 115.05 (s), 116.70 (d), 123.46 (s), 126.37 (s), 128.31 (d × 2), 129.15 (d × 2), 129.31 (d), 130.25 (d), 131.45 (d), 132.44 (d), 132.59 (s), 132.95 (d), 137.01 (d), 137.80 (s), 141.73 (s), 147.75 (s), 162.84 (s), 163.62 (s), 164.15 (s), 164.45 (s) and 186.08 (s) (Found: C, 60.4; H, 4.4; N, 2.7. Calc. for $C_{27}H_{23}NO_9S$: C, 60.33; H, 4.31; N, 2.61%).

Z-*Isomer*.—Pale yellow powder, mp 49–51 °C; ν_{max}(KBr)/cm^{-1} 1720 (CO) and 1640 (CO); *m/z* 537 (M$^+$); δ_H($CDCl_3$) 3.25, 3.34, 3.76 and 3.84 (each 3 H, s, OMe × 4), 6.54 (1 H, s, =CH), 7.36–7.55 (7 H, m, ArH), 7.62 (1 H, s, 5-H) and 7.77–7.79 (2 H, m, ArH); δ_C($CDCl_3$) 51.74 (q), 51.83 (q), 52.10 (q), 52.83 (q), 114.98 (s), 123.17 (s), 123.37 (d), 128.29 (d × 2), 128.95 (d), 129.19 (d × 2), 129.42 (d), 129.79 (d), 131.73 (s), 132.48 (d), 132.84 (d), 132.99 (s), 133.52 (d), 138.09 (s), 139.81 (s), 145.85 (s), 163.00 (s), 164.21 (s), 164.25 (s), 164.98 (s) and 186.19 (s) (Found: C, 59.5; H, 4.35; N, 2.65. Calc. for $C_{27}H_{23}NO_9S \cdot 1/2H_2O$: C, 59.34; H, 4.43; N, 2.56%).

Dimethyl 2-(*p*-bromobenzoyl)-1-[2-(1,2-bismethoxycarbonylvinylsulfanyl)phenyl]pyrrole-3,4-dicarboxylate 19b. E-*Isomer*.—White powder, mp 48–49 °C; ν_{max}(KBr)/cm^{-1} 1720 (CO) and 1650 (CO); *m/z* 615 (M$^+$) and 617 (M$^+$ + 2); δ_H($CDCl_3$) 3.36, 3.59, 3.62 and 3.83 (each 3 H, s, OMe × 4), 5.56 (1 H, s, =CH) and 7.38–7.68 (9-H, m, ArH, 5-H); δ_C($CDCl_3$) 51.76 (q), 51.85 (q), 52.02 (q), 52.82 (q), 115.11 (s), 116.65 (d), 123.43 (s), 126.18 (s), 128.01 (s), 129.29 (d), 130.29 (d), 130.57 (d × 2), 131.43 (d), 131.52 (d × 2), 132.03 (s), 132.54 (d), 136.42 (s), 136.97 (d), 141.48 (s), 147.43 (s), 162.66 (s), 163.48 (s), 164.01 (s), 164.31 (s) and 184.84 (s) (Found: C, 52.55; H, 3.85; N, 2.2. Calc. for $C_{27}H_{22}BrNO_9S$: C, 52.61; H, 3.60; N, 2.27%).

Z-*Isomer*.—Pale yellow powder, mp 57–60 °C; ν_{max}(KBr)/cm^{-1} 1730 (CO) and 1650 (CO); *m/z* 615 (M$^+$) and 617 (M$^+$ + 2); δ_H($CDCl_3$) 3.34, 3.36, 3.75 and 3.82 (each 3 H, s, OMe × 4), 6.51 (1 H, s, =CH), 7.38–7.46 (4 H, m, ArH), 7.56 (2 H, d, *J* 8.5, ArH), 7.63 (1 H, s, 5-H) and 7.67 (2 H, d, *J* 8.5, ArH); δ_C($CDCl_3$) 51.54 (q), 51.67 (q), 51.80 (q), 52.57 (q), 114.67 (s), 122.59 (d), 122.92 (s), 127.59 (s), 128.52 (d), 129.41 (d), 129.58 (d), 130.40 (d × 2), 130.99 (s), 131.24 (d × 2), 132.19 (s), 132.36 (d), 133.51 (d), 136.47 (s), 139.55 (s), 145.65 (s), 162.48 (s), 163.72 (s), 163.80 (s), 164.60 (s) and 184.64 (s) (Found: C, 52.5; H, 3.8; N, 2.2. Calc. for $C_{27}H_{22}BrNO_9S$: C, 52.61; H, 3.60; N, 2.27%).

General procedure for reaction of thiazolium *N*-phenacylides with DMAD in aqueous DMF

Triethylamine (1 mmol) was added dropwise to a mixture of an appropriate thiazolium salt **13** or **14** (1 mmol) and DMAD (1 mmol) in DMF (7 cm^3) containing water (7.7 mmol) with stirring. The reaction mixture was stirred for 2 h at room temperature, and then poured into ice–water. The precipitated solid was filtered off, dried, and recrystallised from an appropriate solvent to afford a hemiacetal **6**, **20**.

Dimethyl 1-hydroxy-4-methyl-1-phenyl-1*H*-pyrrolo[2,1-*c*]-1,4-thiazine-7,8-dicarboxylate 6a. Colourless needles, mp 177–179 °C (from EtOH) (lit.,[2] 172 °C); δ_C($CDCl_3$) 19.69 (q), 51.53 (q), 52.06 (q), 78.72 (s), 104.36 (d), 113.21 (s), 114.29 (s), 121.60 (d), 126.95 (d × 2), 127.82 (d × 2), 128.59 (d), 128.92 (s), 130.93 (s), 140.72 (s), 163.34 (s) and 165.86 (s) (Found: C, 60.0; H, 4.8; N, 3.95. Calc. for $C_{18}H_{17}NO_5S$: C, 60.16; H, 4.77; N, 3.90%).

Dimethyl 1-(*p*-bromophenyl)-1-hydroxy-4-methyl-1*H*-pyrrolo-[2,1-*c*]-1,4-thiazine-7,8-dicarboxylate 6b. Colourless needles, mp 181–182 °C (from EtOH); δ_C($CDCl_3$) 19.72 (q), 51.64 (q), 52.28 (q), 78.41 (s), 104.19 (d), 113.27 (s), 114.62 (s), 121.71 (d), 122.87 (s), 128.70 (d × 2), 129.01 (s), 130.64 (s), 130.95 (d × 2), 140.15 (s), 163.28 (s) and 165.97 (s) (Found: C, 49.5; H, 3.9; N, 3.2. Calc. for $C_{18}H_{16}BrNO_5S$: C, 49.33; H, 3.68; N, 3.20%).

Dimethyl 1-hydroxy-4-methyl-1-(*p*-nitrophenyl)-1*H*-pyrrolo-[2,1-*c*]-1,4-thiazine-7,8-dicarboxylate 6c. Yellow needles, mp 193–194 °C (from EtOH); ν_{max}(KBr)/cm^{-1} 3350 (OH), 1720 (CO), 1690 (CO), 1520, 1340 and 850 (each $ArNO_2$); *m/z* 404 (M$^+$); δ_H($CDCl_3$) 2.37 (3 H, s, Me), 3.35 and 3.81 (each 3 H, s, OMe × 2), 5.22 (1 H, s, OH), 5.91 (1 H, s, 3-H), 7.47 (1 H, s, 6-H), 7.77 and 8.18 (each 2 H, d, *J* 9.0, ArH); δ_C($CDCl_3$) 19.68 (q), 51.74 (q), 52.45 (q), 78.22 (s), 103.97 (d), 112.99 (s), 114.88 (s), 121.94 (d), 122.99 (d × 2), 127.94 (d × 2), 129.29 (s), 130.25 (s), 147.77 (s), 148.26 (s), 163.17 (s) and 166.21 (s) (Found: C, 53.3; H, 4.1; N, 6.9. Calc. for $C_{18}H_{16}N_2O_7S$: C, 53.46; H, 3.99; N, 6.93%).

Dimethyl 1-hydroxy-1,3-diphenyl-1*H*-pyrrolo[2,1-*c*]-1,4-thiazine-7,8-dicarboxylate 6d. White needles, mp 148–152 °C (from CH_2Cl_2–Et_2O); ν_{max}(KBr)/cm^{-1} 3400 (OH), 1730 (CO) and 1680 (CO); *m/z* 421 (M$^+$); δ_H($CDCl_3$) 3.28, 3.73 (each 3 H, s, OMe × 2), 4.99 (1 H, s, OH) and 7.34–7.66 (12 H, m, ArH, 4-H, 6-H); δ_C($CDCl_3$) 51.95 (q), 52.44 (q), 80.38 (s), 112.74 (s), 115.50 (s), 117.58 (d), 124.62 (d), 125.01 (s), 127.05 (d × 2), 127.16 (d × 2), 128.28 (d × 2), 129.03 (d), 129.14 (d × 2), 129.43 (d), 130.36 (s), 135.06 (s), 140.97 (s), 163.72 (s) and 166.03 (s) (Found: C, 65.3; H, 4.5; N, 3.4. Calc. for $C_{23}H_{19}NO_5S$: C, 65.55; H, 4.54; N, 3.32%).

Dimethyl 1-(*p*-bromophenyl)-1-hydroxy-3-phenyl-1*H*-pyrrolo-[2,1-*c*]-1,4-thiazine-7,8-dicarboxylate 6e. Colourless needles, mp 178–181 °C (decomp.) (from CH_2Cl_2–Et_2O); ν_{max}(KBr)/cm^{-1} 3270 (OH), 1720 (CO) and 1680 (CO); *m/z* 499 (M$^+$) and 501 (M$^+$ + 2); δ_H($CDCl_3$) 3.41 and 3.76 (each 3 H, s, OMe × 2), 5.18 (1 H, s, OH) and 7.36–7.53 (11 H, m, ArH, 4-H, 6-H); δ_C($CDCl_3$) 51.76 (q), 52.36 (q), 79.81 (s), 112.40 (s), 115.64 (s), 117.21 (d), 122.99 (s), 124.38 (d), 124.78 (s), 126.92 (d × 2), 128.46 (d × 2) 128.93 (d × 2), 129.33 (d), 129.92 (s), 131.13 (d × 2), 134.56 (s), 140.29 (s), 163.38 (s) and 165.91 (s) (Found: C, 55.1; H, 3.65; N, 2.85. Calc. for $C_{23}H_{18}BrNO_5S$: C, 55.21; H, 3.63; N, 2.80%).

Dimethyl 4-hydroxy-4-phenyl-4*H*-pyrrolo[2,1-*c*]-1,4-benzothiazine-8,9-dicarboxylate 20a. White prisms, mp 171–172 °C (from $CHCl_3$–hexane); ν_{max}(KBr)/cm^{-1} 3350 (OH) and 1720 (CO); *m*/*z* 395 (M^+); δ_H($CDCl_3$) 3.00 and 3.84 (each 3 H, s, OMe × 2), 5.33 (1 H, s, OH), 7.28–7.64 (9 H, m, ArH) and 7.72 (1 H, s, 6-H); δ_C($CDCl_3$) 51.58 (q), 51.91 (q), 79.76 (s), 113.27 (s), 115.26 (s), 118.53 (d), 122.78 (d), 124.26 (s), 126.43 (d), 126.82 (d × 2), 127.48 (d), 127.97 (d × 2), 128.65 (d), 129.10 (d), 133.03 (s), 133.25 (s), 139.69 (s), 163.37 (s) and 165.59 (s) (Found: C, 63.6; H, 4.3; N, 3.5. Calc. for $C_{21}H_{17}NO_5S$: C, 63.79; H, 4.33; N, 3.54%).

Dimethyl 4-(*p*-bromophenyl)-4-hydroxy-4*H*-pyrrolo[2,1-*c*]-1,4-benzothiazine-8,9-dicarboxylate 20b. White prisms, mp 194–196 °C (from $CHCl_3$–hexane); ν_{max}(KBr)/cm^{-1} 3350 (OH), 1740 (CO) and 1690 (CO); *m*/*z* 473 (M^+) and 475 ($M^+ + 2$); δ_H($CDCl_3$) 3.23 and 3.85 (each 3 H, s, OMe × 2), 5.30 (1 H, s, OH), 7.20–7.56 (8 H, m, ArH) and 7.75 (1 H, s, 6-H); δ_C($CDCl_3$) 51.74 (q), 52.27 (q), 79.61 (s), 113.33 (s), 115.75 (s), 118.54 (d), 122.82 (d), 122.99 (s), 123.96 (s), 126.74 (d), 127.74 (d), 128.68 (d × 2), 129.30 (d), 131.13 (d × 2), 133.01 (s), 133.17 (s), 139.26 (s), 163.39 (s) and 165.87 (s) (Found: C, 53.2; H, 3.4; N, 3.0. Calc. for $C_{21}H_{16}BrNO_5S$: C, 53.18; H, 3.40; N, 2.95%).

Reaction of 6b with DMAD

DMAD (0.5 mmol) was added dropwise to a mixture of **6b** (0.5 mmol) and triethylamine (0.5 mmol) in dry DMF (5 cm^3) with stirring. Stirring was continued for 4 h at room temperature after which the mixture was poured into ice–water and extracted with $CHCl_3$ (20 cm^3 × 4). The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure and the residue was purified by PLC on silica gel using hexane–ethyl acetate (2:1) to afford dimethyl 2-(*p*-bromobenzoyl)-1-[2-(1,2-bismethoxycarbonylvinylsulfanyl)-1-methylvinyl]pyrrole-3,4-dicarboxylate **15b** (280 mg, 96%).

Reaction of 6b with ethyl propiolate

Ethyl propiolate (1 mmol) was added dropwise to a mixture of **6b** (1 mmol) and triethylamine (1 mmol) in dry DMF (7 cm^3) with stirring. The mixture was stirred for 4 h at room temperature and then poured into ice–water and extracted with $CHCl_3$ (20 cm^3 × 4). The combined extracts were dried ($MgSO_4$), and concentrated under reduced pressure and the residue was purified by PLC on silica gel using hexane–ethyl acetate (2:1) to afford dimethyl 2-(*p*-bromobenzoyl)-1-[2-(2-ethoxycarbonylvinylsulfanyl)-1-methylvinyl]pyrrole-3,4-dicarboxylate **16** (499 mg, 93%).

E-*Isomer*.—White powder, mp 43–46 °C; ν_{max}(KBr)/cm^{-1} 1720 (CO) and 1650 (CO); *m*/*z* 535 (M^+) and 537 ($M^+ + 2$); δ_H($CDCl_3$) 1.25 (3 H, t, *J* 7.3, CH_2*Me*), 2.33 (3 H, s, Me), 3.35 and 3.83 (each 3 H, s, OMe × 2), 4.13 (2 H, q, *J* 7.3, CH_2Me), 5.74 (1 H, d, *J* 15.1, =CH), 6.28 (1 H, s, =CH), 7.37 (1 H, d, *J* 15.1, =CH), 7.39 (1 H, s, 5-H), 7.58 and 7.65 (each 2 H, d, *J* 8.3, ArH); δ_C($CDCl_3$) 14.13 (q), 23.86 (q), 51.74 (q), 52.00 (q), 60.43 (t), 115.68 (s), 116.83 (d), 118.22 (d), 123.12 (s), 128.08 (s), 129.69 (d), 130.46 (d × 2), 130.99 (s), 131.59 (d × 2), 136.14 (s), 138.47 (s), 141.30 (d), 162.50 (s), 163.85 (s), 164.34 (s) and 184.50 (s) (Found: C, 51.55; H, 4.2; N, 2.6. Calc. for $C_{23}H_{22}BrNO_7S$: C, 51.50; H, 4.13; N, 2.61%).

Z-*Isomer*.—Colourless needles, mp 146 °C (from EtOH); ν_{max}(KBr)/cm^{-1} 1730 (CO) and 1680 (CO); *m*/*z* 535 (M^+) and 537 ($M^+ + 2$); δ_H($CDCl_3$) 1.26 (3 H, t, *J* 7.3, CH_2*Me*), 2.28 (3 H, s, Me), 3.34 and 3.83 (each 3 H, s, OMe × 2), 4.15 (2 H, q, *J* 7.3, CH_2Me), 5.75 (1 H, d, *J* 9.8, =CH), 6.25 (1 H, s, =CH), 6.86 (1 H, d, *J* 9.8, =CH), 7.40 (1 H, s, 5-H), 7.55 and 7.70 (each 2 H, d, *J* 8.5, ArH); δ_C($CDCl_3$) 14.13 (q), 23.64 (q), 51.62 (q), 51.85 (q), 60.29 (t), 114.45 (d), 115.61 (s), 123.12 (s), 123.69 (d), 127.80 (s), 129.65 (d), 130.75 (d × 2), 131.06 (s), 131.43 (d × 2), 135.05 (s), 136.20 (s), 144.21 (d), 162.50 (s), 163.83 (s), 165.75 (s) and 184.83 (s) (Found: C, 51.7; H, 4.2; N, 2.6. Calc. for $C_{23}H_{22}BrNO_7S$: C, 51.50; H, 4.13; N, 2.61%).

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