1*H*-1,4-Benzothiazines. New Cyclic Sulphonium Ylides

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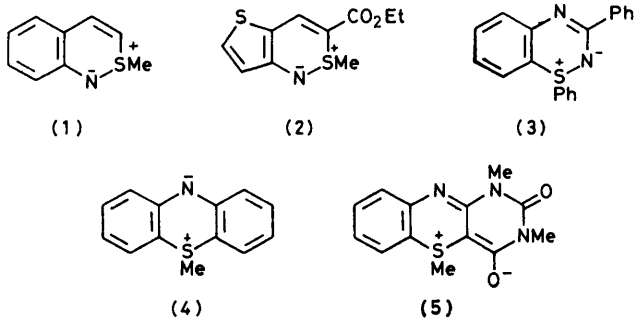
Five derivatives of the 1*H*-1,4-benzothiazine ring system (6) have been prepared by cyclodehydration of the sulphoxides (7) with trifluoroacetic anhydride. The derivative (6a) was also prepared by methylation of 2,3-dihydro-2,2-dimethyl-10*H*-phenothiazin-4(1*H*)-one (11a). ^{1}H and ^{13}C N.m.r. spectra of the compounds indicate that they can be regarded as stabilised sulphonium ylides, the substituents about the sulphur being in a non-planar arrangement. When heated in hydrochloric acid the ylides are demethylated and give the corresponding 4*H*-1,4-benzothiazines.

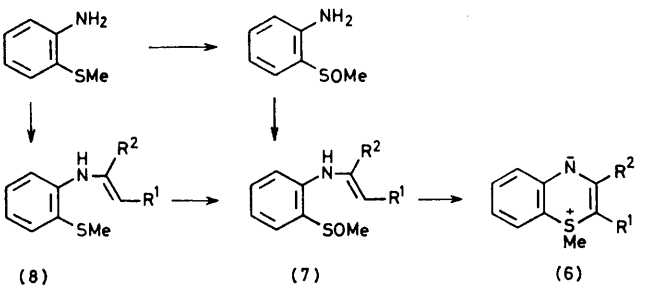
THE preparation and properties of several conjugated six-membered heterocycles containing a sulphur(IV) atom have been described recently. The parent 1*H*-thiazine, or ' thiabenzene ', system was clearly shown by Mislow and his co-workers to be ylidic rather than aromatic in character.[1] Derivatives of this ring system are highly reactive, unless they bear appropriate electron-withdrawing substituents.[2] Analogues containing a nitrogen atom at positions 2, 4, or 6 relative to sulphur should also be stabilised. A few fused aza-analogues of thiabenzene have been prepared: examples are the cyclic sulphimides (1),[3] (2),[4] and (3),[5] and the phenothiazines (4) [6] and (5).[7]



(1) (2) (3) (4) (5)

We have explored a general route to 1*H*-1,4-benzothiazines which is based on an established method for the preparation of acyclic sulphonium ylides, namely, the reaction of a sulphoxide with an activated methylene compound in the presence of a dehydrating agent. The benzothiazines (6) were thus prepared from the sulphoxides (7). These sulphoxides were made by two routes (Scheme). In the first, 2-methylthioaniline reacted with activated methylene compounds to give the sulphides (8), which were then oxidised to the corresponding sulphoxides. In the second, 2-methylsulphinylaniline, prepared from 2-methylthioaniline *via* the acetanilide,[8] was condensed with activated methylene compounds, or, in the case of the diester (7e), was added to dimethyl acetylenedicarboxylate. Although none of these enaminones has previously been prepared, the methods used are well known with other anilines.[9]

An attempt was made to cyclise the sulphide (8e) directly to the benzothiazine (6e) by the use of *N*-chlorosuccinimide, but this was thwarted by the preferential attack of the oxidant at carbon rather than at sulphur, leading to the formation of the chloro-enaminone (9). With hydrogen peroxide in acetic acid, the sulphide (8e) gave a complex mixture of products. In contrast, the sulphides (8a) to (8d) gave the corresponding sulphoxides (7) in moderate yields. The more direct route,



(8) (7) (6)

(6,7,8) a; R^1R^2 = $COCH_2CMe_2CH_2$
b; R^1R^2 = $COCH_2CH_2CH_2$
c; R^1 = COPh, R^2 = Ph
d; R^1 = CO_2Et, R^2 = Ph
e; R^1 = R^2 = CO_2Me

SCHEME

from 2-methylsulphinylaniline, avoids the problem of selective oxidation and is, therefore, probably more general.

Trifluoroacetic anhydride is a very effective reagent for the ' activation ' of dimethyl sulphoxide,[10] and it proved to be suitable for the cyclodehydration of the sulphoxides (7). The benzothiazines (6a) to (6d) were isolated as crystalline solids from the reaction mixtures. Compound (6e) was isolated as an oil; it was characterised as its picrate.

The assignment of cyclic structures to the products is supported by the mass spectra and the ^{1}H and ^{13}C n.m.r. spectra of the compounds. The mass spectra all show, besides a molecular ion, a major fragment ion corresponding to the loss of a methyl radical from the molecule. These fragment ions are assumed to be the thiazinyl cations (10). The ^{1}H n.m.r. spectra all show signals for the *S*-methyl group in the range δ 2.3—2.5, shifted *ca.* 0.4 p.p.m. upfield compared with the *S*-methyl signals in the precursor sulphoxides. The spectrum of the benzothiazine (6a) in trifluoroacetic acid shows an *S*-methyl signal which is shifted downfield, to δ 3.00, as

would be expected if the ylide were protonated. The ^1H and ^{13}C n.m.r. spectra in deuteriochloroform both show the non-planar arrangement of the substituents about sulphur in compound (6a): the ^1H n.m.r. spectrum shows AB patterns for each of the two methylene groups and the ^{13}C n.m.r. spectrum shows separate signals for the carbon atoms of the geminal methyl groups. Tentative assignments of the signals in the ^{13}C n.m.r. spectrum are shown in the Figure. The signal for the carbon atom

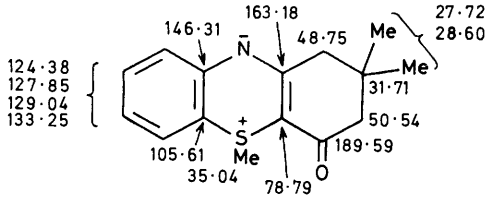
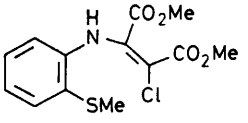


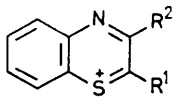
FIGURE ^{13}C N.m.r. spectrum of (6a)

(C-4a) adjacent to sulphur is at 78.79 p.p.m., which is consistent with those observed for other stabilised sulphonium ylides.[11] The chemical shift of the benzene ring carbon atom attached to sulphur (C-5a) is unusually high (105.61 p.p.m.).

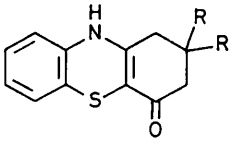
All the ylides show a long-wavelength absorption in the u.v. spectrum. The maxima for compounds (6a), (6b), (6d), and (6e) are in the range 370—375 nm, but for (6c) the maximum is at 400 nm.



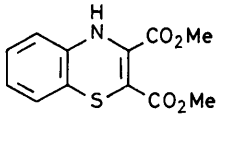
(9)



(10)



(11) a; R = Me
b; R = H



(12)

The structure assigned to compound (6a) was confirmed by an independent synthesis. The known[12] phenothiazine derivative (11a) was methylated by reaction with sodium hydride and iodomethane to give the ylide (6a) directly. This type of *S*-alkylation procedure has previously been used to prepare the ylides (4)[6] and (5).[7] Since the known routes to 4*H*-1,4-thiazines such as (11a) and related derivatives are straightforward[12,13] and appear to be capable of extension, the *S*-alkylation procedure may prove to be a more direct route to the corresponding ylides than the sulphoxide ring-closure.

The reverse of this reaction, the demethylation of the ylides, was readily achieved by heating the ylides with concentrated hydrochloric acid for a short period. In this way the ylides (6a), (6b), and (6e) were converted into the corresponding 4*H*-thiazines (11a), (11b), and (12). Other chemistry of this series of ylides is being explored and will be reported separately.

EXPERIMENTAL

I.r. spectra were recorded for solids as KBr discs on a Perkin-Elmer 125 spectrometer, and ^1H n.m.r. spectra were obtained for solutions in $CDCl_3$ on a Perkin-Elmer R34B instrument (operating at 220 MHz), except where indicated otherwise. U.v. spectra were recorded using a Pye Unicam SP 800 instrument and were calibrated against holmium glass. Mass spectra were measured using an A.E.I. MS12 spectrometer with a direct-insertion probe, at 70 eV. Melting points were obtained on a Kofler hot stage apparatus and are uncorrected. Light petroleum refers to the fraction with b.p. 60—80 °C. 2-Methylthioaniline was obtained from the Aldrich Chemical Company.

Enaminones (8) *derived from 2-Methylthioaniline and Activated Methylene Compounds.*—(a) *5,5-Dimethyl-3-(2-methylthiophenylamino)cyclohex-2-en-1-one* (8a). Dimedone (5.04 g, 0.036 mol), 2-methylthioaniline (5.00 g, 36 mmol) and *p*-tolylsulphonic acid (100 mg) were heated in toluene (70 cm^3) under a Dean and Stark water separator until no more water was produced and the reaction appeared to be complete (by t.l.c.; 10 h). The solvent was evaporated off and the residue was washed with light petroleum, aqueous sodium carbonate, and water. It was then dried and crystallised to give the *enaminone* (8a) (8.00 g, 85%) as colourless needles, m.p. 146—149 °C (from ethyl acetate–hexane) (Found: C, 69.15; H, 7.4; N, 5.1. $C_{15}H_{19}NOS$ requires C, 69.0; H, 7.3; N, 5.4%); $\nu_{max.}$ 3 170, 1 590, and 1 520 cm^{-1}; δ 1.12 (6 H), 2.23 (2 H), 2.38 (3 H), 5.47 (1 H), 6.33 (1 H, m), and 7.14—7.39 (3 H, m).

(b) The following compounds were prepared in a similar manner:

(i) *3-(2-Methylthiophenylamino)cyclohex-2-en-1-one* (8b), from cyclohexane-1,3-dione (94%), m.p. 162—164 °C (from ethyl acetate–ethanol) (Found: C, 67.1; H, 6.4; N, 6.0. $C_{13}H_{15}NOS$ requires C, 66.95; H, 6.4; N, 6.0%); $\nu_{max.}$ 3 210, 1 595, 1 560, and 1 510 cm^{-1}; δ 1.97—2.14 (2 H, m), 2.34 (2 H, t, *J* 7.3 Hz), 2.37 (3 H), 2.50 (2 H, t, *J* 7.3 Hz), 5.41 (1 H), 6.57 (1 H, m), and 7.11—7.35 (3 H, m).

(ii) *3-(2-Methylthiophenylamino)-1,3-diphenylprop-2-en-1-one* (8c), from dibenzoylmethane (58%), yellow plates m.p. 135—138 °C (from ethanol) (Found: C, 76.65; H, 5.5; N, 3.9. $C_{22}H_{19}NOS$ requires C, 76.5; H, 5.5; N, 4.1%); $\nu_{max.}$ 1 590 and 1 565 cm^{-1}; δ 2.49 (3 H), 6.14 (1 H), 6.39 (1 H, d, *J* 7 Hz), 6.69—6.77 (1 H, m), 6.90—6.99 (1 H, m), 7.18—7.48 (9 H, m), and 7.91—8.03 (2 H, m).

(iii) *Ethyl 3-(2-Methylthiophenylamino)-3-phenylpropenoate* (8d), from ethyl benzoylacetate (86%), m.p. 120—123 °C (from ethanol) (Found: C, 69.1; H, 6.1; N, 4.35. $C_{18}H_{19}NO_2S$ requires C, 69.0; H, 6.1; N, 4.5%); $\nu_{max.}$ 1 645, 1 590, and 1 565 cm^{-1}; δ 1.29 (3 H, t, *J* 7 Hz), 2.49 (3 H), 4.22 (2 H, q, *J* 7 Hz), 5.09 (1 H), 6.28 (1 H, d, *J* 8 Hz), 6.70—6.94 (2 H, m), and 7.20—7.37 (6 H, m).

Dimethyl 2-(2-Methylthiophenylamino)but-2-ene-1,4-dioate (8e).—Dimethyl acetylenedicarboxylate (2.13 g, 15 mmol) was added dropwise to a stirred solution of 2-methylthioaniline (2.08 g, 15 mmol) in ethanol (30 cm^3) at room temperature. The reaction was exothermic and the reaction mixture was maintained at 20 °C by external cooling. After 4 h the solvent was removed and the residue was distilled to give the *enamino-ester* (8e) (3.60 g, 85%), b.p. 84—85 °C at

0.1 mmHg. The oil slowly solidified; crystallisation gave a yellow solid, m.p. 48—50 °C (from hexane) (Found: C, 55.4; H, 5.5; N, 4.9. $C_{13}H_{15}NO_4S$ requires C, 55.5; H, 5.3; N, 5.0%); $\nu_{max.}$ 3 240, 1 730, 1 670, and 1 605 cm^{-1}; δ 2.40 (3 H), 3.73 (3 H), 3.81 (3 H), 5.43 (1 H), 6.68 (1 H, m), 6.90—7.11 (2 H, m), 7.25—7.33 (1 H, m), and 9.77 (1 H, NH).

Dimethyl 3-Chloro-2-(2-methylthiophenylamino)but-2-ene-1,4-dioate (9).—The sulphide (8e) (0.56 g, 2.0 mmol) and *N*-chlorosuccinimide (0.27 g, 2.0 mmol) were stirred in dichloromethane (10 cm^3) at 20 °C for 18 h. The solution was washed with aqueous sodium hydroxide and water, dried, and evaporated. The residue, a viscous brown oil (0.62 g), was subjected to layer chromatography (silica; ethyl acetate–light petroleum 1 : 3) which gave the *chloro-ester* (9) (0.50 g, 79%), m.p. 115—117 °C (from hexane) (Found: C, 49.6; H, 4.5; N, 4.4. $C_{13}H_{14}ClNO_4S$ requires C, 49.45; H, 4.4; N, 4.4%); $\nu_{max.}$ 3 260, 1 730, 1 690, and 1 560 cm^{-1}; δ 2.41 (3 H), 3.78 (3 H), 3.79 (3 H), and 7.05—7.45 (5 H, m).

Sulphoxides (7) *by Oxidation of Sulphides.*—(a) *5,5-Dimethyl-3-(2-methylsulphinylphenylamino)cyclohex-2-en-1-one* (7a). A solution of the sulphide (8a) (0.50 g) and hydrogen peroxide (30%) in acetic acid (3 cm^3) was left at 20 °C for 24 h. The solvent was distilled off under reduced pressure and the residual oil was dissolved in dichloromethane (50 cm^3). This solution was washed with aqueous sodium carbonate and water. It was dried and the solvent was removed. The residue was crystallised to give the *sulphoxide* (7a) (0.30 g, 57%), m.p. 184—186 °C (from ethyl acetate) (Found: C, 64.9; H, 6.9; N, 5.0. $C_{15}H_{19}NO_2S$ requires C, 65.0; H, 6.9; N, 5.05%); $\nu_{max.}$ 3 200, 1 630, 1 600, and 1 580 cm^{-1}; δ 1.06 (3 H), 1.13 (3 H), 2.14 and 2.27 (2 H, AB system, *J* 15 Hz), 2.33 and 2.46 (2 H, AB system, *J* 16 Hz), 2.80 (3 H), 5.67 (1 H), 7.15—7.30 (1 H, m), 7.40—7.53 (3 H, m), and 8.60 (1 H, NH).

(b) The following sulphoxides were prepared from the corresponding sulphides in a similar manner:

(i) *3-(2-Methylsulphinylphenylamino)cyclohex-2-en-1-one* (7b) (85%), m.p. 147—149 °C (from ethyl acetate) (Found: C, 62.8; H, 6.1; N, 5.3. $C_{13}H_{15}NO_2S$ requires C, 62.65; H, 6.0; N, 5.6%); $\nu_{max.}$ 3 160, 1 620, 1 600, and 1 570 cm^{-1}; δ 1.83—2.10 (2 H, m), 2.30—2.42 (2 H, m), 2.46—2.56 (2 H, m), 2.78 (3 H), 5.61 (1 H), 7.12—7.27 (1 H, m), 7.38—7.50 (3 H, m), and 8.59 (1 H, NH).

(ii) *3-(2-Methylsulphinylphenylamino)-1,3-diphenylpropenone* (7c) (48%) [after column chromatography (silica; ethyl acetate–light petroleum 1 : 1)], m.p. 126—128 °C (from hexane) (Found: C, 72.8; H, 5.2; N, 3.75. $C_{22}H_{19}NO_2S$ requires C, 73.1; H, 5.3; N, 3.9%); $\nu_{max.}$ 1 590, 1 580, and 1 555 cm^{-1}; δ 2.93 (3 H), 6.25 (1 H), 6.52 (1 H, d, *J* 8 Hz), 7.05—7.15 (1 H, m), 7.19—7.26 (1 H, m), 7.28—7.53 (9 H, m), and 7.85—8.00 (3 H, m).

(iii) *Ethyl 3-(2-methylsulphinylphenylamino)-3-phenylpropenoate* (7d) (10%) [after column chromatography (silica; ethyl acetate–light petroleum 1 : 1)], m.p. 144—146 °C (from hexane) (Found: C, 65.6; H, 5.9; N, 4.2. $C_{18}H_{19}NO_3S$ requires C, 65.65; H, 5.8; N, 4.3%); $\nu_{max.}$ 1 650, 1 605, and 1 580 cm^{-1}; δ 1.25 (3 H, t, *J* 7 Hz), 2.90 (3 H), 4.19 (2 H, q, *J* 7 Hz), 5.18 (1 H), 6.36 (1 H, d, *J* 8 Hz), 7.00—7.60 (7 H, m), and 7.75—7.82 (1 H, m).

Sulphoxides (7) *derived from 2-Methylsulphinylaniline.*—(a) *Compound* (7a). Dimedone (0.90 g, 6.4 mmol), 2-methylsulphinylaniline [8] (1.00 g, 6.5 mmol) and toluene-4-sulphonic acid (100 mg) were heated in toluene (50 cm^3) with a Dean and Stark water separator attached to the apparatus. After 5 h the amine had been consumed. The organic solution was washed with aqueous sodium carbonate and water, dried, and evaporated. The sulphoxide (7a) (1.07 g, 60%) was isolated by crystallisation of the residue.

(b) The following were obtained by a similar procedure: (i) compound (7b) (49%); (ii) compound (7d) (19%).

(c) *Dimethyl 2-(2-methylsulphinylphenylamino)but-2-ene-1,4-dioate* (7e). A solution of dimethyl acetylenedicarboxylate (0.26 g, 1.8 mmol) and 2-methylsulphinylaniline (0.28 g, 1.8 mmol) in ethanol (5 cm^3) was kept at 20 °C for 4 h. The solvent was removed and the residue was extracted with hexane. The hexane solution was concentrated and cooled to give the *sulphoxide* (7e) (0.30 g, 56%) m.p. 108—110 °C (from hexane) (Found: C, 52.3; H, 5.1; N, 4.7. $C_{13}H_{15}NO_5S$ requires C, 52.5; H, 5.05; N, 4.7%); $\nu_{max.}$ 3 260, 1 730, 1 665, 1 615, and 1 585 cm^{-1}; δ 2.85 (3 H), 3.70 (3 H), 3.75 (3 H), 5.69 (1 H), 6.75 (1 H, d, *J* 8 Hz), 7.20—7.45 (2 H, m), and 7.75 (1 H, d, *J* 8 Hz).

Ylides by Cyclodehydration of Sulphoxides.—(a) *2,3-Dihydro-2,2,5-trimethyl-5H-phenothiazin-4(1H)-one* (6a). A solution of the sulphoxide (7a) (0.10 g, 0.36 mmol) in dry dichloromethane (25 cm^3) was stirred at −60 °C while trifluoroacetic anhydride (1 cm^3) in dichloromethane (7 cm^3) was added dropwise.* When the addition was complete the reaction mixture, which contained a solid precipitate, was stirred at −60 °C for a further 1 h, and then at room temperature for 12 h. The reaction mixture, which was now a clear solution, was stirred and cooled in ice and aqueous sodium hydroxide (10%, 5 cm^3) was added dropwise. The organic phase was then separated, washed, dried, and evaporated to leave a solid. Crystallisation gave the *ylide* (6a) (0.06 g, 64%) as pale yellow needles, m.p. 179—181 °C (from ethyl acetate) (Found: C, 69.4; H, 6.7; N, 5.3. $C_{15}H_{17}NOS$ requires C, 69.5; H, 6.6; N, 5.4%); $\nu_{max.}$ 1 575, 1 540, and 1 495 cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 309 (ε 5 900) and 371 (10 950) nm; δ_H ($CDCl_3$) 1.09 (6 H), 2.34 and 2.44 (2 H, AB system, *J* 15 Hz), 2.43 (3 H), 2.57 and 2.73 (2 H, AB system, *J* 16 Hz), 7.18—7.28 (1 H, m), and 7.32—7.63 (3 H, m); δ_H (CF_3CO_2H) 1.27 (6 H), 2.76 (2 H), 2.97 (2 H), 3.00 (3 H), 7.50—7.70 (2 H, m), and 7.75—7.90 (2 H, m); *m/e* 259 (M^+) and 244 ($M^+ - CH_3$, base). The ^{13}C n.m.r. spectrum is given in the Figure.

The filtrate, after removal of the crystalline ylide, was shown by t.l.c. to contain a second, orange-coloured component. This was isolated by column chromatography (alumina) and crystallised as orange plates (8 mg, 8%), m.p. 248—250 °C. This substance was identified as the phenothiazine (11a) by comparison with an authentic specimen prepared from dimedone and 2-aminobenzenethiol.[12]

(b) *2,3-Dihydro-5-methyl-5H-phenothiazin-4(1H)-one* (6b). A procedure similar to that in (a) was used to convert the sulphoxide (7b) (0.10 g) into the *ylide* (6b) (0.07 g, 75%), as yellow needles, m.p. 158—160 °C (from ethyl acetate) (Found: C, 67.3; H, 5.9; N, 5.9. $C_{13}H_{13}NOS$ requires C, 67.5; H, 5.6; N, 6.1%); $\nu_{max.}$ 1 570, 1 550, and 1 495 cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 308 (ε 5 800) and 370 (11 000) nm; δ 1.92—2.07 (2 H, m), 2.39 (3 H), 2.40—2.55 (2 H, m), 2.60—2.89 (2 H, m), 7.08—7.19 (1 H, m), and 7.26—7.43 (3 H, m); *m/e* 231 (M^+) and 216 ($M^+ - CH_3$, base).

A second minor component was obtained from the filtrate and was identified as 2,3-dihydro-10*H*-phenothiazin-4(1*H*)-

* The addition must be carried out slowly and at low temperatures to minimise the possibility of an uncontrolled reaction. The intermediate solid precipitates should be kept under solvent, and should not be isolated.

one (11b) (3 mg), orange plates, m.p. 205—207 °C (from ethanol), by comparison with a specimen prepared from cyclohexane-1,3-dione and 2-aminobenzenethiol.[12]

(c) *2-Benzoyl-1-methyl-3-phenyl-1H-1,4-benzothiazine* (6c). The ylide was prepared by the method described in (a) from the sulphoxide (7c) (0.2 g); it was isolated by column chromatography (silica; ethyl acetate–methanol 3 : 1) and crystallised (0.12 g, 63%) as yellow granules, m.p. 176—180 °C (decomp) (from hexane) (Found: C, 76.6; H, 5.0; N, 4.2. $C_{22}H_{17}NOS$ requires C, 77.0; H, 5.0; 4.1%); $\nu_{max.}$ 1 580 and 1 555 cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 300 (ε 9 500) and 400 (8 800) nm; δ 2.50 (3 H), 6.90—7.10 (6 H, m), 7.21—7.33 (3 H, m), 7.43—7.52 (3 H, m), 7.55—7.65 (1 H, m), and 7.67—7.75 (1 H, m); *m/e* 343 (M^+) and 328 ($M^+ - CH_3$, base).

(d) *Ethyl 1-methyl-3-phenyl-1H-1,4-benzothiazine-2-carboxylate* (6d). The ylide was prepared by the method described in (a) from the sulphoxide (7d) (0.3 g); it was isolated by column chromatography (alumina; ethyl acetate–light petroleum 1 : 1) and crystallised (0.20 g, 71%) as pale yellow granules, m.p. 180—183 °C (decomp.) (from diethyl ether–light petroleum) (Found: C, 69.5; H, 6.1; N, 4.3. $C_{18}H_{17}NO_2S$ requires C, 69.45; H, 5.5; N, 4.5%); $\nu_{max.}$ 1 620 and 1 540 cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 289 (ε 19 000) and 375 (16 000) nm; δ 0.90 (3 H, t, *J* 7 Hz), 2.33 (3 H), 4.02 (2 H, q, *J* 7 Hz), and 7.10—8.00 (9 H, m); *m/e* 311 (M^+), 296 ($M^+ - CH_3$), and 78 (base).

(e) *Dimethyl 1-methyl-1H-1,4-benzothiazine-2,3-dicarboxylate* (6e). The ylide was prepared by the method described in (a) from the sulphoxide (7e) (0.31 g) and was isolated as a viscous oil (0.27 g, 92%) which, although pure by t.l.c., failed to crystallise; $\lambda_{max.}$ ($CHCl_3$) 307 (ε 2 800) and 375 (9 000) nm; δ 2.33 (3 H), 3.75 (3 H), 3.92 (3 H), and 7.00—7.90 (4 H, m); *m/e* 279 (M^+) and 264 ($M^+ - CH_3$, base). It was characterised as its *picrate*, m.p. 179 °C (from ethanol) (Found: C, 44.8; H, 3.3; N, 10.9. $C_{19}H_{16}N_4O_{11}S$ requires C, 44.9; H, 3.15; N, 11.0%).

Methylation of the Phenothiazinone (11a).—A slurry of the phenothiazinone (11a) (0.49 g, 2 mmol) in dry dimethylformamide (10 cm^3) was stirred rapidly at 20 °C and sodium hydride (0.2 g of 50% dispersion in oil) was added in portions. A bright red solution of the anion was produced. Iodomethane was then added dropwise until in slight excess: the red colour of the solution was replaced by a yellow colour. The reaction mixture was poured into ice–water and the product was extracted with dichloromethane (2 × 20 cm^3). The organic phase was washed, dried, and evaporated. Crystallisation of the residue gave the ylide (6a) (0.29 g, 56%), m.p. 179—181 °C, which was identical with the specimen prepared from the sulphoxide (7a).

Demethylation of Ylides.—A solution of the ylide (0.2 g) in concentrated hydrochloric acid (20 cm^3) was heated at 100 °C for 0.5 h. The solution was then cooled and made basic with aqueous sodium hydroxide. The precipitate so produced was then filtered off, washed with water, dried, and identified as indicated below.

In this way the ylide (6a) gave the phenothiazinone (11a) (95%), m.p. 260—262 °C, which was identified by comparison with an independently prepared specimen. The ylide (6b) gave the phenothiazinone (11b) (64%), m.p. 203—204 °C, which was identical with an authentic specimen. The ylide (6e) gave the 1,4-benzothiazine (12) (63%), m.p. 105—107 °C (lit.,[13] 110 °C).

We thank the British Council for financial support (to G. M. I.).

[1/1506 *Received*, 29*th September*, 1981]

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