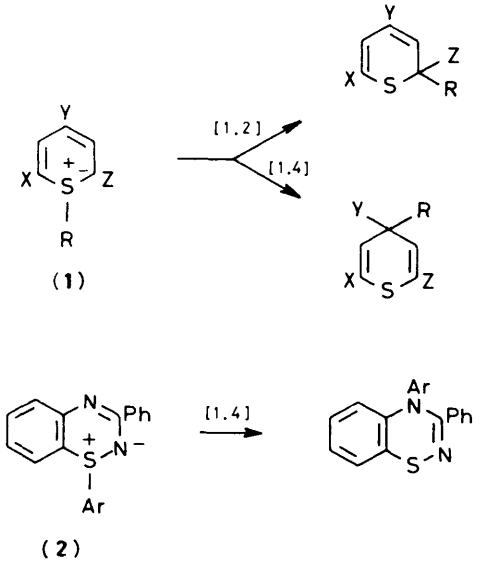
# Thermal Rearrangements of Fused 1λ⁴,2-Thiazines (2-Azathiabenzenes); [1,4] Shifts in Cyclic Sulphur–Nitrogen Ylides

**Raymond S. Gairns, Richard D. Grant, Christopher J. Moody, Charles W. Rees, and Siu Chung Tsoi**
*Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY*

When heated in xylene the fused 1λ⁴,2-thiazines (**3**), with the exception of the benzo compound (**3c**) which is thermally stable, rearrange to the 4a*H*-isomers (**4**). *S*-Phenyl groups migrate exclusively 1,4 to carbon with consequent disruption of the thiophene and furan aromaticity. This thermal [1,4] shift occurs more readily when aromaticity is not disrupted; thus thienothiazine (**7**) isomerises to (**8**) in toluene, and benzothiazine (**11**) isomerises to (**12**) spontaneously on formation in xylene. With the *S*-methyl compound (**3g**) this rearrangement is accompanied by proton tautomerism and [1,2] rearrangement to give the thienothiazepine (**5**) and, at higher temperature (156 °C), the thienopyrrole (**6**) is formed (Scheme 2). The 4a*H*-thienothiazine (**4a**) rearranges more extensively at higher temperatures to give, sequentially, the pyrrolo[1,2-*b*]isothiazole (**13**) at 156 °C (Scheme 5) and the thiophene (**17**) at 180 °C (Scheme 6).

The high reactivity of conjugated six-membered rings containing a sulphur(IV) atom is associated with the fact that these systems are ylidic rather than aromatic in character. For example, thiabenzenes, which are best represented by the cyclic sulphonium ylide structure (**1**), undergo thermal rearrangement involving the transfer of the sulphur substituent, R, to carbon in a [1,2]- or [1,4]-sigmatropic shift, processes typical of acyclic sulphonium ylides[1,2] (Scheme 1). The aza-analogues of thiabenzenes, the 1λ⁴,2,4-benzothiadiazines (**2**) also rearrange by a [1,4] shift of the sulphur aryl substituent when heated, although considerably higher temperatures are required[3] (Scheme 1).




**Scheme 1.**

In the preceding paper[4] we reported the preparation of a series of fused 1λ⁴,2-thiazines (2-azathiabenzenes), and showed that their spectral properties are in accord with an ylidic structure. We now report in detail the thermal rearrangements of these cyclic sulphur-nitrogen ylides (sulphimides).[5]

## Results and Discussion

*Thermal Rearrangement of* 1λ⁴,2-*Thiazines*.—The fused 1λ⁴,2-thiazines (**3**) are thermally stable up to *ca.* 120 °C but on being heated in xylene (138 °C) or bromobenzene (156 °C) are gradually consumed. In the case of the *S*-phenylthienothiazine (**3a**), being heated under reflux in xylene for 10 h led to the formation of a new product in excellent yield (94%). The product, which was isomeric with the starting sulphimide and was unstable to further heating (see later), was assigned the 4a*H*-thienothiazine structure (**4a**) on the basis of its spectral properties. In particular, the $^1$H n.m.r. spectrum showed a non-aromatic thiophene β-proton at δ 6.50 as a doublet (*J* 5.8 Hz), and the $^{13}$C n.m.r. spectrum contained a highfield low-intensity signal at δ 59.3 indicating a sp³ quaternary carbon which was assigned to C-4a. Alkaline hydrolysis of (**4a**) gave the corresponding carboxylic acid, which showed no tendency to undergo decarboxylation. The corresponding *S*-phenylfurothiazine (**3b**) rearranged similarly to give (**4b**) in excellent yield (Table 1), but the benzothiazine (**3c**), which was much more thermally stable and required prolonged refluxing in 1,2-dichlorobenzene to effect any change, did not rearrange cleanly. The other *S*-phenyl thienothiazine derivatives (**3d**—**f**), however, all rearranged when heated in xylene to give the corresponding 4a*H*-isomers in good yield (Table 1). Thus the fused

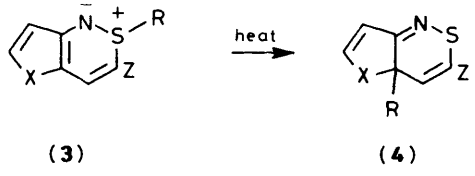
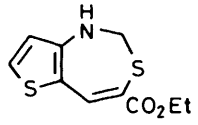



**Table 1.** Thermal rearrangement of 1λ⁴,2-thiazine derivatives

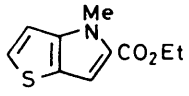
| (3)/(4) | X | R | Z | Yield (%) |
|---|---|---|---|---|
| **a** | S | Ph | $CO_2Et$ | 94 |
| **b** | O | Ph | $CO_2Et$ | 98 |
| **c** | CH=CH | Ph | $CO_2Et$ | — |
| **d** | S | Ph | COMe | 80 |
| **e** | S | Ph | CHO | 54 |
| **f** | S | Ph | CN | 88 |
| **g** | S | Me | $CO_2Et$ | 40 |

azathiabenzenes (**3a**, **b**, **d**—**f**) undergo thermal rearrangement which involves migration of the *S*-phenyl substituent to carbon and consequent disruption of the thiophene and furan aromaticity. In the case of the benzo derivative (**3c**), the corresponding migration with its consequent disruption of the benzenoid aromaticity is now much less favoured. This migration of the sulphur substituent to carbon is formally a [1,4]-sigmatropic shift involving six electrons, and is clearly closely related to the corresponding shift observed in thiabenzenes by Mislow and co-workers.[1,2]

For the *S*-phenylthiazines the alternative [1,2]-shift to nitrogen was not observed, and indeed this simple process is rarely observed in sulphimides generally.[6] However, in the rearrangement of the *S*-methylthienothiazine (**3g**), although the [1,4]-rearrangement leading to (**4g**) was the major (40%) pathway, other products were also observed. The cyclic sulphimide (**3g**) when heated in xylene gave the 4a*H*-thiazine (**4g**) (40%) and the thieno-1,3-thiazepine (**5**) (26%). When the rearrangement was carried out at a higher temperature in boiling bromobenzene the products were the 4a*H*-thiazine (**4g**) (40%) and the *N*-methyl thienopyrrole (**6**) (9%). The structure of the 4a*H*-thiazine (**4g**) was assigned by comparison with the corresponding phenyl substituted derivatives and was confirmed by *X*-ray crystallography.* The *N*-methyl thienopyrrole structure (**6**) was confirmed by *N*-methylation of the known[7] *N*-H thienopyrrole, and the thienothiazepine (**5**) was assigned on the basis of its $^1$H n.m.r. spectrum which in particular showed the presence of an NH adjacent to a $CH_2$ group. The formation



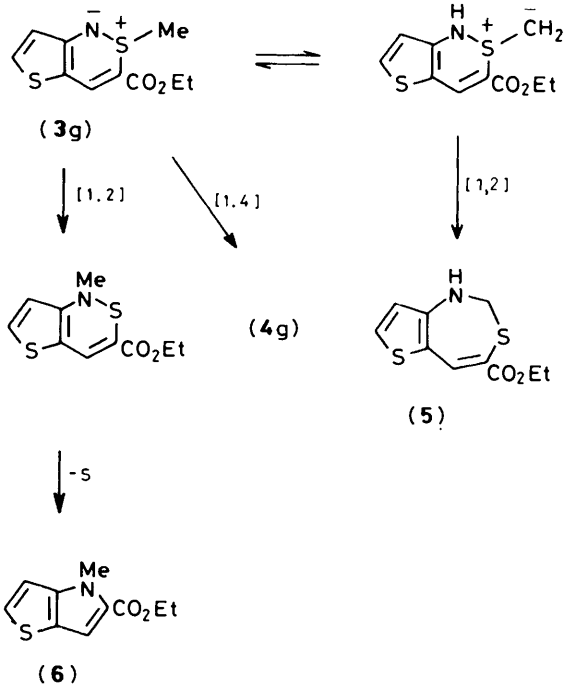
(**5**)



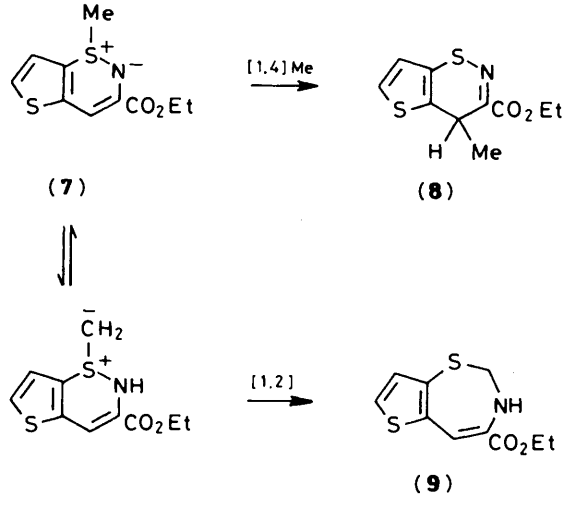
(**6**)

of the thiazepine (**5**) is not unexpected; it is presumably formed by tautomerisation of (**3g**) into the isomeric sulphonium ylide followed by a [1,2]-nitrogen shift to the carbanionic centre (Scheme 2). This type of reaction is well known in acyclic sulphimides,[6] and has also been observed in the thermal rearrangement of 9-methyl-9-thia-10-aza-phenanthrene.[8] The origin of the small amount of the *N*-methyl thienopyrrole (**6**) is not known for certain. One possible mechanism would involve a [1,2]-methyl shift from sulphur to nitrogen followed by extrusion of sulphur (Scheme 2).

The thermal [1,4]-sigmatropic rearrangement of the sulphur substituent occurs more readily in isomeric fused azathiabenzenes when the fused aromatic ring is not directly involved. The *S*-methylthienothiazine (**7**) is less thermally stable than the isomeric ylide (**3g**) and decomposes in boiling toluene to give a very complex mixture of products. The two main components were separated by careful chromatography and identified as the 4*H*-thienothiazine (**8**) (4%) and the thienothiazepine (**9**) (14%). The formation of these rearrangement products is again rationalised in terms of a competing [1,4]-methyl shift, and a [1,2]-rearrangement, with ring expansion, of the sulphonium ylide tautomer of the starting sulphimide (**7**) (Scheme 3). The corresponding [1,4]-rearrangement of the benzo-fused *S*-phenyl sulphimides (**11**) was so fast that the sulphimides themselves could not be isolated. The azides (**10**), prepared from the corresponding benzaldehydes by condensation with ethyl azidoacetate, needed to be heated in boiling xylene to effect their decomposition. Under these conditions, the sulphimides (**11**) were not isolated, and the products were the corresponding



Scheme 2.

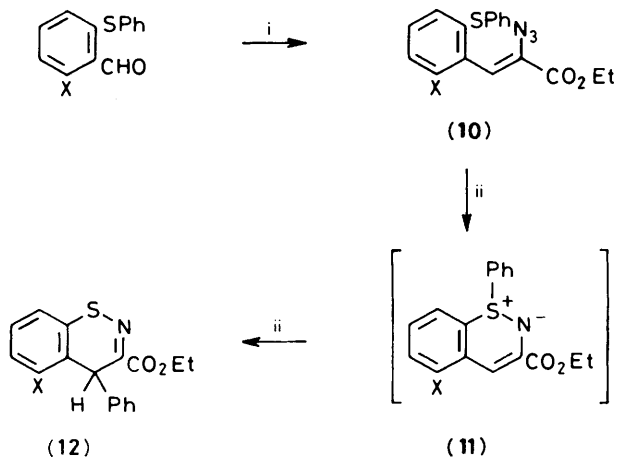


Scheme 3.

benzothiazines (**12**), formed by [1,4]-sigmatropic shift of the *S*-phenyl substituent in the intermediate cyclic sulphimide (Scheme 4). Thus, there is a thermal rearrangement pathway common to these cyclic sulphur–nitrogen ylides which involves a [1,4]-sigmatropic shift of the sulphur substituent to carbon. This parallels closely the thermal rearrangement of the thiabenzes investigated by Mislow and co-workers.[1,2]

*Thermal Decomposition of the* 4aH-*Thienothiazine* (**4a**).—When the cyclic sulphimide (**3a**) was heated in boiling bromobenzene, as opposed to xylene, for 2.5 h the rearrangement product, the 4a*H*-thienothiazine (**4a**), was accompanied by another compound from which it was inseparable by chromatography. However, on prolonged heating in bromobenzene (36 h). this mixture was converted

* Determined by Dr. D. J. Williams of this department.

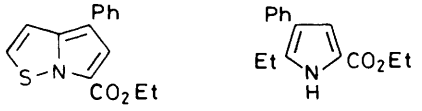



a, X = Cl; b, X = SPh

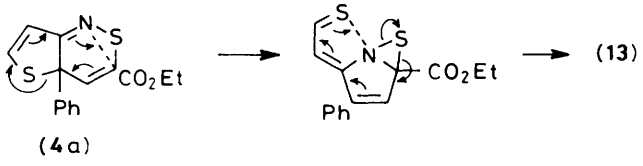
**Scheme 4.** *Reagents:* i, $EtO_2CCH_2N_3$, EtOH, NaOEt, −15 °C; ii, heat, xylene.

into the new product in 80% yield. The same product was obtained in 82% yield by heating the pure 4a*H*-thienothiazine (**4a**) in bromobenzene, confirming that it was derived from the 4a*H*-isomer (**4a**) rather than the starting 1λ⁴-isomer (**3a**). In both cases elemental sulphur was also isolated, the yield in the second reaction being 63%.

Microanalysis and mass spectrometry established that the product contained one less sulphur atom than (**4a**), and the $^{13}C$ n.m.r. spectrum indicated that the $sp^3$ quaternary and C=N carbons were no longer present. The presence of an ester carbonyl at 1 670 $cm^{-1}$ in the i.r. spectrum and a vinylic proton with a small coupling to a proton α- to sulphur in the $^1H$ n.m.r. spectrum suggested the structure (**13**). Further evidence in support of the pyrrolo[1,2-*b*]isothiazole structure (**13**) was obtained by desulphurisation of the product with Raney nickel to give ethyl 5-ethyl-4-phenylpyrrole-2-carboxylate (**14**). The relative positions of the substituents in the pyrrole (**14**) were confirmed by n.m.r. n.O.e. difference experiments.

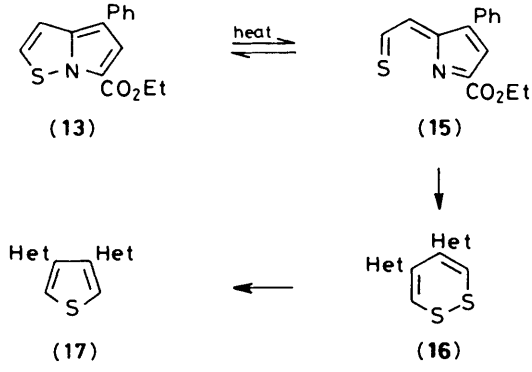



The mechanism by which the pyrroloisothiazole (**13**) is formed from the thienothiazine (**4a**) is not known, although it is likely that it is the sulphur atom adjacent to nitrogen in the starting material that is extruded. One possible mechanism which involves an electrocyclic breaking of the C(**4a**)–S bond followed by recyclisation is shown in Scheme 5.




**Scheme 5.**

The pyrroloisothiazole (**13**) itself is also thermally unstable at higher temperatures, and when heated in boiling 1,2-dichlorobenzene is converted into a compound assigned the thiophene structure (**17**), in 49% yield. The same thiophene (**17**) was also obtained (28%) by thermolysis of the thienothiazine (**4a**) in 1,2-dichlorobenzene. In both cases elemental sulphur was isolated, and hydrogen sulphide was evolved during the thermolysis. The symmetrical structure of the thiophene (**17**) was assigned on the basis of its spectroscopic properties, but unfortunately attempts to confirm the structure by desulphurisation were unsuccessful. The thermal instability of the pyrroloisothiazole (**13**) is presumably associated with the weak N–S bond, breaking of which would lead to the unstable thioaldehyde (**15**). Dimerisation of (**15**) in a head-to-head fashion would give the 1,2-dithian (**16**), and hence the thiophene (**17**) (Scheme 6). The alternative head-to-tail dimerisation of (**15**) would give a 1,4-dithiin, and hence a 2,4-disubstituted thiophene, which would not possess the element of symmetry required by the spectral properties of the product.




**Scheme 6.** Het = 2-ethoxycarbonyl-4-phenylpyrrol-5-yl.

## Experimental

*Fused* 1λ⁴,2-*Thiazines*.—The starting thiazines (**3a**—**g**) and (**7**) were prepared as described in the preceding paper.[4]

*Thermolysis of the Thiazine* (**3a**).—A solution of the thiazine (**3a**) (99 mg) in xylene (8 ml) was heated under reflux for 10 h. Evaporation of the solvent and chromatography gave *ethyl* 4a-*phenyl*-4a*H*-*thieno*[3,2-c][1,2]*thiazine*-3-*carboxylate* (**4a**) (93 mg, 94%), b.p. 140 °C at 0.02 mmHg (Kugelrohr) (Found: C, 59.7; H, 4.4; N, 4.6; S, 21.3. $C_{15}H_{13}NO_2S_2$ requires C, 59.4; H, 4.3; N, 4.6; S, 21.1%); $\nu_{max.}$ ($CCl_4$) 1 725 $cm^{-1}$; $\lambda_{max.}$ (EtOH) 260sh (log ε 3.89), 267 (3.89), 272sh (3.87), 296 (3.78), and 330 nm (3.82); δ (250 MHz, $CDCl_3$) 1.33 (3 H, t), 4.26 (2 H, q), 6.50 (1 H, d, *J* 5.8 Hz), 7.13—7.26 (5 H, m), 7.34 (1 H, d, *J* 5.8 Hz), and 7.38 (1 H, s); $\delta_C$($CDCl_3$) 14.0, 59.3, 62.0, 120.2, 120.7, 125.6, 128.4, 128.5, 131.1, 137.9, 141.9, 162.4, and 165.6; *m/z* 303 ($M^+$), 274, 230 (base), 226, 198, and 186.

*Thermolysis of the Thiazine* (**3b**).—A solution of the thiazine (**3b**) (123 mg) in xylene (10 ml) was heated under reflux for 1 h. Evaporation of the solvent and chromatography gave *ethyl* 4a-*phenyl*-4a*H*-*furo*[3,2-c][1,2]*thiazine*-3-*carboxylate* (**4b**) (120 mg, 98%) as a gum, $\nu_{max.}$ (neat) 1 715 $cm^{-1}$; δ (250 MHz, $CDCl_3$) 1.40 (3 H, t), 4.30 (2 H, q), 6.1 (1 H, d, *J* 3 Hz), 7.1 (1 H, s), 7.1—7.4 (5 H, m), and 7.4 (1 H, d, *J* 3 Hz); $\delta_C$($CDCl_3$) 14.0, 62.0, 83.4, 105.3, 119.2, 126.1, 128.6, 129.3, 131.4, 134.9, 161.5, 162.3, and 164.7; *m/z* 287 ($M^+$), 258, 231, and 186.

*Thermolysis of the Thiazine* (**3c**).—The thiazine (**3c**) (201 mg) was heated under reflux in 1,2-dichlorobenzene (15 ml) for 45 h.

The solvent was evaporated to leave a complex mixture with no major product (t.l.c., n.m.r.).

*Thermolysis of the Thiazine* (**3d**).—A solution of the thiazine (**3d**) (100 mg) in xylene (50 ml) was heated under reflux until starting material was consumed (t.l.c.). Evaporation of the solvent and chromatography gave *3-acetyl-4a-phenyl-4aH-thieno*[3,2-c][1,2]*-thiazine* (**4d**) (80 mg, 80%) as an oil (Found: C, 61.5; H, 4.2; N, 5.0. $C_{14}H_{11}NOS_2$ requires C, 61.5; H, 4.1; N, 5.1%); $\nu_{max.}$ (neat) 1 680 $cm^{-1}$; δ (90 MHz, $CDCl_3$) 2.48 (3 H, s), 7.06—7.30 (6 H, m), and 7.36 (1 H, d, *J* 6.5 Hz); $\delta_C$($CDCl_3$) 26.5, 59.4, 120.1, 125.5, 128.6, 137.5, 139.1, 142.1, 166.2, and 193.0; *m/z* 273 ($M^+$), 257, and 230 (base).

*Thermolysis of the Thiazine* (**3e**).—A solution of the thiazine (**3e**) (100 mg) in xylene (50 ml) was heated under reflux until starting material was consumed (t.l.c.). Evaporation of the solvent and chromatography gave 4a-*phenyl*-4aH-*thieno*[3,2-c]-[1,2]*thiazine-3-carbaldehyde* (**4e**) (54 mg, 54%), m.p. 90 °C (Found: C, 60.2; H, 3.4; N, 5.4. $C_{13}H_9NOS_2$ requires C, 60.2; H, 3.5; N, 5.4%); $\nu_{max.}$($CCl_4$) 1 690 $cm^{-1}$; δ (90 MHz, $CDCl_3$) 6.53 (1 H, d, *J* 6.4 Hz), 7.25 (6 H, m), 7.39 (1 H, d, *J* 6.4 Hz), and 9.67 (1 H, s); $\delta_C$($CDCl_3$) 29.7, 59.2, 120.3, 125.6, 127.5, 128.8, 137.2, 139.4, 142.1, 166.5, and 186.4; *m/z* 259 ($M^+$) and 230 (base).

*Thermolysis of the Thiazine* (**3f**).—A solution of the thiazine (**3f**) (100 mg) in xylene (50 ml) was heated under reflux until starting material was consumed (t.l.c.). Evaporation of the solvent and chromatography gave 4a-*phenyl*-4aH-*thieno*[3,2-c]-[1,2]*thiazine-3-carbonitrile* (**4f**) (88 mg, 88%), m.p. 161—162 °C (Found: 61.2; H, 3.1; N, 10.9. $C_{13}H_8N_2S_2$ requires C, 60.9; H, 3.15; N, 10.9%); $\nu_{max.}$($CCl_4$) 2 220 $cm^{-1}$; δ (90 MHz, $CDCl_3$) 6.53 (1 H, d, *J* 6.4 Hz), 7.02—7.36 (6 H, m), and 7.46 (1 H, d, *J* 6.4 Hz); $\delta_C$($CDCl_3$) 59.1, 112.8, 113.5, 119.8, 125.5, 125.8, 128.8, 128.9, 136.2, 144.4, and 166.1; *m/z* 256 ($M^+$, base).

*Thermolysis of the Thiazine* (**3g**).—(*a*) *In xylene.* A solution of the thiazine (**3g**) (100 mg) in xylene (50 ml) was heated under reflux until starting material was consumed (t.l.c.) Evaporation of the solvent and chromatography gave (i) ethyl 4a-methyl-4a*H*-thieno[3,2-*c*][1,2]thiazine-3-carboxylate (**4g**) (40 mg, 40%), data given below, and (ii) *ethyl 2,3-dihydrothieno*[3,2-d][1,3]*thiazepine-4-carboxylate* (**5**) (26 mg, 26%), m.p. 117—118 °C (Found: C, 49.8; H, 4.5; N, 5.6. $C_{10}H_{11}NO_2S_2$ requires C, 49.8; H, 4.6; N, 5.8%); $\nu_{max.}$($CCl_4$) 3 340 and 1 700 $cm^{-1}$; δ (250 MHz, $CDCl_3$) 1.34 (3 H, t), 4.29 (2 H, q), 4.37 (2 H, d, *J* 4 Hz), 5.48 (1 H, t, *J* 4 Hz), 6.63 (1 H, d, *J* 5 Hz), 7.36 (1 H, d, *J* 5 Hz), and 8.10 (1 H, s); $\delta_C$($CDCl_3$) 14.4, 53.3, 61.5, 114.7, 122.4, 124.3, 129.5, 134.3, 148.1, and 169.9; *m/z* 241 ($M^+$, base), 212, 209, and 196.

(*b*) *In bromobenzene.* A solution of the thiazine (**3g**) (176 mg) in bromobenzene (10 ml) was heated under reflux for 2 h. Evaporation of the solvent and chromatography gave (i) *ethyl 4-methyl-4H-thieno*[3,2-b]*pyrrole-5-carboxylate* (**6**) (14 mg, 9%), b.p. 110 °C at 0.08 mmHg (Kugelrohr), m.p. 24—26 °C (from light petroleum at 0 °C) (Found: C, 57.2; H, 5.5; N, 6.7. $C_{10}H_{11}NO_2S$ requires C, 57.4; H, 5.3; N, 6.7%); $\nu_{max.}$ (neat) 1 705 $cm^{-1}$; δ (250 MHz, $CDCl_3$) 1.37 (3 H, t), 4.03 (3 H, s), 4.32 (2 H, q), 6.91 (1 H, dd, *J* 5.1, 0.7 Hz), 7.17 (1 H, d, *J* 0.7 Hz), and 7.30 (1 H, d, *J* 5.1 Hz); $\delta_c$($CDCl_3$) 14.5, 34.5, 60.1, 109.0, 110.1, 121.9, 127.1, 128.9, 145.7, and 161.8; *m/z* 209 ($M^+$, base); and (ii) *ethyl* 4a-*methyl*-4aH-*thieno*[3,2-c][1,2]*thiazine-3-carboxylate* (**4g**) (71 mg, 40%), m.p. 71—72 °C (Found: C, 50.0; H, 4.6; N, 5.8; S, 26.6. $C_{10}H_{11}NO_2S_2$ requires C, 49.8; H, 4.6; N, 5.8; S, 26.6%); $\nu_{max.}$(Nujol) 1 720 $cm^{-1}$; δ (250 MHz, $CDCl_3$) 1.19 (3 H, s), 1.36 (3 H, t), 4.32 (2 H, q), 6.30 (1 H, d, *J* 5.9 Hz), 7.02 (1 H, s), and 7.28 (1 H, d, *J* 5.9 Hz); $\delta_C$($CDCl_3$) 14.2, 20.3, 53.1, 62.0, 119.6, 121.8, 129.8, 141.5, 162.3, and 167.7; *m/z* 241 ($M^+$), 226, 209, 198, 181, 168 (base), and 141.

*Independent Synthesis of the Thienopyrrole* (**6**).—Ethyl 4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate[7] (47 mg, 0.24 mmol) in dry dimethylformamide (1 ml) was added to a stirred suspension of sodium hydride (7 mg, 0.29 mmol) in dimethylformamide (1 ml) at room temperature. After 30 min, an excess of iodomethane was added, and the mixture stirred for a further 2 h. Aqueous work-up and chromatography gave the *N*-methylthienopyrrole (**6**) (38 mg, 75%), identical with the previously obtained sample.

*Thermolysis of the Thiazine* (**7**).—A solution of the thiazine (**7**) (188 mg) in toluene (18 ml) was heated under reflux for 2 h. Evaporation of the solvent and chromatography gave (i) *ethyl* 4-*methyl*-4H-*thieno*[2,3-e][1,2]*thiazine-3-carboxylate* (**8**) (7 mg, 4%) as an oil, $\nu_{max.}$ (neat) 1 710 $cm^{-1}$; δ (250 MHz, $CDCl_3$) 1.31 (3 H, d, *J* 7.7 Hz), 1.40 (3 H, t), 4.37 (2 H, q), 4.77 (1 H, q, *J* 7.7 Hz), 6.80 (1 H, d, *J* 5.0 Hz), and 7.30 (1 H, d, *J* 5.0 Hz); *m/z* 241 ($M^+$), 226 (base), 198, 195, 167, 154, 141, and 97; and (ii) *ethyl* 2,3-*dihydrothieno*[2,3-f][1,3]*thiazepine-4-carboxylate* (**9**) (27 mg, 14%) as an oil, $\nu_{max.}$ (neat) 3 400 and 1 705 $cm^{-1}$; δ (250 MHz, $CDCl_3$) 1.37 (3 H, t), 4.32 (2 H, q), 4.48 (2 H, d, *J* 6.8 Hz), 5.79 (1 H, br), 6.78 (1 H, dd, *J* 1.3 Hz, 0.4 Hz), 6.82 (1 H, dd, *J* 5.3, 0.4 Hz), and 7.18 (1 H, d, *J* 5.3 Hz); *m/z* 241 ($M^+$, base).

*Ethyl 2-Azido-3-*[*2-chloro-6-*(*phenylthio*)*phenyl*]*propenoate* (**10a**).—A mixture of 2,6-dichlorobenzaldehyde (1.75 g), thiophenol (1.1 ml), potassium carbonate (1.5 g) in propan-2-ol (9 ml), and hexamethylphosphoric triamide (1 ml) was stirred at room temperature for 3 days. The mixture was poured into water, and extracted with ethyl acetate. The combined organic extracts were washed with water, dried, evaporated, and the residue crystallised from methanol to give *2-chloro-6-*(*phenylthio*)*benzaldehyde* (1.25 g, 50%), m.p. 59—60 °C (Found: C, 62.4; H, 3.6; Cl, 14.6; S, 12.9. $C_{13}H_9ClOS$ requires C, 62.7; H, 3.7; Cl, 14.3; S, 12.9%; $\nu_{max.}$ (Nujol) 1 685 $cm^{-1}$; δ (60 MHz, $CDCl_3$) 6.6—7.7 (8 H, m) and 10.7 (1 H, s).

The above aldehyde was condensed with ethyl azidoacetate under the usual conditions[4] to give the *title compound* (**10a**) as a yellow oil (30%), $\nu_{max.}$ (neat) 2 115 and 1 715 $cm^{-1}$; δ (60 MHz, $CDCl_3$) 1.4 (3 H, t), 4.3 (2 H, q), and 6.8—7.5 (9 H, m).

*Ethyl 2-Azido-3-*[*2,6-bis*(*phenylthio*)*phenyl*]*propenoate* (**10b**).—A mixture of 2,6-dichlorobenzaldehyde (1.75 g), thiophenol (3.0 ml), and potassium carbonate (3.0 g) in hexamethylphosphoric triamide (5 ml) was stirred at room temperature under nitrogen for 2 days. The mixture was poured into water and extracted with ethyl acetate. The combined organic extracts were washed with water, dried, evaporated and the residue crystallised from methanol to give *2,6-bis*(*phenylthio*)*benzaldehyde* (2.1 g, 65%), m.p. 119—120 °C (Found: C, 70.8; H, 4.4; S, 19.6. $C_{19}H_{14}OS_2$ requires C, 70.8; H, 4.4; S, 19.6%); $\nu_{max.}$ (Nujol) 1 665 $cm^{-1}$; δ (60 MHz, $CDCl_3$) 6.7—7.6 (13 H, m) and 10.8 (1 H, s).

The above aldehyde was condensed with ethyl azidoacetate under the usual conditions[4] to give the *title compound* (**10b**) as a yellow oil (37%), $\nu_{max.}$ (neat) 2 115 and 1 720 $cm^{-1}$; δ (60 MHz, $CDCl_3$) 1.4 (3 H, t), 4.3 (2 H, q), and 7.0—7.6 (14 H, m).

*Thermolysis of the Azide* (**10a**).—A solution of the azide (**10a**) (0.9 g) in xylene (200 ml) was heated under reflux for 5 h. Evaporation of the solvent and crystallisation of the residue from methanol gave *ethyl 5-chloro-4-phenyl-4H-benzo*[e][1,2]-*thiazine-3-carboxylate* (**12a**) (0.51 g, 61%), m.p. 100—102 °C (Found: C, 61.5; H, 4.2; Cl, 10.9; N, 4.2; S, 9.8. $C_{17}H_{14}ClNO_2S$ requires C, 61.5; H, 4.3; Cl, 10.7; N, 4.2; S, 9.7%); $\nu_{max.}$ (Nujol) 1 710 $cm^{-1}$; δ (60 MHz, $CDCl_3$) 1.35 (3 H, t), 4.35 (2 H, q), 6.15 (1 H, s), and 7.0—7.4 (8 H, m); $\delta_C$($CDCl_3$) 14.1, 40.8, 62.4, 120.2, 127.4, 127.8, 128.4 (2 carbons), 128.7, 129.2, 134.3, 134.9, 138.2, 154.6, and 161.6.

*Thermolysis of the Azide* (**10b**).—A solution of the azide (**10b**) (1.0 g) in xylene (200 ml) was heated under reflux for 6 h. Evaporation of the solvent gave an oil which was distilled at 170—190 °C and 0.07 mmHg, and then crystallised from methanol to give *ethyl 4-phenyl-5-(phenylthio)-4H-benzo*[e]-[1,2]*thiazine-3-carboxylate* (**12b**) (0.12 g, 13%), m.p. 95—96 °C (Found: C, 68.1; H, 4.7; N, 3.5; S, 15.9. $C_{23}H_{19}NO_2S_2$ requires C, 68.1; H, 4.7; N, 3.5; S, 15.8%); δ (60 MHz, $CDCl_3$) 1.35 (3 H, t), 4.2 (2 H, q), 6.45 (1 H, s), and 7.1—7.4 (13 H, m); *m/z* 405 ($M^+$), 359, 332, and 305.

*Thermolysis of the* 4aH-*Thienothiazine* (**4a**).—A solution of the thiazine (**4a**) (92 mg) in bromobenzene (10 ml) was heated under reflux for 72 h. The solvent was evaporated and the residue was distilled at 140—150 °C and 0.02 mmHg (Kugelrohr). The distillate was dissolved in dichloromethane, and the insoluble pale yellow solid was filtered off and identified as elemental sulphur (6 mg, 63%). The filtrate was evaporated to give *ethyl 4-phenylpyrrolo*[1,2-b]*isothiazole-6-carboxylate* (**13**) (68 mg, 82%), m.p. 108—109 °C (from light petroleum) (Found: C, 66.6; H, 4.85; N, 5.2. $C_{15}H_{13}NO_2S$ requires C, 66.4; H, 4.8; N, 5.2%); $\nu_{max.}$ (Nujol) 1 670 and 1 660 $cm^{-1}$; δ (250 MHz, $CDCl_3$) 1.43 (3 H, t), 4.43 (2 H, q), 7.14 (1 H, d, *J* 6.0 Hz), 7.19—7.28 (1 H, m), 7.36—7.45 (2 H, m), 7.48 (1 H, d, *J* 1.0 Hz), 7.56—7.62 (2 H, m), and 7.68 (1 H, dd, *J* 6.0, 1.0 Hz); $\delta_C$($CDCl_3$) 14.6, 60.6, 111.1, 117.3, 118.1, 120.2, 125.8, 125.9, 128.9, 129.8, 135.2, 143.2, and 161.1; *m/z* 271 ($M^+$, base).

*Desulphurisation of the Pyrroloisothiazole* (**13**).—A mixture of the pyrroloisothiazole (**13**) (37 mg) and freshly prepared Raney nickel[9] (*ca.* 0.5 g) in ethanol (7 ml) was heated under reflux for 1 h. After cooling, the mixture was filtered through Celite, and the latter washed with hot ethanol. The filtrate was evaporated, and the residue chromatographed to give *ethyl 5-ethyl-4-phenylpyrrole-2-carboxylate* (**14**) (27 mg, 81%), m.p. 113—114 °C (Found: C, 73.9; H, 7.1; N, 5.7. $C_{15}H_{17}NO_2$ requires C, 74.05; H, 7.0; N, 5.8%); $\nu_{max.}$ (Nujol) 3 280 and 1 685 $cm^{-1}$; δ (250 MHz, $CDCl_3$) 1.29 (3 H, t, *J* 7.8 Hz), 1.37 (3 H, t, *J* 7.0 Hz), 2.83 (2 H, q, *J* 7.8 Hz), 4.36 (2 H, q, *J* 7.0 Hz), 7.01 (1 H, d, *J* 2.6 Hz), 7.20—7.29 (1 H, m), 7.33—7.39 (4 H, m), and 9.51 (1 H, br); *m/z* 243 ($M^+$, base), 228, 215, 197, 182, 170, 169, 168, 166, and 154; nuclear Overhauser effect difference experiment in n.m.r. spectrum: pre-irradiation at δ 9.51 (N–H) caused enhancement at δ 2.83 and 1.29; pre-irradiation at δ 7.01 (H-3) caused enhancement at δ 7.33 (Ph group), and pre-irradiation at δ 2.83 (5-ethyl $CH_2$ group) caused enhancement at δ 9.51 and 7.33.

*Thermolysis of the Pyrroloisothiazole* (**13**),—A solution of the pyrroloisothiazole (**13**) (22 mg) in 1,2-dichlorobenzene (2 ml) was heated under reflux for 20 h. Evaporation of the solvent and chromatography gave the thiophene (**17**) (10 mg, 49%), data given below.

*Higher Temperature Thermolysis of the Thienothiazine* (**4a**).—A solution of the thienothiazine (**4a**) (180 mg) in 1,2-dichlorobenzene (15 ml) was heated under reflux for 15 h. Evaporation of the solvent and chromatography gave 3,4-*bis*(2-*ethoxycarbonyl-4-phenylpyrrol-5-yl*)*thiophene* (**17**) (43 mg, 28%), m.p. 246—248 °C (Found: $M^+$, 510.1616. $C_{30}H_{26}N_2O_4S$ requires *M*, 510.1613); $\nu_{max.}$ (Nujol) 3 280 and 1 685 $cm^{-1}$; δ [250 MHz, $(CD_3)_2SO$] 1.30 (2 × 3 H, t), 4.23 (2 × 2 H, q), 6.75 (2 × 1 H, d, *J* 2.4 Hz), 7.02 (10 H, m), 7.58 (2 × 1 H, s), and 11.26 (2 × 1 H, br d, *J* 2.4 Hz); *m/z* 510 ($M^+$, base), 464, 421, 418, 393, 391, 390, 365, 363, 336, and 285.

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