Novel Rearrangements of Cyano-stabilised Cyclic Sulfur Ylides, 2-Alkyl-1-cyano-3,4-dihydro-1*H*-2-thionianaphthalen-1-ides: Spiro-compound Formation and Ring Expansion Reactions

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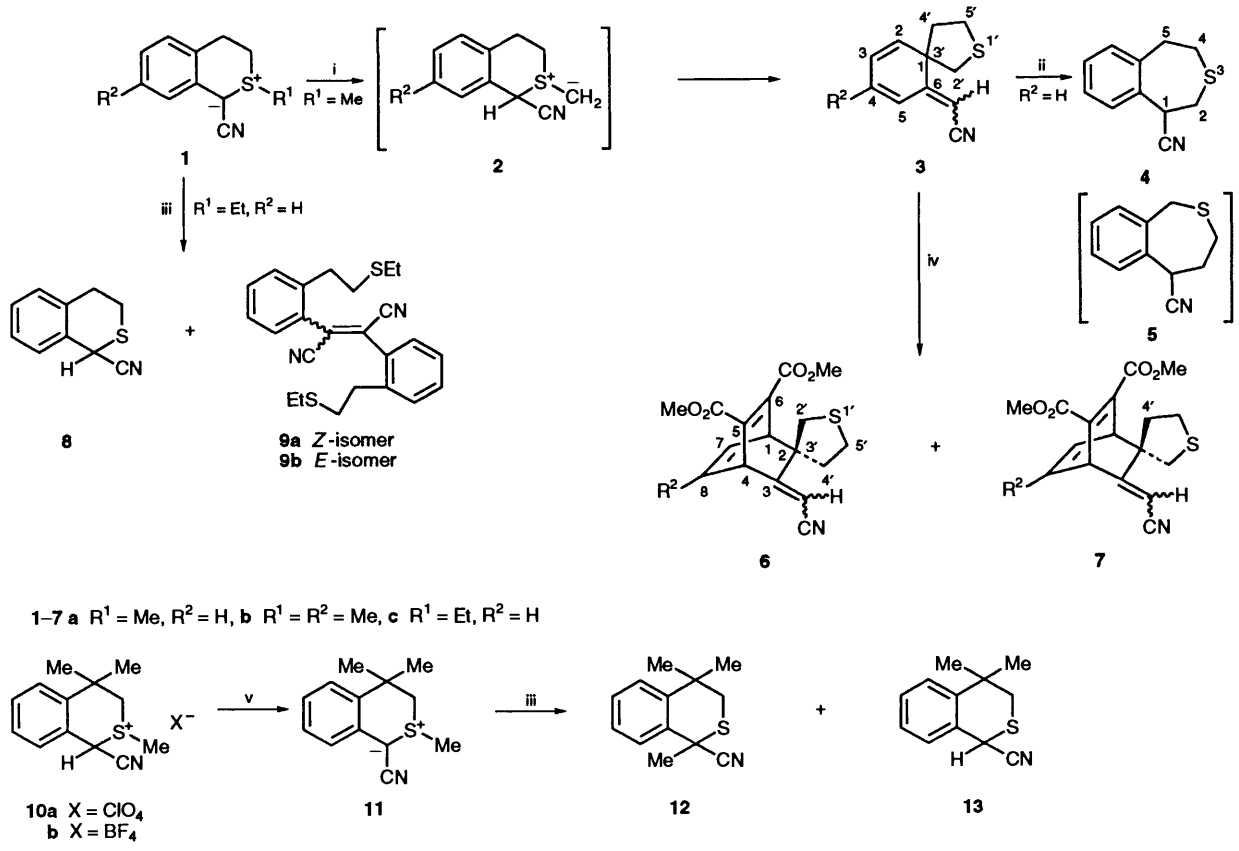
Thermal reaction of 1-cyano-2-methyl-3,4-dihydro-1*H*-2-thionianaphthalen-1-ides **1** in ethanol afforded the spiro compounds **3** in good yields, which underwent thermal rearrangement and Diels–Alder reaction to give tetrahydro-3-benzothiepine **4** and a pair of cycloadducts **6** and **7**, respectively. Treatment of **1** with succinimide similarly provided **3** *via* the processes of protonation, ylide formation and [2,3]sigmatropic rearrangement. In contrast, treatment of **1a** with *N*-chlorosuccinimide, chloramine B or T formed the chloroketenimine **16** *via* an S ⟶ N [2,3]sigmatropic rearrangement of the *exo*-methanide **15**. The *exo*-ylide **19** generated by deprotonation of the sulfonium salt **18** with sodium hydride underwent a similar [2,3]rearrangement to give the ketenimine **20**. Hydrolysis of the ketenimines **16** and **20** with dilute hydrochloric acid produced amides **17** and **21**, respectively. Reactions of **1** with dimethyl acetylenedicarboxylate proceeded *via* Michael addition followed by two different routes of ring-expansion to give the nine-membered cyclic sulfides **30** and the eight-membered cyclic sulfur ylides **32**.

We have studied rearrangements and ring transformation reactions of cyclic sulfur ylides in detail.[1] Reactions of thionianaphthalenides (thianaphthalenes) stabilised by a cyano group with dimethyl acetylenedicarboxylate (DMAD) afforded the nine- or seven-membered ring compounds through the addition of DMAD and subsequent ring-expansion reactions.[2,3] The ylides stabilised by a benzoyl group produced a 1,3-oxathionine derivatives through a [2,3]sigmatropic rearrangement.[4] After we reported the first example of a [2,3]sigmatropic rearrangement forming a spiro compound,[5] similar rearrangements were found in sulfur and nitrogen ylides.[6,7] This paper describes novel rearrangements and ring-transformation reactions of 2-alkyl-1-cyano-3,4-dihydro-1*H*-2-thionianaphthalen-1-ides.

Results and Discussion

Formation of Spiro Compounds.—Thermal reaction of 1-cyano-2-methyl-3,4-dihydro-1*H*-2-thionianaphthalen-1-ides **1** in toluene afforded 1-benzyl-1-cyano-3,4-dihydro-1*H*-2-benzothiopyrans of which the benzyl group is derived from toluene.[8] In order to examine the thermal reaction in a protic solvent, ylide **1a** was heated in ethanol to give 6-cyanomethylene-4-methylcyclohexa-2,4-dienespiro-3′-thiolane **3a** in 83% yield (Scheme 1). The ^{1}H NMR spectrum showed the absence of an *S*-methyl group and the presence of a new methylene group. Signals of the 4′-methylene group shifted to a higher field at δ 1.96 and 2.16 than those of the 4-methylene group of 3,4-dihydro-1*H*-2-benzothiopyran **8**, and moreover signals of olefinic protons at δ 6.13–6.77 appeared higher than those of aromatic protons of **8** at δ 7.22. The ^{13}C NMR spectrum exhibited a quaternary carbon at δ 53.3. The spiro structure **3a** was deduced from these spectral data and confirmed by the chemical reactions described below. Since the *exo*-methylenecyclohexadiene derivatives thermally isomerise to aromatic compounds,[9] a solution of the spiro compound **3a** in benzene was heated in a sealed tube at 205 °C to afford 1-cyano-1,2,4,5-tetrahydro-3-benzothiepine **4** as the sole product in 82% yield. If the 4′-carbon had undergone [1,3]sigmatropic rearrangement, 5-cyano tetrahydro-2-benzothiepine **5** would have been formed. The structure of the product was determined to be not tetrahydro-2-benzothiepine **5** but tetrahydro-3-benzothiepine **4** by the use of decoupled ^{1}H NMR spectroscopy. The 2-H appeared as two doublets at δ 2.95 and 3.06 on irradiation of 1-H at δ 4.50, and the 5-H appeared as two doublets at δ 3.23 and 3.48 on irradiation of the 4-H at δ 2.73. The rearrangement of **3a** to **4** or **5** is thermally forbidden and proceeds through a radical pathway.[9] The α-thiomethyl radical is more stabilised by sulfur than the β-thiomethyl radical[10] and therefore the $C_{2'}$–$C_{3'}$ bond would be selectively cleaved. On the other hand, the spiro compound **3a** bearing a cyclohexadiene moiety reacted with DMAD to afford two isomeric Diels–Alder adducts **6a** and **7a** in 58.5 and 20% yields, respectively. The stereochemistry of the adducts **6a** and **7a** was determined by ^{1}H NMR spectroscopy. One of the 2′-methylene protons of **6a** was deshielded at δ 2.94 by the ester group at 6-position and one of the 4′-methylene protons of **7a** similarly shifted to a lower field at δ 2.14. On the basis of this observation, the 2′-methylene group of **6a** and 4′-methylene group of **7a** lie on the same side as the ester. Since the spiro compounds **3** had not been obtained from the thermal reaction in aprotic solvents[8] but had been obtained from thermolysis in ethanol, we propose the following mechanism for formation of **3**. The ylide carbanion is protonated by alcohol and then a methyl group of the resulting sulfonium ion is deprotonated by an alkoxide ion to form the *exo*-methanide **2**. The *exo*-ylide **2** undergoes the Sommelet–Hauser [2,3]sigmatropic rearrangement to give the spiro compound **3**. From this mechanism, we expected that **3** would be produced in good yield by a reagent which readily donates a proton and of which the conjugate base exhibits very low nucleophilicity. Succinimide was selected and treated with the ylide **1a** in benzene. The spiro compound **3a** was obtained, as expected, in 85% yield. It is very interesting that the spiro compound formation proceeds towards the loss of aromaticity of the benzene ring. Thermal reaction of the 7-methyl derivative **1b** in ethanol similarly afforded the spiro compound **3b**, but the reaction of *S*-ethyl derivative **1c** afforded 1-cyano-3,4-dihydro-1*H*-2-benzothiopyran **8** and dimeric products **9**. The 4,4-



Scheme 1 *Reagents and conditions:* i, reflux in MeOH or EtOH, or succinimide in C_6H_6; ii, heating in C_6H_6 at 205 °C in a sealed tube; iii, reflux in EtOH; iv, $MeO_2CC{\equiv}CCO_2Me$; v; Et_3N in EtOH

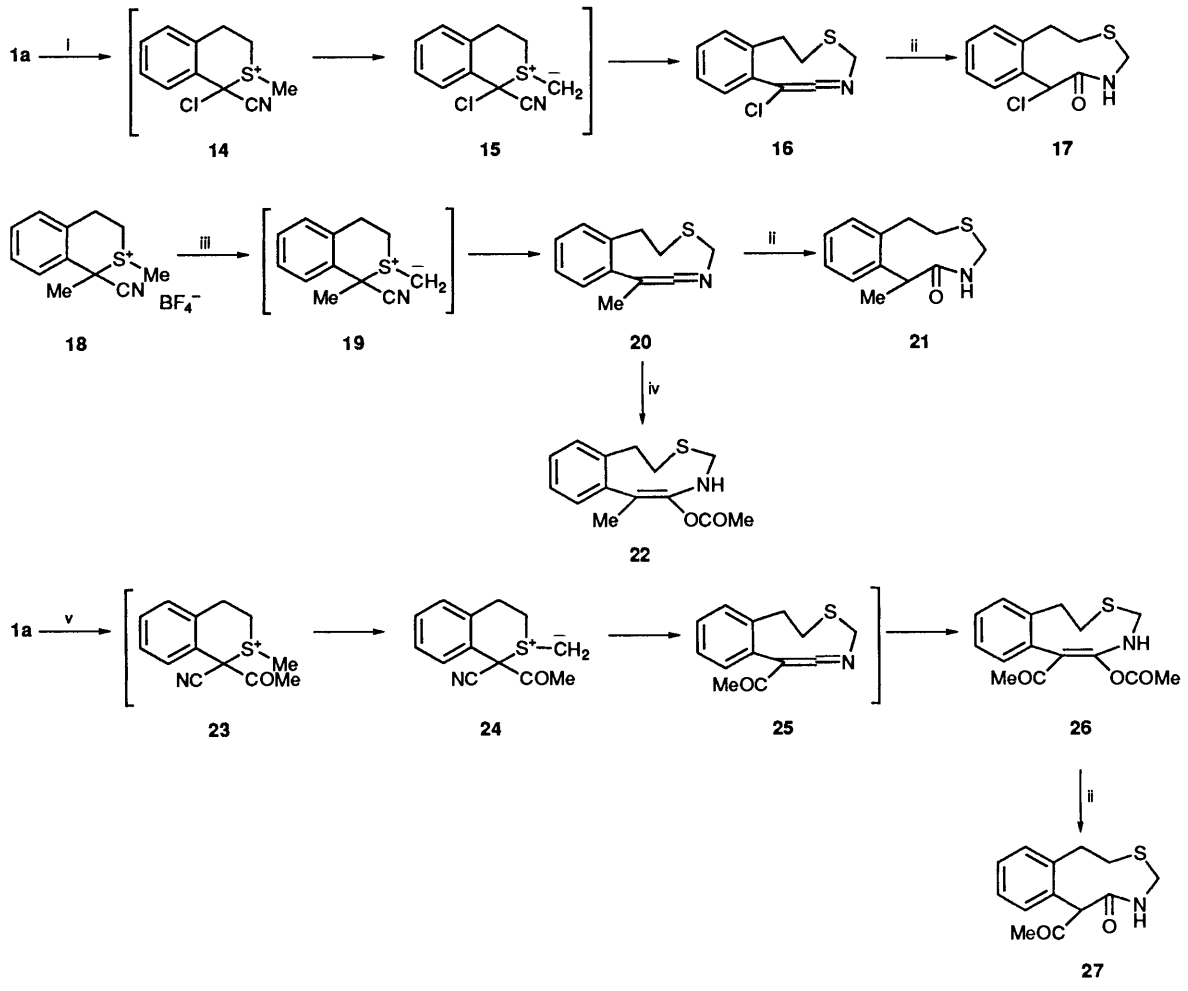
dimethyl derivative **11**, prepared from the sulfonium salt **10**, underwent thermal reaction in ethanol to afford the rearranged product **12** and the demethylated product **13** in 45 and 18% yields, respectively. This finding shows that the 4-methyl groups hinder the orbital interaction between the *exo*-methanide and 4a-carbon of the benzene ring and consequently spiro compound formation did not take place.

Formation of Ketenimines.—An aliphatic sulfur ylide stabilised by a cyano group has been reported to undergo a [2,3]sigmatropic rearrangement in which a substituent on the sulfur atom transferred onto the nitrogen atom of the cyano group to give a ketenimine.[11] Since this is only one example of S⟶N [2,3]sigmatropic rearrangement, we planned to investigate the S ⟶ N rearrangement of cyano-stabilised cyclic sulfur ylides. If the cyano and the *exo*-methanide moieties in the bicyclic ylides are proximate, the methanide group may rearrange to the nitrogen atom of the cyano group. When a bulkier group than the cyano group is introduced into 1-position, the cyano and the methanide groups would be in the *cis*-configuration. First, we examined the reaction of **1a** with *N*-chlorosuccinimide (NCS) because the reaction of **1a** with succinimide had given the spiro compound **3a** in good yield as mentioned above. The reaction readily gave the expected ketenimine, 7-chloro-5,6-didehydro-1,2,4,5-tetrahydro-3,5-benzothiazonine **16** in 57% yield (Scheme 2). The ketenimine structure of **16** was determined from the spectral data showing a broad and strong absorption band at 2000–1900 cm^{-1} owing to the ketenimine moiety in the IR spectrum, and two signals at δ 78.2 and 196.6 in the ^{13}C NMR spectrum.[12] Furthermore, the structure of **16** was chemically confirmed by acid-catalysed hydrolysis[13] giving 7-chloro-1,2,4,5-tetrahydro-3,5-benzothiazonin-6-(7*H*)-one **17**. The ketenimine **16** was also produced by the reactions with chloramine B or T in 23 or 26% yield, respectively. Formation of ketenimine **16** can be explained by a reaction mechanism initiated by chlorination at the 1-position. The 1-chlorosulfonium ion **14** is deprotonated by the imide or sulfonamide anion to form the *exo*-methanide **15** which undergoes the cyano-promoted [2,3]sigmatropic rearrangement. Ylide **1a** was treated with *N*-bromosuccinimide, but the product was too unstable to be isolated. If the halogen atom of the intermediate **14** or the 1-bromo derivative, is replaced by a methyl group, which is as large as a chlorine atom and is bound covalently with the carbon atom at 1-position, the ketenimine would be neatly produced. Therefore, we prepared 1-cyano-1,2-dimethyl-3,4-dihydro-2-thionianaphthalene salt **18** and treated it with sodium hydride in tetrahydrofuran (THF). The ketenimine **20** was produced in good yield *via* the exo-methanide intermediate **19**. Solvolysis of the ketenimine **20** with water or acetic acid provided the amide **21** or the enol acetate **22**, respectively.

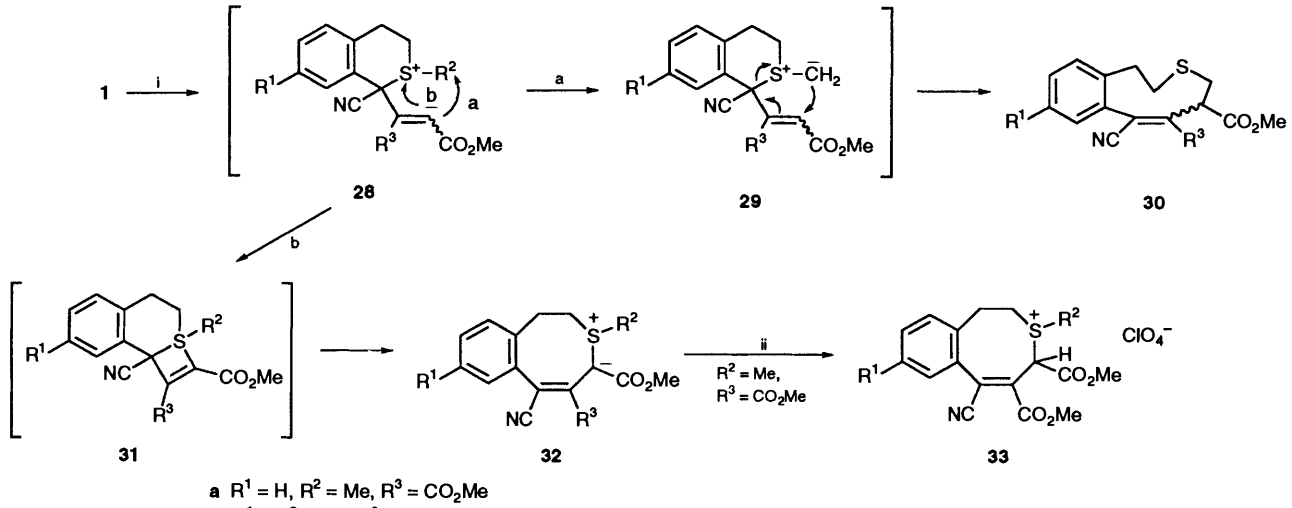
Treatment of **1a** with acetic anhydride gave 6-acetoxy-7-acetyl-1,2,4,5-tetrahydrobenzothiazonine **26** in 63% yield. This can be explained by the assumption that the ketenimine moiety of **25** is activated by the acetyl group and undergoes nucleophilic attack of the acetate anion formed in the reaction. The resulting enol acetate **26** is hydrolysed to the amide **27**.

Ring-expansion Reactions.—Thiabenzene derivatives stabilised by a cyano group react with DMAD to cause ring-transformation reactions.[2,3,6] We have described above the novel rearrangements of *exo*-ylide intermediates formed by addition of nucleophiles to the 1-positions of the ylides **1**. Therefore, ring-transformation reactions can be expected in the reaction of **1** with DMAD.

Treatment of **1a** with DMAD gave a couple of 1 : 1 adducts, 7-cyano-5,6-bis(methoxycarbonyl)-1,2,4,5-tetrahydro-3-benzothionine **30a** and 6-cyano-4,5-bis(methoxycarbonyl)-3-methyl-



Scheme 2 *Reagents and conditions:* i, NCS, chloramine B or T; ii, dil. HCl; iii, NaH in THF; iv, AcOH; v, Ac_2O



a R^1 = H, R^2 = Me, R^3 = CO_2Me
b R^1 = R^2 = Me, R^3 = CO_2Me
c R^1 = H, R^2 = Et, R^3 = CO_2Me
d R^1 = R^3 = H, R^2 = Me

Scheme 3 *Reagents:* i, $MeO_2CC{\equiv}CCO_2Me$ or $HC{\equiv}CCO_2Me$; ii, $HClO_4$

1,2-dihydro-4*H*-3-thioniabenzocycloocten-4-ide **32a** in 37 and 38% yields, respectively (Scheme 3). The 7-methyl derivative **1b** similarly reacted with DMAD. The *S*-ethyl derivative **1c** afforded the eight-membered cyclic ylide **32c** in 31% yield but did not afford the nine-membered ring product **30c**. The structure of the product **30a** was determined from the ^1H and ^{13}C NMR spectral data. The ^1H NMR spectrum exhibited no signals owing to *S*-methyl and vinyl protons, and the ^{13}C NMR spectrum showed three methylene carbons (δ 32.5, 33.1, 36.5), a methine carbon (δ 49.4) and tetra-substituted olefinic carbons (δ 123.3, 132.8). Another product **32a** showed remarkable features of the ylidic structure. The strong and lower-shifted absorptions

due to the cyano group and one of two carbonyl groups appeared at 2180 and 1650 cm^{-1}, respectively, in the IR spectrum. In addition to the spectral evidence, treatment of **32a** with perchloric acid provided an isomeric mixture of the sulfonium salts **33**. A plausible mechanism for formation of **30** and **32** is shown in Scheme 3. An acetylenic carbon of DMAD attacks at the carbanion of the ylide **1** to form the betaine **28**, which leads to the *exo*-methanide **29** by an intramolecular proton abstraction of the *S*-methyl group. The ylide **29** undergoes [2,3]sigmatropic rearrangement giving the nine-membered cyclic sulfide **30**. On the other hand, the nucleophilic attack of the vinyl anion of **28** at the positive sulfur atom generates the σ-sulfurane intermediate **31**, which is presumably unstable and collapses to the eight-membered cyclic ylide **32**. Since the ylide **32a** is stabilised by both the cyano and the ester groups, it underwent neither the thermal reaction on refluxing in ethanol nor the reaction with DMAD on refluxing in dichloromethane.

Experimental

M.p.s were determined on a Yanagimoto micro melting apparatus and are uncorrected. IR spectra of solids (KBr) and liquids (film) were recorded on a JASCO IRA-100 spectrophotometer. ^1H NMR spectra were obtained for solutions in $CDCl_3$ on a Hitachi R-20B (60 MHz) or a JEOL GX-270 spectrometer with tetramethylsilane as an internal standard, unless otherwise indicated. *J* values are given in Hz. ^{13}C Spectra were run on a JEOL GX-270 spectrometer. Mass spectra were obtained using a JEOL JMS-D 300 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.

Thermal Reaction of 1-*Cyano*-2-*methyl*-3,4-*dihydro*-1H-2-*thionianaphthalen*-1-*ide* **1a** *in Ethanol*.—A solution of **1a**[8] (447 mg, 2.4 mmol) in dry ethanol (90 cm^3) was refluxed for 5 h under a nitrogen atmosphere and then concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using hexane–ethyl acetate (10:1) to give 6-*cyanomethylenecyclohexa*-2,4-*dienespiro*-3′-*thiolane* **3a** (369 mg, 83%) as colourless prisms, m.p. 91–92 °C (from dichloromethane–hexane); ν_{max}/cm^{-1} 2200 (CN); δ_H(400 MHz; $CDCl_3$) 1.96, 2.16 (each 1 H, dt, *J* 13.0, 6.5, 4′-H), 2.79 (1 H, d, *J* 11.3, 2′-H), 2.96–3.08 (2 H, m, 5′-H_2), 3.04 (1 H, d, *J* 11.3, 2′-H), 5.58 (1 H, s, =CHCN), 6.13–6.14 (2 H, m, =CH), 6.32–6.36 (1 H, m, =CH) and 6.77 (1 H, d, *J* 9.6, =CH); δ_C(100 MHz; $CDCl_3$) 29.1 (t, C-4′), 45.4, 46.0 (each t, C-2′ and-5′), 53.3 (s, C-1), 93.9 (d, *C*HCN), 116.8 (s, CN), 121.6, 123.8, 124.9, 138.3 (each d, C-2, -3, -4 and -5) and 162.9 (s, C-6); *m/z*189 (M^+) (Found: C, 69.6; H, 5.7; N, 7.4. $C_{11}H_{11}NS$ requires C, 69.8; H, 5.9; N, 7.4%).

Thermal Reaction of 1-*Cyano*-2,7-*dimethyl*-3,4-*dihydro*-1H-2-*thionianaphthalen*-1-*ide* **1b** *in Ethanol*.—A solution of **1b**[8] (100 mg, 0.5 mmol) in dry ethanol (20 cm^3) was heated under the same reaction conditions as for **1a** and similarly worked up. The residue was purified by PLC on silica gel using hexane–ethyl acetate (5:1) to afford 6-*cyanomethylene*-4-*methylcyclohexa*-2,4-*dienespiro*-3′-*thiolane* **3b** (59 mg, 59%) as pale-yellow prisms, m.p. 70–72 °C (from dichloromethane–hexane); ν_{max}/cm^{-1} 2200 (CN); $\delta_H(CDCl_3)$ 1.75–2.23 (2 H, m, 4′-H_2), 2.05 (3 H, d, *J* 1.5, 4-CH_3), 2.70–3.18 (4 H, m, 2′- and 5′-H_2), 5.48 (1 H, s, =CHCN), 5.95–6.33 (2 H, m, 2- and 3-H), 6.60–6.70 (1 H, m, 5-H); *m/z* 203 (M^+) (Found: C, 70.65; H, 6.4; N, 6.9. $C_{12}H_{13}NS$ requires C, 70.9; H, 6.45; N, 6.9%).

Thermal Reaction of 1-*Cyano*-2-*ethyl*-3,4-*dihydro*-1H-2-*thionianaphthalen*-1-*ide* **1c** *in Ethanol*.—Triethylamine (101 mg, 1 mmol) was added to a suspension of 1-cyano-2-ethyl-3,4-dihydro-1*H*-2-thionianaphthalene perchlorate[8] (152 mg, 0.5 mmol) in dry ethanol (10 cm^3) under a nitrogen atmosphere. The reaction mixture was stirred for 2.5 h at room temperature, then poured into water and extracted with dichloromethane. The extracts were dried ($MgSO_4$) and concentrated to dryness to leave the ylide **1c** as a pale yellow oil; $\delta_H(CDCl_3)$ 1.25 (3 H, t, *J* 7.0, CH_3), 2.30 (2 H, q, *J* 7.0, SCH_2CH_3), 2.78–3.23 (4 H, m, 3- and 4-H_2) and 6.55–7.13 (4 H, m, ArH). The ylide **1c** gradually decomposed at room temperature and, therefore, it was used for the thermal reaction without further purification. A solution of **1c** in dry ethanol (20 cm^3) was refluxed for 3 h under a nitrogen atmosphere. The reaction mixture was worked up as for **1a** and gave 1-cyano-3,4-dihydro-1*H*-2-benzothiopyran **8** (72 mg, 82%), (*Z*)- **9a** (5 mg) and (*E*)-2,3-bis[*o*-(ethylthioethyl)phenyl]but-2-enedinitrile **9b** (6 mg). Compound **8** was identical with an authentic sample.[8] Authentic samples of dimeric products **9** were alternatively prepared as described below and the products **9a**, **b** were identified by comparison with them.

Dimerisation of the S-*Ethyl Ylide* **1c**.—The ylide **1c** was prepared from 1-cyano-2-ethyl-3,4-dihydro-1*H*-2-thionianaphthalene perchlorate[8] (456 mg, 1.5 mmol) as described above. A mixture of the ylide **1c** and tetracyanoethylene (5 mg) in dry acetonitrile (20 cm^3) was stirred at room temperature for a day. The solvent was evaporated and the residue was separated by PLC on silica gel using hexane–dichloromethane (1:2). (*Z*)-(**9a**) (65 mg, 21%) and (*E*)-2,3-*Bis*[o-(2-*ethylthioethyl*)-*phenyl*]*but*-2-*enedinitrile* (**9b**) (70 mg, 23%) were obtained. **9a**: colourless prisms, m.p. 82.5 °C (from dichloromethane–hexane); ν_{max}/cm^{-1} 2220 (CN); $\delta_H(CDCl_3)$ 1.31 (6 H, t, *J* 7.5, 2 × CH_3), 2.63 (4 H, q, *J* 7.5, 2 × CH_2CH_3), 2.8–3.05 (8 H, m, 2 × CH_2CH_2) and 6.79–7.36 (8 H, m, ArH); *m/z* 406 (M^+) (Found: C, 70.85; H, 6.5; N, 6.9. $C_{24}H_{26}N_2S_2$ requires C, 70.9; H, 6.45; N, 6.9%). **9b**: pale-yellow oil; ν_{max}/cm^{-1} 2230 (CN); $\delta_H(CDCl_3)$ 1.24 (6 H, t, *J* 7.5, 2 × CH_3), 2.56 (4 H, q, *J* 7.5, 2 × CH_2CH_3), 2.69–3.3 (8 H, m, 2 × CH_2CH_2) and 7.34–7.53 (8 H, m, ArH); HRMS (Found: M^+, 406.1565. Calc. for $C_{24}H_{26}N_2S_2$, *M*, 406.1538). *Z*- and *E*-structures of the products **9a**, **b** were determined by comparison of their ^1H NMR spectra with those of the *S*-methyl derivatives.[8]

Reaction of **1a** *with Succinimide*.—A mixture of **1a** (103 mg, 0.54 mmol) and succinimide (540 mg, 5.4. mmol) in dry benzene (20 cm^3) was refluxed for 6 h under a nitrogen atmosphere, cooled and filtered. The filtrate was concentrated under reduced pressure and the residue was washed with diethyl ether. The washings were condensed and then submitted to PLC on silica gel using hexane–ethyl acetate (7 : 1). The spiro compound **3a** (88 mg, 85%) was obtained as colourless prisms.

Reaction of the Spiro Compound **3a** *with Dimethyl Acetylenedicarboxylate* (*DMAD*).—A solution of **3a** (51 mg, 0.3 mmol) and DMAD (117 mg, 0.8 mmol) in benzene (10 cm^3) was refluxed for 5 h under a nitrogen atmosphere and then concentrated to dryness under reduced pressure. The residue was separated by PLC on silica gel using hexane–ethyl acetate (4:1) to give (1R*, 2R*, 4S*)-3-*cyanomethylene*-5,6-*bis*(*methoxycarbonyl*)*bicyclo*[2.2.2]*octa*-5,7-*diene*-2-*spiro*-3′-*thiolane* **6a** (52 mg, 58.5%) and (1R*, 2S*, 4S*)-*isomer* **7a** (17 mg, 20%). **6a**: colourless prisms, m.p. 156–157 °C (from dichloromethane–hexane); ν_{max}/cm^{-1} 2220 (CN), 1730 and 1710 (CO); δ_H(400 MHz, $CDCl_3$) 1.85 (1 H, dt, *J* 13.2, 7.8 4′-H), 2.00 (1 H, dt, *J* 13.2, 5.7, 4′-H), 2.60, 2.94 (each 1 H, d, *J* 11.6, 2′-H_2), 2.90–3.00 (2 H, m, 5′-H_2), 3.83, 3.84 (each 3 H, s, CO_2CH_3), 4.12 (1 H, dd, *J* 5.9, 1.4, 1-H), 5.27 (1 H, dd, *J* 5.9, 1.4, 4-H), 5.45 (1 H, s, =CHCN) and 6.56 and 6.63 (each 1 H, ddd, *J* 6.8, 5.9, 1.4, 7- and 8-H); *m/z*

331 (M^+) (Found: C, 61.75; H, 5.3; N, 4.2. $C_{17}H_{17}NO_4S$ requires C, 61.6; H, 5.2; N, 4.2%). **7a**: colourless prisms, m.p. 156–157 °C (from dichloromethane–hexane); ν_{max}/cm^{-1} 2220 (CN), 1735 and 1715 (CO); δ_H(400 MHz; $CDCl_3$) 1.85 (1 H, ddd, *J* 13.2, 9.2, 7.8, 4'-H), 2.14 (1 H, ddd, *J* 13.2, 6.5, 3.5, 4'-H), 2.69 (2 H, s, 2'-H_2), 2.98 (1 H, ddd, *J* 11.1, 7.8, 3.5, 5'-H), 3.08 (1 H, ddd, *J* 11.1, 9.2, 6.5, 5'-H), 3.82, 3.84 (each 3 H, s, CO_2CH_3), 4.21 (1 H, dd, *J* 5.7, 1.9, 1-H), 5.25 (1 H, dd, *J* 5.7, 1.9, 4-H), 5.37 (1 H, s, =CHCN) and 6.60 and 6.63 (each 1 H, td, *J* 5.7, 1.9, 7- and 8-H); *m/z* 331 (M^+) (Found: C, 61.4; H, 5.3; N, 4.2. $C_{17}H_{17}NO_4S$ requires C, 61.6; H, 5.2; N, 4.2%).

Reaction of **3b** *with DMAD.*—The spiro compound **3b** was treated with DMAD in the same way as described for **3a**. (1R*,2R*,4S*)-3-*Cyanomethylene*-5,6-*bis*(*methoxycarbonyl*)-8-*methylbicyclo*[2.2.2]*octa*-5,7-*diene*-2-*spiro*-3'-*thiolane* **6b** and (1R*,2S*,4S*)-*isomer* **7b** were obtained in 32.5 and 11% yield, respectively. **6b**: colourless prisms, m.p. 122 °C (from dichloromethane–hexane); ν_{max}/cm^{-1} 2220 (CN), 1740 and 1710 (CO); δ_H(400 MHz: $CDCl_3$) 1.86 (1 H, dt, *J* 13.2, 8.4, 4'-H), 1.97 (3 H, d, *J* 1.6, 8-CH_3), 2.00 (1 H, dt, *J* 13.2, 5.7, 4'-H), 2.63, 2.92 (each 1 H, d, *J* 11.6, 2'-H_2), 2.95 (2 H, dd, *J* 8.4, 5.7, 5'-H_2), 3.82, 3.83 (each 3 H, s, CO_2CH_3), 3.96 (1 H, d, *J* 6.2, 1-H), 5.00 (1 H, d, *J* 1.6, 4-H), 5.41 (1 H, s, =CHCN) and 6.13 (1 H, ddq, *J* 6.2, 1.6, 1.6, 7-H); *m/z* 345 (M^+) (Found: C, 62.8; H, 5.5; N, 4.1. $C_{18}H_{19}NO_4S$ requires C, 62.6; H, 5.5; N, 4.1%). **7b**: colourless prisms, m.p. 87–88 °C (from dichloromethane–hexane); ν_{max}/cm^{-1} 2200 (CN), 1740 and 1725 (CO); δ_H(400 MHz: $CDCl_3$) 1.81 (1 H, ddd, *J* 13.2, 9.2, 7.8, 4'-H), 1.98 (3 H, d, *J* 1.6 Hz, 8-CH_3), 2.12 (1 H, ddd, *J* 13.2, 6.8, 4.1, 4'-H), 2.71 (2 H, s, 2'-H_2), 2.96 (1 H, ddd, *J* 11.1, 7.8, 4.1, 5'-H), 3.06 (1 H, ddd, *J* 11.1, 9.2, 6.8, 5'-H), 3.82, 3.83 (each 3 H, s, CO_2CH_3), 4.03 (1 H, d, *J* 5.9, 1-H), 4.97 (1 H, d, *J* 1.6, 4-H), 5.38 (1 H, s, =CHCN) and 6.31 (1 H, ddq, *J* 5.9, 1.6, 1.6, 7-H); *m/z* 345 (M^+) (Found: C, 62.65; H, 5.5; N, 4.1. $C_{18}H_{19}NO_4S$ requires C, 62.6; H, 5.5; N, 4.1%).

Thermal Rearrangement of the Spiro Compound **3a**.—A solution of **3a** (100 mg, 0.5 mmol) in dry benzene (20 cm^3) was heated at 205 °C under a nitrogen atmosphere in a sealed tube for 5 h. The reaction mixture was concentrated to dryness and the residue was purified by PLC on silica gel using hexane–ethyl acetate (9:1) to give 1-*cyano*-1,2,4,5-*tetrahydro*-3-*benzothiepine* **4** (82 mg, 82%), colourless prisms, m.p. 104.5–106.5 °C (from dichloromethane–hexane); ν_{max}/cm^{-1} 2240 (CN); δ_H(200 MHz; $CDCl_3$) 2.73 (2 H, t, *J* 5, 4-H_2), 2.95 (1 H, dd, *J* 13, 7, 2-H), 3.06 (1 H, dd, *J* 13, 2, 2-H), 3.23 (1 H, dt, *J* 16, 5, 5-H), 3.48 (1 H, dt, *J* 16, 5, 5H), 4.50 (1 H, dd, *J* 2, 7, 1-H), 7.10–7.33 (3 H, m, ArH) and 7.35–7.46 (1 H, m, ArH); δ_C($CDCl_3$) 29.3 (t, C-4), 32.9 (t, C-2), 39.4 (t, C-5), 41.3 (d, C-1), 119.0 (s, CN), 127.4, 128.4, 128.7, 131.1 (each d, ArC), 134.9 and 140.4 (each s, ArC): *m/z* 189 (M^+) (Found: C, 69.6; H, 6.0; N, 7.4. $C_{11}H_{11}NS$ requires C, 69.8; H, 5.9; N, 7.4%).

1-*Cyano*-2,4,4-*trimethyl*-3,4-*dihydro*-1H-2-*thionianaphthalene Salts* **10**.—(a) A mixture of 1-cyano-4,4-dimethyl-1*H*-2-benzothiopyran **13**[14] (2.03 g, 10 mmol), iodomethane (14.2 g, 0.1 mol) and silver perchlorate (90% pure; 2.3 g, 10 mmol) in 1,2-dichloroethane (50 cm^3) was stirred for two days at room temperature. The precipitate was filtered off and washed with hot acetone several times. The filtrate and the washings were combined and concentrated to dryness. The crystals were recrystallised from acetone–chloroform to give the *thionianaphthalene perchlorate* **10a** as colourless prisms (2.8 g, 88%), m.p. 164–165 °C; ν_{max}/cm^{-1} 2240 (CN), 1100 (ClO_4^-); δ_H(CF_3CO_2H) 1.69, 1.78 (each 3 H, s, 4-CH_3), 3.39 (3 H, s, SCH_3), 3.62 (1 H, d, *J* 11.3 3-H), 4.03 (1 H, dd, *J* 11.3, 1.5, 3-H), 6.13 (1 H, d, *J* 1.5, 1-H) and 7.35–7.80 (4 H, m, ArH) (Found: C, 48.95; H, 5.1; N, 4.2. $C_{13}H_{16}ClNO_4S$ requires C, 49.1; H, 5.1; N, 4.4%). The coupling between the 1-H_{eq} and 3-H_{eq} indicates that the conformation of 1-cyano group is axial. The 3-H_{eq} signal of **10a** is shifted downfield in comparison to the 3-H signal of 1-cyano-4,4-dimethyl-3,4-dihydro-1*H*-benzothiopyran **13** (δ 2.66) and, therefore, the lone pair electrons of the sulfur atom lie in the equatorial position and the *S*-methyl group occupies the axial position, namely the sulfonium salt **10a** has a *trans* configuration. When a solution of **10a** in CF_3CO_2H was warmed to 55 °C, a new *S*-methyl signal appeared at δ 3.49.

(b) Dimethoxycarbenium tetrafluoroborate was prepared from trimethyl orthoformate (0.49 g, 4.6 mmol) and boron trifluoride etherate (0.75 g, 4.6 mmol) in dry dichloromethane (1 cm^3).[15] A solution of **13** (470 mg, 2.3 mmol) in dry dichloromethane (1 cm^3) was added dropwise to the suspension of the carbenium salt in dichloromethane at −30 °C, stirred for 1 h at that temperature and gradually warmed to ambient temperature. After the mixture had been stirred overnight, the solvent was removed under reduced pressure. The residual oil was rinsed with diethyl ether and then ethyl acetate was added to the oil. The crystals that precipitated were filtered, washed with ethyl acetate and diethyl ether, successively, and recrystallised from acetone–diethyl ether to give the *thionianaphthalene tetrafluoroborate* **10b** as colourless prisms (0.60 g, 85%), m.p. 138–139 °C; ν_{max}/cm^{-1} 2240 (CN) and 1100 (BF_4^-) (Found: C, 51.1; H, 5.3; N, 4.6. $C_{13}H_{16}BF_4NS$ requires C, 51.2; H, 5.3; N, 4.6%). The ^1H NMR spectrum in CF_3CO_2H (60 MHz) was almost the same as that of the perchlorate **10a**.

1-*Cyano*-2,4,4-*trimethyl*-3,4-*dihydro*-1H-2-*thionianaphthalen*-1-*ide* **11**.—Triethylamine (637 mg, 3.3 mmol) was added to an ice-cold suspension of **10a** (1.00 g, 3.2 mmol) with stirring under a nitrogen atmosphere. The mixture was stirred for 8 h at room temperature, poured into water and extracted with dichloromethane. The extracts were dried ($MgSO_4$) and evaporated to dryness. Diethyl ether was added to the residue and the crystals were filtered off. Recrystallisation from diethyl ether gave pale-yellow prisms (568 mg, 83%), m.p. 120–122 °C; ν_{max}/cm^{-1} 2120 (CN); δ_H($CDCl_3$) 1.43 (3 H, s, CH_3), 1.53 (3 H, s, CH_3), 2.50 (3 H, s, SCH_3), 3.28 (2 H, q, *J* 13.5 CH_2) and 6.70–7.40 (4 H, m, ArH); *m/z* 217 (M^+) (Found: C, 71.6; H, 7.0; N, 6.4. $C_{13}H_{15}NS$ requires C, 71.85; H, 6.95; N, 6.4%). The ylide **11** was similarly prepared from the sulfonium tetrafluoroborate **10b**.

Thermal Reaction of the Ylide **11** *in Ethanol.*—A solution of the ylide **11** (349 mg, 1.6 mmol) in dry ethanol (30 cm^3) was refluxed for 6 h under a nitrogen atmosphere and then evaporated to dryness. The residue was separated by PLC on silica gel using dichloromethane–hexane (3:10) to give 1-*cyano*-1,4,4-*trimethyl*-3,4-*dihydro*-1H-2-*benzothiopyran* **12** (158 mg, 45%) and the demethylated product **13** (59 mg, 18%). **12**: colourless prisms, m.p. 82–83 °C (from dichloromethane–hexane); ν_{max}/cm^{-1} 2225 (CN); δ_H($CDCl_3$) 4.40 (6 H, s, 2 × CH_3), 2.00 (3 H, s, 1-CH_3), 2.66, 3.31 (1 H, d, *J* 14.3, 3-H) and 7.05–7.60 (4 H, m, ArH); *m/z* 217 (M^+) (Found: C, 71.6; H, 7.0; N, 6.5. $C_{13}H_{15}NS$ requires C, 71.85; H, 6.95; N, 6.4%). Compound **13** was identical with an authentic sample.[14]

Reaction of the Ylide **1a** *with* N-*Chlorosuccinimide.*—*N*-Chlorosuccinimide (43 mg, 0.3 mmol) was added to a solution of **1a** (57.5 mg, 0.3 mmol) in dry dichloromethane (20 cm^3) with stirring at 0 °C. After the reaction mixture had been stirred for 10 min, the solvent was evaporated under reduced pressure and the residue was separated by PLC on silica gel using hexane–ethyl acetate (8:1) to give 7-*chloro*-5,6-*didehydro*-1,2,4,5-*tetrahydro*-3,5-*benzothiazonine* **16** (38 mg, 57%), a yellow oil; ν_{max}/cm^{-1} 2010 (C=C=N); δ_H($CDCl_3$) 2.51–3.16 (4 H, m, CH_2CH_2), 4.83 (2 H, s, SCH_2N) and 7.08–7.79 (4 H, m, ArH);

$\delta_C(CDCl_3)$ 30.3, 37.0 (each t, C-1 and -2), 56.5 (t, C-4), 78.2 (s, C-7), 127.1, 127.3, 127.5, 130.4 (each d, ArC), 130.5, 136.1 (each s, ArC) and 196.6 (s, C-6); HRMS (Found: M^+, 223.0238 and 225.0211. Calc. for $C_{11}H_{10}ClNS$, *M*, 223.0213, Cl = 34.9689 and Cl = 36.9659, respectively).

Reaction of the Ylide **1a** *with Chloramine B or T.*—Chloramine B dihydrate (170 mg, 0.7 mmol) was added to a solution of **1a** (127 mg, 0.7 mmol) in dichloromethane (20 cm^3). The reaction mixture was stirred for 3 h at room temperature and then filtered. The filtrate was concentrated to dryness and the residue was separated by PLC on silica gel using hexane–ethyl acetate (8:1) to give the ketenimine **16** (34 mg, 23%). The ketenimine was obtained by the reaction of **1a** with chloramine T trihydrate in 26% yield.

Hydrolysis of the Ketenimine **16**.—Reaction of **1a** (301 mg, 1.6 mmol) with *N*-chlorosuccinimide (290 mg, 1.6 mmol) was conducted and worked up in the same way as described above. The raw product was dissolved in acetonitrile (45 cm^3) and treated with a mixture of water (10 cm^3) and concentrated hydrochloric acid (2 drops) for a day at room temperature. Acetonitrile was removed under reduced pressure and the residue was extracted with dichloromethane. The extracts were dried ($MgSO_4$) and concentrated to dryness. The residual oil was separated by PLC on silica gel using hexane–ethyl acetate (5:1) to give 7-*chloro*-1,2,4,5-*tetrahydro*-3,5-*benzothiazonin*-6-(7H)-*one* **17** (151 mg, 39% from **1a**), colourless prisms, m.p. 111 °C (from hexane–dichloromethane); ν_{max}/cm^{-1} 3250 (NH) and 1660 (CO); $\delta(CDCl_3)$ 2.13–2.55 (4 H, m, 1- and $2H_2$), 3.95 (1 H, br d, *J* 12.8, 4-H), 5.37 (1 H, s, 7-H), 5.52 (1 H, d, *J* 12.8, 4-H), 6.30–6.50 (1 H, br s, NH) and 6.79–7.55 (4 H, m, ArH); *m/z* 241 (M^+, Cl = 35), 243 (M^+, Cl = 37) (Found: C, 54.7; H, 5.0; N, 5.8. $C_{11}H_{12}ClNOS$ requires C, 54.7; H, 5.0: N, 5.8%).

1-*Cyano*-1,2-*dimethyl*-3,4-*dihydro*-1H-2-*thionianaphthalene Tetrafluoroborate* **18**.—A mixture of 1-cyano-1-methyl-3,4-dihydro-1*H*-2-benzothiopyran[16] (1.0 g, 5.3 mmol), iodomethane (7.5 g, 53 mmol) and silver tetrafluoroborate (1.0 g, 5.3 mmol) in dry dichloromethane (20 cm^3) was refluxed for 48 h under shielding from the light. The precipitate was filtered off and washed with hot acetonitrile. The washings were concentrated to dryness to give colourless prisms (1.9 g, 81.5%), m.p. 209–210 °C (from acetone); ν_{max}/cm^{-1} 2240 (CN) and 1100 (BF_4^-); $\delta_H(CF_3CO_2H)$ 2.42 (3 H, s, 1-CH_3), 3.33 (3 H, s, SCH_3), 3.50–4.40 (4 H, m, 2 × CH_2) and 7.50–7.85 (4 H, m, ArH) (Found: C, 49.35; H, 4.7; N, 4.8. $C_{12}H_{14}BF_4NS$ requires C, 49.5; H, 4.8; N, 4.8%).

Reaction of **18** *with Sodium Hydride*.—Sodium hydride (60% dispersion in mineral oil; 207 mg, 5.2 mmol) was added to a suspension of the sulfonium salt **18** (500 mg, 1.7 mmol) in dry THF (30 cm^3) under a nitrogen atmosphere at 0 °C. The mixture was stirred for 5 h at that temperature and concentrated to dryness. The residue was dissolved in dichloromethane and the precipitate was filtered off. The filtrate was washed with ice-water, dried ($MgSO_4$) for 10 min and then concentrated under reduced pressure. Purification of the residue by column chromatography on silica gel using dichloromethane–hexane (1:2) gave 7-*methyl*-5,6-*didehydro*-1,2,4,5-*tetrahydro*-3,5-*benzothiazonine* **20**, a pale-yellow oil (221 mg, 63%); $\nu_{max}/cm,^{-1}$ 2010 (C=C=N); $\delta_H(CDCl_3)$ 2.05 (3 H, s, CH_3), 2.45–4.30 (4 H, m, CH_2CH_2), 4.60 (2 H, s, SCH_2N) and 6.95–7.40 (4 H, m, ArH): HRMS (Found: M^+, 203.0764. Calc. for $C_{12}H_{13}NS$, *M*, 203.0767). When the raw product was purified by PLC on silica gel, a part of the ketenimine **20** was hydrolysed to give 7-*methyl*-1,2,4,5-*tetrahydro*-3,5-*benzothiazonin*-6-(7H)-*one* **21** as colourless prisms, m.p. 177–178 °C (from ethanol); ν_{max}/cm^{-1} 3260 (NH) and 1645 (CO); δ_H(270 MHz; $CDCl_3$) 1.54 (3 H, d, *J* 6.8, CH_3), 2.69 (1 H, ddd, *J* 3.4, 11.1, 14.2, 2-H), 2.95–3.23 (2 H, m, 1-H_2), 3.44 (1 H, ddd, *J* 3.4, 10.7, 14.2, 2-H), 3.70 (1 H, dd, *J* 2.4, 14.6, 4-H), 4.50 (1 H, dd, *J* 8.5, 14.6, 4-H), 4.92 (1 H, q, *J* 6.8, 7-H), 5.65–5.85 (1 H, br s, NH) and 7.15–7.30 (4 H, m, ArH); *m/z* 221 (M^+) (Found: C, 64.9; H, 7.0; N, 6.4. $C_{12}H_{15}NOS$ requires C, 65.1; H, 6.8; N, 6.3%).

Reaction of the Ketenimine **20** *with Acetic Acid*.—Acetic acid (83 mg, 1.5 mmol) was added to a solution of the ketenimine **20** (61 mg, 0.3 mmol) in dry dichloromethane (5 cm^3). The mixture was stirred for 10 min at room temperature and poured into a cold solution of sodium hydrogen carbonate. The organic layer was separated, washed with water, dried ($MgSO_4$) and concentrated. The residue was separated by PLC on silica gel using hexane–ethyl acetate (1:10) to give 6-*acetoxy*-7-*methyl*-1,2,4,5-*tetrahydro*-3,5-*benzothiazonine* **22** (56 mg, 71%) as colourless prisms, m.p. 102–103 °C (from diethyl ether–hexane); ν_{max}/cm^{-1} 3360 (NH), 1765 and 1695 (CO); $\delta_H(CDCl_3)$ 1.83 (3 H, s, $COCH_3$), 2.24 (3 H, s, 7-CH_3), 2.95–3.35 (4 H, m, 1- and 2-H_2), 3.70–4.10 (2 H, m, 4-H_2) and 7.24 (4 H, br s, ArH); *m/z* 263 (M^+) (Found: C, 63.6; H, 6.5; N, 5.3. $C_{14}H_{17}NO_2S$ requires C, 63.85; H, 6.5; N, 5.3%).

Reaction of **1a** *with Acetic Anhydride*.—A mixture of **1a** (104 mg, 0.55 mmol) and acetic anhydride (5.6 g, 55 mmol) in dry dichloromethane (20 cm^3) was stirred for 20 h at room temperature under a nitrogen atmosphere and then poured into saturated aqueous sodium hydrogen carbonate. The mixture was stirred until evolution of carbon dioxide ceased and then it was extracted with dichloromethane. The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was separated by PLC on silica gel using benzene–acetone (7:1) to give 6-*acetoxy*-7-*acetyl*-1,2,4,5-*tetrahydro*-3,5-*benzothiazonine* **26** (101 mg, 63%) as colourless prisms, m.p. 174 °C (from dichloromethane–hexane); ν_{max}/cm^{-1} 3200 (NH), 1750 (CO_2CH_3) and 1660 (CO); δ_H(100 MHz; $CDCl_3$) 1.78 (3 H, s, $COCH_3$), 2.17 (3 H, s, $OCOCH_3$), 2.50–3.30 (4 H, m, 1- and 2-H_2), 4.20–4.70 (2 H, m, 4-H_2), 6.45 (1 H, t, *J* 7.5, NH) and 6.95–7.50 (4 H, m, ArH); $\delta_C(CDCl_3)$ 16.6, 20.9 (each q, CH_3), 30.9, 31.9 (each t, C-1 and -2), 41.5 (t, C-4) 123.6 (s), 127.0 (d), 128.8 (d), 130.2 (d), 133.7, 138.9, 146.6 (each s), 169.2 and 170.8 (each s, CO); *m/z* 291 (M^+) (Found: C, 61.6; H, 5.9; N, 4.75. $C_{15}H_{17}NO_3S$ requires C, 61.8; H, 5.9; N, 4.8%).

Hydrolysis of **26**.—A sodium hydroxide solution (5%; 15 cm^3) was added to a solution of **26** (155 mg, 0.53 mmol) in ethanol (15 cm^3). The mixture was stirred for 2 h at room temperature, poured into water and extracted with dichloromethane. The extracts were dried ($MgSO_4$) and concentrated to dryness. The residue was recrystallised from diethyl ether–hexane to give 7-*acetyl*-1,2,4,5-*tetrahydro*-3,5-*thiazonin*-6-(7H)-*one* **27** (27 mg, 20%) as colourless prisms, m.p. 131 °C; ν_{max}/cm^{-1} 3240 (NH) and 1605 (CO); δ_H 1.80 (3 H, s, CH_3), 2.35–3.93 (6 H, m, 1-, 2- and 4-H_2), 5.10–5.60 (1 H, m, NH) and 7.00–7.28 (4 H, m, ArH); *m/z* 249 (M^+) (Found: C, 62.4; H, 6.1; N, 5.55. $C_{13}H_{15}NO_2S$ requires C, 62.6; H, 6.1; N, 5.6%).

Reaction of **1a** *with DMAD*.—DMAD (83 mg, 0.6 mmol) was added to a solution of **1a** (108 mg, 0.6 mmol) in dry dichloromethane (20 cm^3) with stirring at 0 °C under a nitrogen atmosphere. The reaction mixture was stirred overnight at room temperature and then concentrated to dryness under reduced pressure. The residue was separated by PLC on silica gel using hexane–ethyl acetate (5:1) to give *dimethyl* 7-*cyano*-1,2,4,5-*tetrahydro*-3-*benzothionine*-5,6-*dicarboxylate* **30a** (69 mg, 37%) and 6-*cyano*-4,5-*bis*(*methoxycarbonyl*)-3-*methyl*-1,2-*dihydro*-4H-3-*thioniabenzocycloocten*-4-*ide* **32a** (72 mg, 38%).

30a: colourless prisms, m.p. 154–155 °C (from dichloromethane–hexane); ν_{max}/cm^{-1} 2210 (CN) and 1740 (CO); δ_H(100 MHz; $CDCl_3$) 2.12–3.40 (7 H, m, 1-, 2-, 4- and 5-H), 3.65, 3.93 (each 3 H, s, CH_3) and 7.12–7.56 (4 H, m, ArH); δ_C(25 MHz; $CDCl_3$) 32.5, 33.1, 36.5 (each t, C-1, 2 and 4), 49.4 (d, C-5), 52.6, 52.9 (each q, CH_3), 115.8 (s, CN), 123.3 (s, ArC), 127.5, 127.6, 130.3, 130.9 (each d, ArC), 132.8 (s, ArC), 140.2, 146.1 (each s, C-6 and -7), 163.2 and 170.1 (each s, CO); *m/z* 331 (M^+) (Found: C, 61.4; H, 5.15; N, 4.2. $C_{17}H_{17}NO_4S$ requires C, 61.6; H, 5.2; N, 4.2%). **32a**: yellow prisms, m.p. 179–180 °C (decomp.) (from dichloromethane–diethyl ether); ν_{max}/cm^{-1} 2180 (CN), 1715 and 1650 (CO); δ_H(100 MHz; $CDCl_3$) 2.85 (3 H, br s, SCH_3), 2.50–3.60 (4 H, m, CH_2CH_2), 3.69, 3.95 (each 3 H, s, CO_2CH_3), 7.00–7.50 (3 H, m, ArH) and 7.50–7.75 (1 H, m, ArH); δ_C 24.72 (q, SCH_3), 29.56, 38.84 (t, C-1 and -2), 51.31, 53.16 (s, OCH_3), 91.60 (s, C-4), 122.17 (s, CN), 128.16, 128.75, 129.87, 130.51 (each d), 133.65, 134.86 (each s), 149.76 (s, C-5 or -6), 164.59 and 168.79 (each s, CO); *m/z* 331 (M^+) (Found: C, 61.3; H, 5.25; N, 4.3. $C_{17}H_{17}NO_4S$ requires C, 61.6; H, 5.2; N, 4.2%).

Reaction of **1b** *with DMAD.*—A mixture of **1b** (102 mg, 0.5 mmol) and DMAD (83 mg, 0.6 mmol) in dichloromethane (20 cm^3) was stirred overnight at room temperature and then concentrated to dryness. The residue was separated by PLC on silica gel using hexane–ethyl acetate (4:1) to give *dimethyl 7-cyano-9-methyl-1,2,4,5-tetrahydro-3-benzothionine-5,6-dicarboxylate* **30b** (45 mg, 26%) and *6-cyano-4,5-bis(methoxycarbonyl)-3,8-dimethyl-1,2-dihydro-4H-3-thioniabenzocyclooctene-4-ide* **32b** (57 mg, 33%). **30b**: colourless oil; ν_{max}/cm^{-1} 2210 (CN) and 1740 (CO); $\delta_H(CDCl_3)$ 2.38 (3 H, s, 9-CH_3), 2.65–3.45 (7 H, m, 1-, 2-, 4-H_2 and 5-H), 3.68, 3.95 (each 3 H, s, CO_2CH_3) and 7.03–7.45 (3 H, m, ArH); HRMS (Found: M^+, 345.1038. Calc. for $C_{18}H_{19}NO_4S$, *M*, 345.1035). **31b**: yellow powder, m.p. 174–175 °C (decomp., from dichloromethane–diethyl ether); ν_{max}/cm^{-1} 2180 (CN), 1730 and 1645 (CO_2CH_3); $\delta_H(CDCl_3)$ 2.34 (3 H, s, 8-CH_3), 2.81 (3 H, s, SCH_3), 2.60–3.55 (4 H, m, 2 × CH_2), 3.69, 3.94 (each 3 H, s, CO_2CH_3), 6.94–7.23 (2 H, m, ArH) and 7.40–7.58 (1 H, m, ArH); *m/z* 345 (M^+) (Found: C, 62.4; H, 5.5; N, 4.0. $C_{18}H_{19}NO_4S$ requires C, 62.6; H, 5.5; N, 4.1%).

Reaction of **1c** *with DMAD.*—The ylide **1c** was prepared from 2-ethyl-3,4-dihydro-1*H*-2-thionianaphthalene perchlorate[8] (607 mg, 2.0 mmol) in the same way as described in the thermal reaction of **1c** and then dissolved in dry dichloromethane (50 cm^3). DMAD (290 mg, 2.0 mmol) was added to the solution under a nitrogen atmosphere and the reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and the residue was separated by PLC on silica gel using hexane–ethyl acetate (4:1) to afford *6-cyano-3-ethyl-4,5-bis(methoxycarbonyl)-1,2-dihydro-4H-3-thioniabenzocyclooctene-4-ide* **32c** (211 mg, 31%) as a pale-yellow powder, m.p. 159–160 °C (decomp.; from dichloromethane–hexane); ν_{max}/cm^{-1} 2180 (CN), 1730 and 1640 (CO_2CH_3); $\delta_H(CDCl_3)$ 1.20 (3 H, t, *J* 7.5, CH_2CH_3), 2.58–3.53 (6 H, m, 3-, 4-H and 2-CH_2), 3.68, 3.95 (each 3 H, s, CO_2CH_3), 7.01–7.50 (3 H, m, ArH) and 7.58–7.85 (1 H, m, ArH); $\delta_C(CDCl_3)$ 9.77 (q, CH_2CH_3), 29.27, 37.05 (each d, C-1 and -2), 35.70 (t, SCH_2CH_3), 51.27, 52.98 (each q, OCH_3), 122.28 (s, CN), 128.07, 128.68, 129.83, 130.31 (each d, ArC), 133.75, 134.75, 134.79 (each s, ArC), 150.87 (s, C-5 or -6), 164.75, 168.89 (each s, CO); *m/z* 345 (M^+) (Found: C, 62.5; H, 5.4; N, 4.0. $C_{18}H_{19}NO_4S$ requires C, 62.6; H, 5.5; N, 4.1%).

Reaction of **1a** *with Methyl Propiolate* (*MP*).—A mixture of **1a** (103 mg, 0.54 mmol) and MP (46 mg, 0.55 mmol) in dry dichloromethane (20 cm^3) was stirred overnight under a nitrogen atmosphere and then concentrated to dryness. The residue was separated by PLC on silica gel using hexane–acetone (4:1) to give *6-cyano-4-methoxycarbonyl-3-methyl-1,2-dihydro-4H-3-thioniabenzocycloocten-4-ide* **32d** (30 mg, 20%), pale-yellow prisms, m.p. 192–193 °C (decomp.; from acetone–hexane); ν_{max}/cm^{-1} 2180 (CN), 1650 and 1550 (CO_2CH_3); $\delta_H(CDCl_3)$ 2.10 (3 H, br s, SCH_3), 2.75–3.55 (4 H, m, 2 × CH_2), 3.75 (3 H, s, CO_2CH_3), 7.00–7.45 (3 H, m, ArH), 7.45–7.64 (1 H, m, ArH) and 7.98 (1 H, s, =CH); $\delta_C(CDCl_3)$ 21.05 (q, SCH_3), 29.4, 38.1 (each d, C-1 and -2), 51.5 (q, OCH_3), 86.8 (s, 4-C), 124.9 (s, CN), 128.3, 128.6 (each d, ArC), 134.8, 136.4 (each s, ArC), 143.1 (s, C-5 or -6) and 164.9 (s CO); *m/z* 273 (M^+) (Found: C, 65.8; H, 5.4; N, 5.1. $C_{15}H_{15}NO_2S$ requires C, 65.9; H, 5.5; N, 5.1%).

Reaction of Ylide **32a** *with Perchloric Acid.*—Perchloric acid (70%; 44 mg, 0.3 mmol) was added to a solution of **32a** (101 mg, 0.3 mmol) in acetonitrile (20 cm^3) and the mixture was stirred for 2 h at room temperature. The solvent was removed under reduced pressure and dichloromethane (1 cm^3) was added to the residual oil. The resulting crystals were filtered and recrystallised from acetonitrile–diethyl ether to give *6-cyano-4,5-bis(methoxycarbonyl)-3-methyl-1,2-dihydro-4H-3-thioniabenzocyclooctene perchlorate* **33** (100 mg, 76%) as colourless prisms, m.p. 173–176 °C; ν_{max}/cm^{-1} 2220 (CN), 1770, 1745, 1720 (CO_2CH_3) and 1100–1070 (ClO_4^-); δ_H(270 MHz; CD_3CN) 2.88 (3 H, s, SCH_3), 2.93–3.04 (1 H, m, CH_2), 3.40–3.53 (2 H, m, CH_2) 3.68–3.83 (1 H, m, CH_2), 3.76, 3.98 (each 3 H, s, OCH_3), 4.98 (1 H, s, CH) and 7.40–7.72 (4 H, m, ArH) (Found: C, 47.1; H, 4.2; N, 3.2. $C_{17}H_{18}ClNO_8S$ requires C, 47.3; H, 4.2; N, 3.2%).

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