Selective Rearrangements of 1λ⁴,2,4-Benzothiadiazines

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1-Aryl-1λ⁴,2,4-benzothiadiazines (1) rearrange when heated above 180 °C to give the isomeric 4-aryl-4*H*-1,2,4-benzothiadiazines (2) by an intramolecular pathway, a [1,4]-sigmatropic shift. The 1-phenyl-1λ⁴,2,4-benzoselenadiazine (4) rearranges in a similar way, but 1-alkyl- and 1-morpholino-1λ⁴,2,4-benzothiadiazines (6) and (8) give 2*H*-1,2,4-benzothiadiazines (7) with loss of the 1-substituent. On irradiation, the 1-aryl- and 1-alkyl-benzothiadiazines (1), (6), and (13) rearrange to give benzimidazoles by cleavage of the sulphur–nitrogen ylide bond; an intermediate nitrene can be intercepted by dimethyl sulphoxide.

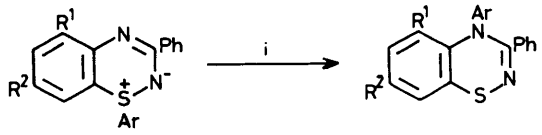
Thermal Reactions

A characteristic feature of the chemistry of thiabenzenes is their thermal instability. For example, the 1,2,4,6-tetraphenyl derivative is unstable above 0 °C.[1] The major pathways of thermal reaction of 1-alkyl- and 1-aryl-thiabenzenes appear to involve intramolecular 1,2- and 1,4-shifts of the 1-substituents from sulphur to carbon.[2] Similar migrations of sulphur substituents have also been observed in related ylides derived from the 1λ⁴,4-benzothiazine system.[3] In contrast, thermal reactions of acyclic sulphur–nitrogen ylides (sulphimides) do not normally involve the migration of simple aryl or alkyl groups from sulphur:[4] more commonly, the reactions require cleavage of the sulphur–nitrogen bond of the ylides.[4,5]

We set out to determine whether the thermal reactions of 1λ⁴,2,4-benzothiadiazines,[6] as cyclic sulphimides, would parallel those of the thiabenzenes or those of the acyclic sulphimides. In contrast with thiabenzenes, the 1-arylbenzothiadiazines (1) were thermally quite stable, and required heating in solution at about 180 °C before any change was observed. For small-scale reactions, it was found convenient to heat the ylides (1) without a solvent at 220—225 °C. In all instances, this resulted in the formation of one major product from each of the ylides, these products being isomers of the starting ylides. The rearrangement products, which were bright yellow solids, were isolated by layer chromatography.

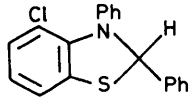
The mass spectra of the rearrangement products all showed a strong molecular ion, with a major fragment ion corresponding to the loss of PhCN, irrespective of the nature of the 1-substituent of the starting ylide. From this, it appeared likely that the 1-aryl substituent had migrated to N-2 or to N-4 rather than to C-3. The major evidence for the structures of the rearrangement products was provided by the reductive cleavage of the product from the ylide (1b), using zinc dust in acetic acid. This reduction product contained both phenyl groups but only one of the nitrogen atoms of the original ylide. It was assigned the structure 4-chloro-2,3-dihydro-2,3-diphenylbenzothiazole (3), the single hydrogen atom at C-2 appearing in the ^{1}H n.m.r. spectrum as a singlet at δ 6.30. On this basis, the rearrangement products are formulated as 3,4-diaryl-4*H*-1,2,4-benzothiadiazines (2) (Scheme 1), the reduction having involved the elimination of ammonia.

The ^{1}H n.m.r. spectra of the rearrangement products revealed one feature which allowed them to be classified into two groups. Compounds (2b), (2c) and (2f) showed multiplets (2 H), typical of the *ortho*-hydrogen atoms of a conjugated phenyl group, in the region δ 8.0—8.2, but in the spectra of compounds (2a), (2d), and (2e) these signals were not distinguishable from those of the other aryl hydrogen atoms, the lowest field signals appearing at about δ 7.3. It thus appears that the 3-phenyl substituent is conjugated with the ring imidoyl group in the former set of compounds but not in the latter. The former set all bear a 5-substituent, whereas the latter do not, suggesting that the presence of a 5-substituent forces the 4-aryl group out of planarity with the ring and hence allows the 3-phenyl group to lie coplanar.



a; $R^1 = R^2 = H$, Ar = Ph
b; R^1 = Cl, R^2 = H, Ar = Ph
c; R^1 = Me, R^2 = H, Ar = Ph
d; R^1 = H, R^2 = Me, Ar = Ph
e; $R^1 = R^2 = H$, Ar = 4-MeC_6H_4
f; R^1 = Me, R^2 = H, Ar = 4-MeC_6H_4
g; R^1 = Cl, R^2 = H, Ar = 4-MeC_6H_4

Scheme 1. i, 220—225 °C



(3)

An experiment was carried out with the object of determining whether the rearrangement was inter- or intra-molecular. Ylides (1c) and (1g), bearing different 1-aryl substituents, were pyrolysed together at 225 °C and the rearrangement products were isolated as a mixture. The mass spectrum of the mixture showed only the ions derived from the intramolecular rearrangement products (2c) and (2g); molecular ions corresponding to ' crossover ' products (2b) and (2f) were absent. This indicates that the reaction is probably an intramolecular one, a [1,4]-sigmatropic shift, and indeed it seems to bear a close parallel to those observed by Mislow and coworkers in the thiabenzene series.[2]

A similar type of rearrangement took place when the analogous 1λ⁴-benzoselenadiazine (4) was heated at 180 °C: a single major product was isolated by layer chromatography and was assigned structure (5). An attempt to observe a similar methyl migration in the 1-methyl-1λ⁴,2,6-benzothiadiazine (6) was, however, unsuccessful: the compound

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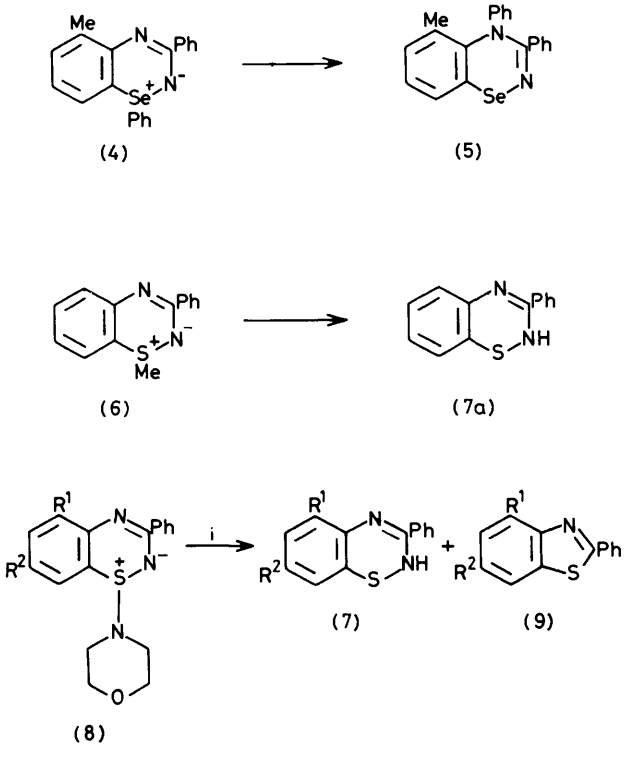


a; $R^1 = R^2 = H$
b; $R^1 = Cl$, $R^2 = H$
c; $R^1 = H$, $R^2 = Cl$
d; $R^1 = H$, $R^2 = Me$

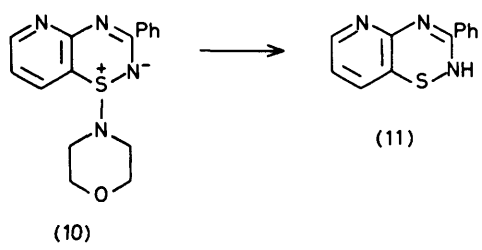
Scheme 2. *Reagents*: i, PhCl, 132 °C, 1—4 h, N_2

decomposed at a much lower temperature (80 °C) and gave as the major product the demethylated compound (7a).

The 1-morpholino-1λ⁴,2,4-benzothiadiazines (8) proved to be intermediate in stability between the 1-aryl and 1-methyl derivatives. The compounds decomposed when heated in chlorobenzene at 132 °C for 1—4 h and gave, as major products, the 2*H*-benzothiadiazines (7) in which the morpholino-group has been lost (Scheme 2). In several cases, the corresponding benzothiazoles (9) were also detected as minor products, but it is likely that these are formed from the benzothiadiazines (7).[7] We did not determine whether the benzothiadiazines (7) were formed by a concerted β-elimination process, of the type which commonly occurs with sulphimides bearing substituents with a β-hydrogen atom, or whether they were derived by a radical cleavage process. We were not able to detect products derived from ' 3,4-dehydromorpholine ', which would be the residual fragment of a concerted β-elimination process. The same type of thermal reaction was observed with the thiadiazine (10) derived from *N*-(2-pyridyl)benzamidine, the product being the 2*H*-thiadiazine (11). The overall reaction sequence thus provides a convenient route to 2*H*-thiadiazines such as (7) and (11) from *N*-arylbenzamidines: only a few such compounds have previously been prepared.[7,8]

Light-induced Rearrangements

When sulphimides are subjected to ultraviolet irradiation, the most common result is cleavage of the sulphur–nitrogen bond to give a sulphide and a nitrene which then reacts further.[4] Such reactions have been observed in a range of acyclic sulphimides, including imidoylsulphimides,[5] and, more recently, with some cyclic sulphimides.[9] The 1λ⁴,2,4-benzothiadiazines (1) conformed to the expected pattern, and were cleaved at the sulphur–nitrogen bond when irradiated in acetonitrile.



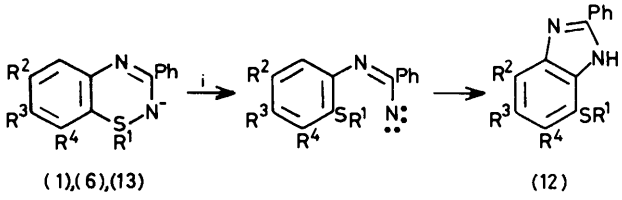
The results of the photolyses are summarised in Scheme 3. The benzothiadiazines were cleaved, presumably to give the nitrenes, which then cyclised onto the free *ortho*-positions of the benzene rings to give the benzimidazoles (12), the second step being a known reaction of imidoylnitrenes.[5] The 1-phenyl-1,2,4-benzothiadiazines were cleaved rapidly and the crystalline benzimidazoles (12a), (12b), and (12c) were isolated in good yields. The less stable 1-alkyl-1,2,4-benzothiadiazines similarly gave benzimidazoles (12d) and (12e), but in lower overall yields.

With all these benzothiadiazines, there was a free 5-position available for the intermediate nitrene to attack. We also investigated the light-induced reactions of benzothiadiazine (1b), with a chloro-substituent at the 5-position, in order to determine whether a group other than hydrogen could be displaced by the nitrene. The benzothiadiazine (1b) was apparently stable to irradiation in acetonitrile: it was recovered after irradiation for 1 h (the time taken for the others to rearrange completely) and even after 18 h, more than 50% was recovered, the remainder having been converted into a large number of minor products. When the irradiation was repeated in the presence of dimethyl sulphoxide, a different result was obtained: the benzothiadiazine was consumed much more rapidly, and a new major product was isolated in good yield, to which the sulphoximide structure (14) was assigned. Apparently, in the absence of a suitable pathway for diversion of the nitrene, the latter is reversibly intercepted intramolecularly by the neighbouring sulphur group; that is, the starting structure is reversibly regenerated. Dimethyl sulphoxide can compete effectively for the nitrene and divert it to the sulphoximide (14). Attack at the carbon atom bearing chlorine does not appear to occur to any significant extent. These observations are summarized in Scheme 4.

Experimental

General directions and preparations of the 1λ⁴,2,4-benzothiadiazines are described in the preceding paper.[6]

Thermal Rearrangement of 1-Arylbenzothiadiazines.—(*a*) *1,3-Diphenyl-1λ⁴,2,4-benzothiadiazine* (1a). (i) The benzothiadiazine (416 mg) was heated in 1,2-dichlorobenzene (10 cm^3) under reflux (180 °C) for 45 h. The solvent was removed by distillation and the residue was subjected to layer chromatography [silica; chloroform–ethyl acetate (9 : 1)]. This gave the starting benzothiadiazine (155 mg) and, as a single fast-running yellow component, *3,4-diphenyl-4H-1,2,4-benzothiadiazine* (2a) (184 mg), m.p. 144—145 °C (from dichloromethane–hexane) (Found: C, 75.4; H, 4.9; N, 9.3. $C_{19}H_{14}N_2S$ requires C, 75.5; H, 4.7; N, 9.3%); $\nu_{max.}$ 1 609, 1 467, 1 438, 1 312, 1 302, and 1 204 cm^{-1}; δ 6.42 (1 H, d, *J* 8 Hz), 6.80—7.00 (3 H, m), and 7.12—7.26 (10 H, m); *m/e* 302 (M^+, base), 200, and 199 (M^+ − PhCN). A third component of the mixture was identified as *N*-(2-phenylthiophenyl)benzamidine

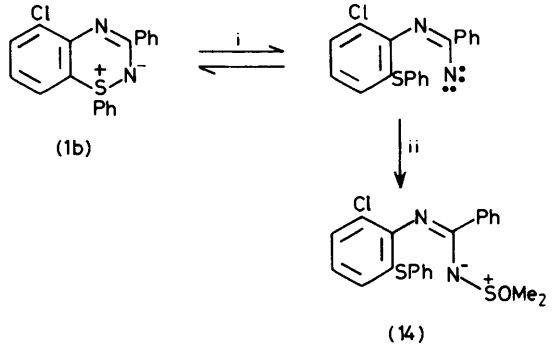


(1),(6),(13) (12)

(1) a; R^1 = Ph, R^2 = R^3 = R^4 = H
d; R^1 = Ph, R^2 = R^4 = H, R^3 = Me
h; R^1 = Ph, R^2 = Me, R^3 = R^4 = H
(6) R^1 = Me, R^2 = R^3 = R^4 = H
(13) R^1 = Et, R^2 = R^4 = H, R^3 = Me

(12) a; R^1 = Ph, R^2 = R^3 = R^4 = H
b; R^1 = Ph, R^2 = Me, R^3 = R^4 = H
c; R^1 = Ph, R^2 = R^4 = H, R^3 = Me
d; R^1 = Me, R^2 = R^3 = R^4 = H
e; R^1 = Et, R^2 = R^4 = H, R^3 = Me

Scheme 3. *Reagents:* i, *hν*, MeCN



(1b) (14)

Scheme 4. *Reagents:* i, *hν*, MeCN; ii, *hν*, MeCN–Me_2SO

(58 mg), m.p. 104 °C. (ii) The benzothiadiazine (265 mg) was heated without solvent at 220 °C for 1.5 h. Layer chromatography gave the starting material (166 mg) and 3,4-diphenyl-4*H*-1,2,4-benzothiadiazine (40 mg).

(*b*) 5-*Chloro*-1,3-*diphenyl*-1λ⁴,2,4-*benzothiadiazine* (1b). This compound (580 mg) was heated at 225 °C for 1.5 h. Layer chromatography gave the starting material (128 mg) and 5-*chloro*-3,4-*diphenyl*-4H-1,2,4-*benzothiadiazine* (2b) (300 mg), m.p. 156—157 °C (from dichloromethane–hexane) (Found: C, 67.9; H, 4.0; N, 8.5. $C_{19}H_{13}ClN_2S$ requires C, 67.7; H, 3.9; N, 8.3%); $\nu_{max.}$ 1 590, 1 578, 1 490, 1 335, and 1 260 cm^{-1}; δ 6.70 (2 H, d, *J* 7.5 Hz), 6.90 (1 H, t, *J* 6.7 Hz), 7.12 (2 H, t, *J* 7.5 Hz), 7.21—7.25 (2 H, m), 7.38—7.50 (4 H, m), and 8.15—8.22 (2 H, m); *m/e* 336 and 338 (M^+) and 233 and 235 (M^+ – PhCN, base).

The benzothiadiazine (2b) (90 mg) in acetic acid (10 cm^3) at 80 °C was reductively cleaved by the addition of zinc dust (300 mg) in portions. Layer chromatography [silica; ether–hexane (7 : 3)] gave as a single major product an oil (54 mg) which was assigned the structure 4-*chloro*-2,3-*dihydro*-2,3-*diphenylbenzothiazole* (3) (Found: M^+ 323.051. $C_{19}H_{14}ClN_2S$ requires *M* 323.054); δ 6.30 (1 H, 2-H) and 6.80—7.55 (13 H, m); *m/e* 323 and 325 (M^+) and 246 and 248 (M^+ – Ph, base).

(*c*) 5-*Methyl*-1,3-*diphenyl*-1λ⁴,2,4-*benzothiadiazine* (1c). This compound (304 mg) was heated at 220 °C for 2 h and gave 5-*methyl*-3,4-*diphenyl*-4H-1,2,4-*benzothiadiazine* (2c) (250 mg), m.p. 174—176 °C (from ethanol) (Found: C, 75.8; H, 5.1; N, 8.5. $C_{20}H_{16}N_2S$ requires C, 75.9; H, 5.1; N, 8.9%); $\nu_{max.}$ 1 587, 1 488, and 1 255 cm^{-1}; δ 2.48 (3 H), 6.63 (2 H, d, *J* 8.3 Hz), 6.90 (1 H, t, *J* 6.7 Hz), 7.12 (2 H, t, *J* 7.8 Hz), 7.20—7.35 (3 H, m), 7.45—7.55 (3 H, m), and 8.10—8.17 (2 H, m); *m/e* 316 (M^+) and 213 (M^+ – PhCN).

(*d*) 7-*Methyl*-1,3-*diphenyl*-1λ⁴,2,4-*benzothiadiazine* (1d). This compound (440 mg) was heated at 225 °C for 1 h and gave, by layer chromatography, the starting material (210 mg) and 7-*methyl*-3,4-*diphenyl*-4H-1,2,4-*benzothiadiazine* (2d) (155 mg), m.p. 169—170 °C (from methanol) (Found: C, 75.8; H, 5.0; N, 9.0. $C_{20}H_{16}N_2S$ requires C, 75.9; H, 5.1; N, 8.9%); $\nu_{max.}$ 1 545, 1 450, 1 430, 1 320, and 1 242 cm^{-1}; δ 2.15 (3 H), 6.30 (1 H, d, *J* 7.8 Hz), 6.59 (1 H), 6.65 (1 H, d, *J* 7.8 Hz), 7.05—7.23 (8 H, m), and 7.25—7.32 (2 H, m); *m/e* 316 (M^+) and 213 (M^+ – PhCN, base).

(*e*) 1-(4-*Methylphenyl*)-3-*phenyl*-1λ⁴,2,4-*benzothiadiazine* (1e). This compound (393 mg) was heated at 225 °C for 1.5 h. Layer chromatography gave starting material (185 mg) and 4-(4-*methylphenyl*)-3-*phenyl*-4H-1,2,4-*benzothiadiazine* (2e) (110 mg), m.p. 138—140 °C (from dichloromethane–hexane) (Found: C, 75.2; H, 5.3; N, 8.7. $C_{20}H_{16}N_2S$ requires C, 75.9; H, 5.1; N, 8.9%); $\nu_{max.}$ 1 603, 1 465, 1 438, and 1 292 cm^{-1}; δ 2.22 (3 H), 6.30 (1 H, d, *J* 7.4 Hz), 6.75 (1 H, t, *J* 7.3 Hz), 6.80—6.95 (2 H, m), 7.05—7.10 (4 H, m), 7.10—7.20 (3 H, m), and 7.23—7.31 (2 H, m); *m/e* 316 (M^+) and 213 (M^+ – PhCN).

(*f*) 5-*Methyl*-1-(4-*methylphenyl*)-1λ⁴,2,4-*benzothiadiazine* (1f). The compound (300 mg) was heated at 225 °C for 1.5 h. Layer chromatography gave starting material (80 mg) and 5-*methyl*-4-(4-*methylphenyl*)-3-*phenyl*-4H-1,2,4-*benzothiadiazine* (2f) (160 mg), m.p. 160—162 °C (from dichloromethane–hexane) (Found: C, 76.05; H, 5.6; N, 8.4. $C_{21}H_{18}N_2S$ requires C, 76.3; H, 5.5; N, 8.5%); $\nu_{max.}$ 1 608, 1 500, 1 440, and 1 255 cm^{-1}; δ 2.18 (3 H), 2.44 (3 H), 6.54 (2 H, d, *J* 8 Hz), 6.90 (2 H, *J* 8 Hz), 7.15—7.30 (3 H, m), 7.35—7.50 (3 H, m), and 8.06—8.13 (2 H, m); *m/e* 330 (M^+), 227 (M^+ – PhCN), and 212 (base).

Thermal Rearrangement of a Mixture of Benzothiadiazines (1c) *and* (1g).—A mixture of compounds (1c) (240 mg) and (1g) (200 mg) was heated at 225 °C for 1.5 h. The mixture of products was isolated by t.l.c. as a single yellow band (98 mg). The n.m.r. spectrum showed two methyl signals at δ 2.20 and 2.48 (ratio 1 : 3); the mass spectrum showed *m/e* 350 and 352, and 316; no peaks were discernible at *m/e* 330 or 336.

Thermal Rearrangement of 5-*Methyl*-1,3-*diphenyl*-1λ⁴,2,4-*benzoselenadiazine* (4).—The benzoselenadiazine (358 mg) was heated without solvent at 180 °C for 1 h and gave 5-*methyl*-3,4-*diphenyl*-4H-1,2,4-*benzoselenadiazine* (5) (203 mg), m.p. 171—173 °C (from ethanol) (Found: C, 66.2; H, 4.7; N, 7.4. $C_{20}H_{16}N_2Se$ requires C, 66.1; H, 4.4; N, 7.7%); $\nu_{max.}$ 1 580, 1 540, 1 490, and 1 250 cm^{-1}; δ 2.52 (3 H), 6.60 (2 H, d, *J* 8 Hz), 6.88 (1 H, t, 7 Hz), 7.07—7.17 (2 H, m), 7.23—7.37 (3 H, m), 7.42—7.52 (3 H, m), and 8.13—8.22 (2 H, m); *m/e* 362 and 364 (M^+), 259 and 261 (M^+ – PhCN), and 184 (base).

Thermolysis of 1-*Alkyl- and* 1-*Morpholino*-1λ⁴,2,4-*benzothiadiazines.*—(*a*) 1-*Methyl*-3-*phenyl*-1λ⁴,2,4-*benzothiadiazine* (6). A specimen of the compound was freshly prepared as described earlier [6] from *N*-phenylbenzamidine (392 mg, 2.0 mmol), *N*-chlorosuccinimide (532 mg), and dimethyl disulphide (94 mg). The oil was heated at 80 °C for 1 h. Column chromatography [silica; chloroform–ethyl acetate (9 : 1)] gave a single yellow product, 3-*phenyl*-2H-1,2,4-*benzothiadiazine* (7a) (235 mg, 52%), m.p. 119—120 °C (from dichloromethane–hexane) (Found: C, 68.7; H, 4.6; N, 12.4. $C_{13}H_{10}N_2S$ requires C, 69.0; H, 4.5; N, 12.4%); $\nu_{max.}$ 3 220, 1 590, 1 550, 1 455, and 1 420 cm^{-1}; δ 6.35—6.42 (1 H, m), 6.60—6.71 (2 H, m), 6.80—6.93 (2 H, m), 7.27—7.43 (3 H, m), and 7.52—7.60 (2 H, m); *m/e* 226 (M^+), 211 (M^+ − NH), 123 (M^+ − PhCN), and 96 (base).

(*b*) 5-*Chloro*-1-*morpholino*-3-*phenyl*-1λ⁴,2,4-*benzothiadiazine* (8b). The benzothiazine (190 mg, 0.55 mmol) was heated in chlorobenzene (5 cm^3) containing hydroquinone (20 mg) under nitrogen for 4 h. The solvent was removed; layer chromatography gave 5-*chloro*-3-*phenyl*-2H-1,2,4-*benzothiadiazine* (7b) (110 mg, 76%), m.p. 128—129 °C (from ethanol) (Found: C, 59.8; H, 3.55; N, 10.6. $C_{13}H_9ClN_2S$ requires C, 59.9; H, 3.5; N, 10.7%); $\nu_{max.}$ 3 400, 1 613, 1 475, 1 445, and 1 410 cm^{-1}; δ 6.65 (1 H, d, *J* 7.3 Hz), 6.85 (1 H, t, 7.3 Hz), 7.02 (1 H, d, *J* 7.3 Hz), 7.26 (1 H), 7.40—7.53 (3 H, m), and 7.67—7.75 (2 H, m); *m/e* 260 and 262 (M^+), 157 and 159 (M^+ − PhCN), and 122 (base). A second product was 4-chloro-2-phenylbenzothiazole (9b) (5 mg, 4%), m.p. 96—98 °C (from light petroleum); this was isolated in 33% yield when the thermolysis was carried out in decalin at 190 °C (Found: C, 63.25; H, 3.25; N, 5.65. $C_{13}H_8ClNS$ requires C, 63.5; H, 3.3; N, 5.7%); *m/e* 245 and 247 (M^+).

(*c*) 7-*Chloro*-1-*morpholino*-3-*phenyl*-1λ⁴,2,4-*benzothiadiazine* (8c). This compound (300 mg, 0.87 mmol) was heated in chlorobenzene (10 cm^3) under reflux for 4 h to give 7-chloro-3-phenyl-2*H*-1,2,4-benzothiadiazine (7c) (20 mg, 9%), m.p. 169 °C (from hexane) (lit.,[8] m.p. 166.5 °C) and 6-chloro-2-phenylbenzothiazole (9c) (13 mg, 6%), m.p. 156 °C (from hexane) (lit.,[10] m.p. 157 °C).

(*d*) 7-*Methyl*-1-*morpholino*-3-*phenyl*-1λ⁴,2,4-*benzothiadiazine* (8d). The benzothiadiazine (398 mg, 1.2 mmol) gave, after heating in chlorobenzene (10 cm^3) for 4 h, 7-*methyl*-3-*phenyl*-2H-1,2,4-*benzothiadiazine* (7d) (122 mg, 42%), m.p. 105—106 °C (from hexane) (Found: C, 70.2; H, 5.0; N, 11.7. $C_{14}H_{12}N_2S$ requires C, 70.0; H, 5.0; N, 11.7%); $\nu_{max.}$ 3 350, 1 605, 1 558, and 1 465 cm^{-1}; δ 2.20 (3 H), 6.35 (1 H, d, *J* 7.2 Hz), 6.55 (2 H, br), 6.73 (1 H, d, *J* 7.2 Hz), 7.35—7.50 (3 H, m), and 7.60—7.67 (2 H, m); *m/e* 240 (M^+, base), 225 (M^+ − NH), and 137 (M^+ − PhCN). A second product was 6-methyl-2-phenylbenzothiazole (9d) (55 mg, 20%), m.p. 123 °C (from cyclohexane) (lit.,[11] m.p. 125 °C).

1-*Morpholino*-3-*phenylpyrido*[2,3-e][1λ⁴,2,4]*thiadiazine* (10). —Compound (10) was prepared (32%) by the general method described in the preceding paper,[6] from 4,4′-thiobismorpholine, *N*-(2-pyridyl)benzamidine, and *N*-chlorosuccinimide. It was characterised only by its ^{1}H n.m.r. spectrum, δ (60 MHz) 2.80—3.00 (4 H, m), 3.50—3.70 (4 H, m), 7.15—7.55 (4 H, m), 7.70—7.90 (1 H, dd, *J* 2 and 8 Hz, 8-H), 8.40—8.65 (2 H, m), and 8.75—8.95 (1 H, dd, *J* 2 and 5 Hz, 6-H).

The thiadiazine (230 mg, 0.74 mmol) gave on thermolysis 3-*phenyl*-2H-*pyrido*[2,3-e][1,2,4]*thiadiazine* (11) (128 mg, 76%), m.p. 150—151 °C (from ethanol) (Found C, 63.6; H, 4.0; N, 18.2. $C_{12}H_9N_3S$ requires C, 63.4; H, 4.0; N, 18.5%); $\nu_{max.}$ 3 150 (br), 1 620, 1 495, 1 480, and 1 410 cm^{-1}; δ 6.70—6.78 (1 H, m), 6.91 (1 H, dd, *J* 2 and 8 Hz), 7.36—7.52 (4 H, m), 7.65—7.72 (2 H, m), and 8.20 (1 H, br, NH); *m/e* 227 (M^+) and 124 (M^+ − PhCN, base).

Photolysis of 1λ⁴,2,4-*Benzothiadiazines. General Procedure.* —The benzothiadiazines were dissolved in dry acetonitrile (0.5% w/w) and the solutions were irradiated in a Rayonet reactor at 253.7 nm under nitrogen. The course of the reaction was followed by t.l.c.; most reactions were complete after 1 h. Products were isolated by layer chromatography (silica). (*a*) 1,3-Diphenyl-1λ⁴,2,4-benzothiadiazine (1a) (406 mg, 1.34 mmol) gave 2-*phenyl*-7-(*phenylthio*)*benzimidazole* (12a) (300 mg, 74%), m.p. 182—184 °C (after sublimation at 228 °C and 0.5 mmHg) (Found: C, 75.45; H, 4.6; N, 9.5. $C_{19}H_{14}N_2S$ requires C, 75.5; H, 4.7; N, 9.3%); $\nu_{max.}$ 2 500—3 100 (br) cm^{-1}; δ 7.15—7.50 (10 H, m), 7.70—7.90 (1 H, m), 7.95—8.05 (2 H, m), and 9.55 (1 H, br, NH); *m/e* 302 (M^+, base). (*b*) 6-Methyl-1,3-diphenyl-1λ⁴,2,4-benzothiadiazine (1h) (160 mg, 0.51 mmol) gave 4-*methyl*-2-*phenyl*-7-(*phenylthio*)*benzimidazole* (12b) (110 mg, 69%), m.p. 73—76 °C (after sublimation at 220 °C and 0.5 mmHg) (Found: C, 75.5; H, 5.2; N, 8.8. $C_{20}H_{16}N_2S$ requires C, 75.9; H, 5.1; N, 8.9%); $\nu_{max.}$ 2 500—3 200 cm^{-1}; δ 2.67 (3 H), 7.00—7.40 (10 H, m), 7.92—8.05 (2 H, m), and 8.65 (1 H, br, NH); *m/e* 316 (M^+, base). (*c*) 7-Methyl-1,3-diphenyl-1λ⁴,2,4-benzothiadiazine (1d) (166 mg, 0.52 mmol) gave 4-*methyl*-2-*phenyl*-7-(*phenylthio*)*benzimidazole* (12c) (125 mg, 75%), m.p. 188—190 °C (from ethyl acetate) (Found: C, 75.7; H, 5.2; N, 8.9. $C_{20}H_{16}N_2S$ requires C, 75.9; H, 5.1; N, 8.9%); $\nu_{max.}$ 2 800—3 200 cm^{-1}; δ 2.43 (3 H), 7.15—7.30 (6 H, m), 7.37—7.46 (3 H, m), 7.52 (1 H, br, NH), and 7.90—8.00 (2 H, m); *m/e* 316 (M^+, base). (*d*) 1-Methyl-3-phenyl-1λ⁴,2,4-benzothiadiazine (6), prepared immediately before photolysis from *N*-phenylbenzamidine (392 mg, 2.0 mmol), gave 4-*methylthio*-2-*phenylbenzimidazole* (12d) (160 mg, 33%), m.p. 215—217 °C (from ethyl acetate) (Found: C, 69.4; H, 5.0; N, 11.4. $C_{14}H_{12}N_2S$ requires C, 70.0; H, 5.0; N, 11.7%); $\nu_{max.}$ 2 500—3 200 cm^{-1}; δ 2.60 (3 H), 7.03 (1 H, d, *J* 8 Hz), 7.15—7.25 (1 H, m), 7.35 (1 H, d, *J* 8 Hz), 7.50—7.62 (3 H, m), and 8.15—8.25 (2 H, m); *m/e* 240 (M^+, base). (*e*) 1-Ethyl-7-methyl-3-phenyl-1λ⁴,2,4-benzothiadiazine (13), freshly prepared from 4-methylphenylbenzamidine (420 mg, 2.0 mmol), gave 7-*ethylthio*-5-*methyl*-2-*phenylbenzimidazole* (12e) (118 mg, 22%), m.p. 145 °C (from ethyl acetate) (Found: M^+, 268.1023. $C_{16}H_{16}N_2S$ requires M^+, 268.1034); $\nu_{max.}$ 2 500—3 200 cm^{-1}; δ 1.25 (3 H, t), 2.38 (3 H), 3.00 (2 H, q), 7.06 (1 H), 7.21 (1 H), 7.25—7.35 (3 H, m), 8.00—8.12 (2 H, m), and 9.70 (1 H, br, NH); *m/e* 260 (M^+, base) and 240 (M^+ − C_2H_4). (*f*) 5-Chloro-1,3-diphenyl-1λ⁴,2,4-benzothiadiazine (1b) was irradiated under different conditions as follows. (i) The compound was recovered unchanged after irradiation in acetonitrile for 1 h. (ii) The benzothiadiazine (262 mg, 0.78 mmol) was irradiated in acetonitrile for 17 h and gave a dark brown solution. Layer chromatography (silica) showed the presence of several minor components, none of which was identified; the starting material (140 mg, 53%) was recovered from the plate. (iii) The benzothiadiazine (261 mg, 0.78 mmol) was irradiated in acetonitrile (150 cm^3) containing dimethyl sulphoxide (606 mg, 7.8 mmol) for 3.5 h. Layer chromatography gave the starting material (86 mg, 33%) and N-[N-(2-*chloro*-6-*phenylthiophenyl*)*benzimidoyl*]-S,S-*dimethylsulphoximide* (14) (137 mg, 64% based on starting material consumed), m.p. 121—122 °C (from ethanol) (Found: C, 60.7; H, 4.75; N, 6.7. $C_{21}H_{19}ClN_2OS_2$ requires C, 60.8; H, 4.6; N, 6.8%); $\nu_{max.}$ 1 560, 1 205, and 1 010 cm^{-1}; δ 3.38 (3 H), 3.51 (3 H), 6.70—6.85 (2 H, m), 7.12 (1 H, d, *J* 8 Hz), and 7.18—8.05 (10 H, m); *m/e* 414 and 416 (M^+, base), and 321 (M^+ − Me_2SONH).

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