Thermal Reactions of 2-Alkyl (or Aryl)-1-benzoyl-3,4-dihydro-1*H*-2-thionianaphthalen-1-ides with Compounds possessing an Acidic Hydrogen [1]

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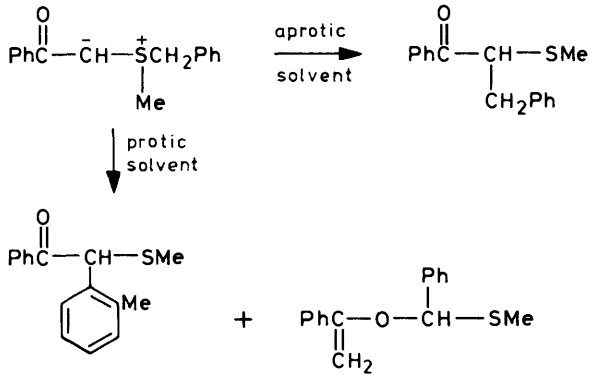
Thermal reactions of 2-alkyl-1-benzoyl-3,4-dihydro-1*H*-2-thionianaphthalen-1-ides (1a—d) in ethanol afforded alkyl *o*-vinylbenzyl sulphides (2a—d) along with ethyl benzoate, whereas that of the 2-phenyl congener (1e) gave *o*-(ethoxymethyl)phenethyl phenyl sulphide (3) together with the sulphide (2e). The ylides (1a and e) reacted with boiling water to afford the benzoates (9a and e). Reactions of the ylides (1a—e) with carboxylic acids and thiols gave the ring-opening products (11)—(17), cleaving the C(1)–S bond. Reactions of the ylide (1a) with succinimide or phthalimide yielded the ring-expansion product 2-phenyl-4,5-dihydro-3,5-benzoxathionine (19). In the reaction of the ylide (1a) with phenol, the product proportions changed with amounts of phenol. When 2 equiv. of phenol were used, the oxathionine (19) was obtained. However, the ring-opening products (22) and (23) were formed by using 10 or 100 equiv. of phenol.

These reactions are initiated by protonation on the ylidic carbanion to form the sulphonium salt (5). The conjugate base formed concurrently attacks a different reaction site, *viz.* a carbonyl carbon, C(1), or a methyl proton of the sulphonium salt (5), depending on its character.

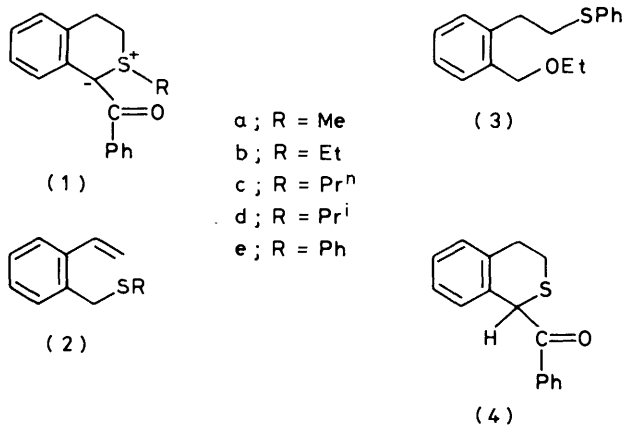
It is known that solvents alter the mechanisms of thermal reactions of sulphur ylides.[2] α-(*S*-Benzyl-*S*-methylsulphonio)-acetophenon-α-ide underwent a [1,2]-shift (Stevens-type rearrangement) in aprotic solvents to give 1,3-diphenyl-2-methylthiopropan-1-one, whereas it underwent a [2,3]-sigmatropic rearrangement in protic solvents (Scheme 1).



Scheme 1.

In our previous paper [3] we reported the thermal rearrangements of 1-benzoyl-1*H*-2-thionianaphthalen-1-ides and 1-benzoyl-3,4-dihydro-1*H*-2-thionianaphthalen-1-ides in aromatic hydrocarbons. This report deals with the thermal reactions of 2-alkyl- or 2-aryl-1-benzoyl-3,4-dihydro-1*H*-2-thionianaphthalen-1-ides in protic solvents and their reactions with reagents possessing an acidic hydrogen. It is well known that sulphur ylides react with acids to form sulphonium salts. However, little study has been made on further reactions of the sulphonium salts.[4,5]

First, we investigated the thermal reactions of the cyclic sulphur ylides in alcohols. Refluxing the ylide (1a) in ethanol for 3 h yielded methyl *o*-vinylbenzyl sulphide (2a) in 85.4% yield along with ethyl benzoate. The structure of the sulphide (2a) was deduced by the presence of three pairs of doublets for a vinyl group at δ 5.28, 5.63, and 7.09 in the ^{1}H n.m.r. spectrum, and confirmed by comparison with the spectral data



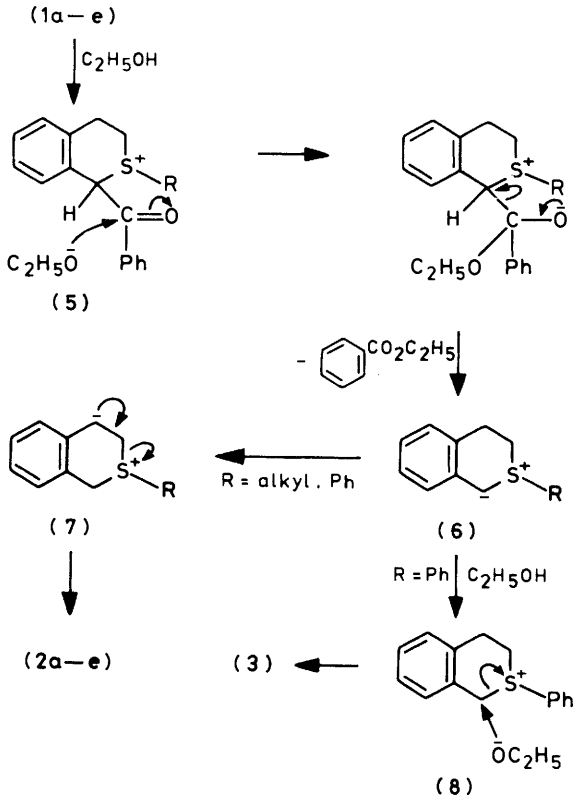
obtained for an authentic sample prepared from dimethyl sulphoxide (DMSO) and *o*-vinylphenylmagnesium chloride. Similarly, ylides (1b—d) formed sulphides (2b—d) and ethyl benzoate, whereas the 2-phenyl derivative (1e) formed *o*-(ethoxymethyl)phenethyl phenyl sulphide (3) in 12.1% yield together with phenyl *o*-vinylbenzyl sulphide (2e) and ethyl benzoate.

The structure of the sulphide (3) was determined on the basis of its spectral data. The high-resolution mass spectrum gave a molecular formula of $C_{17}H_{20}OS$ and the ^{1}H n.m.r. spectrum showed signals for an ethoxy group [δ 1.19 (t) and 3.49 (d)], two adjacent methylene groups [δ 2.90—3.25 (m)], and an isolated methylene group [δ 4.43 (s)]. Thermal reaction of the *S*-isopropyl congener (1d) in ethanol afforded 1-benzoylisothiochroman (4) in 10.5% yield together with the sulphide (2d). When methanol was used instead of ethanol, methyl benzoate was formed.

From these results, summarised in Table 1, the reactions would proceed through the pathways shown in Scheme 2. Ethanol protonates the C(1) carbanion of the ylides (1a—e) to form sulphonium salts (5), whose carbonyl carbon is attacked by ethoxide ion. A new ylide (6) formed concurrently with ethyl benzoate undergoes β-elimination through compound (7) to give the products (2a—e). In the case of the *S*-phenyl

Table 1. Thermal reactions of 2-alkyl (or aryl)-1-benzoyl-3,4-dihydro-1*H*-2-thionianaphthalen-1-ides (1a—e) in alcohols or water

Compd.	Solvent (*t*/h)	Product (% yield)
(1a)	C_2H_5OH (3)	(2a) (85.4)
(1b)	C_2H_5OH (3)	(2b) (83.5)
(1c)	C_2H_5OH (3)	(2c) (80.1)
(1d)	C_2H_5OH (3)	(2d) (69.8), (4) (10.5)
(1e)	C_2H_5OH (8)	(2e) (67.2), (3) (12.1)
(1a)	CH_3OH (3)	(2a) (80.0)
(1a)	t-C_4H_9OH (28)	(9a) (44.0)
(1e)	t-C_4H_9OH (45)	(9e) (26.0)
(1a)	Water (0.3)	(9a) (45.0)



Scheme 2.

derivative, the ylide (6) is partly protonated because the ylide (6; R = Ph) would be more stable than the ylide (6; R = alkyl). The resulting sulphonium salt (8) is attacked by ethoxide anion and C–S bond cleavage leads to the ring-opened product (3).[6]

Ylide (1a) was refluxed for 28 h in t-butyl alcohol to give *o*-(methylthioethyl)benzyl benzoate (9a) in 44.0% yield. The product was the same compound as that obtained from the reaction of the ylide (1a) in water. This finding showed that protonation of the ylide (1a) by t-butyl alcohol was difficult and that traces of water in t-butyl alcohol must have reacted with the ylide (1a). The plausible pathways are shown in Scheme 3. The sulphonium salt (5) is attacked at the carbonyl carbon by the hydroxide ion to generate the ylidic intermediate (6) and benzoic acid. They react together to form 2-methylisothiochromanium benzoate. Another possible pathway through epoxide (10) to the product (9a) was ruled out by the crossover experiment of (1f) and (1g). The mass spectrum

Table 2. Thermal reactions of 1-benzoyl-2-methyl-3,4-dihydro-1*H*-2-thionianaphthalen-1-ide (1a) with acids or thiols

RH (molar ratio)	Time (h)	Product (% yield)
CH_3CO_2H (1)	7	(11) (89.0)
$C_6H_5CO_2H$ (10)	9	(12) (81.8)
C_6H_5COSH (1)	2	(13) (94.1)
o-$H_2NC_6H_4CO_2H$ (2)	17	(14) (53.4)
o-$HOC_6H_4CO_2H$ (2)	18	(15) (66.0)
C_6H_5SH (1)	23	(16) (95.2)
$C_6H_5CH_2SH$ (1)	25	(17) (44.0)

Table 3. Thermal reactions of 1-benzoyl-2-methyl-3,4-dihydro-1*H*-2-thionianaphthalen-1-ide (1a) with phenol

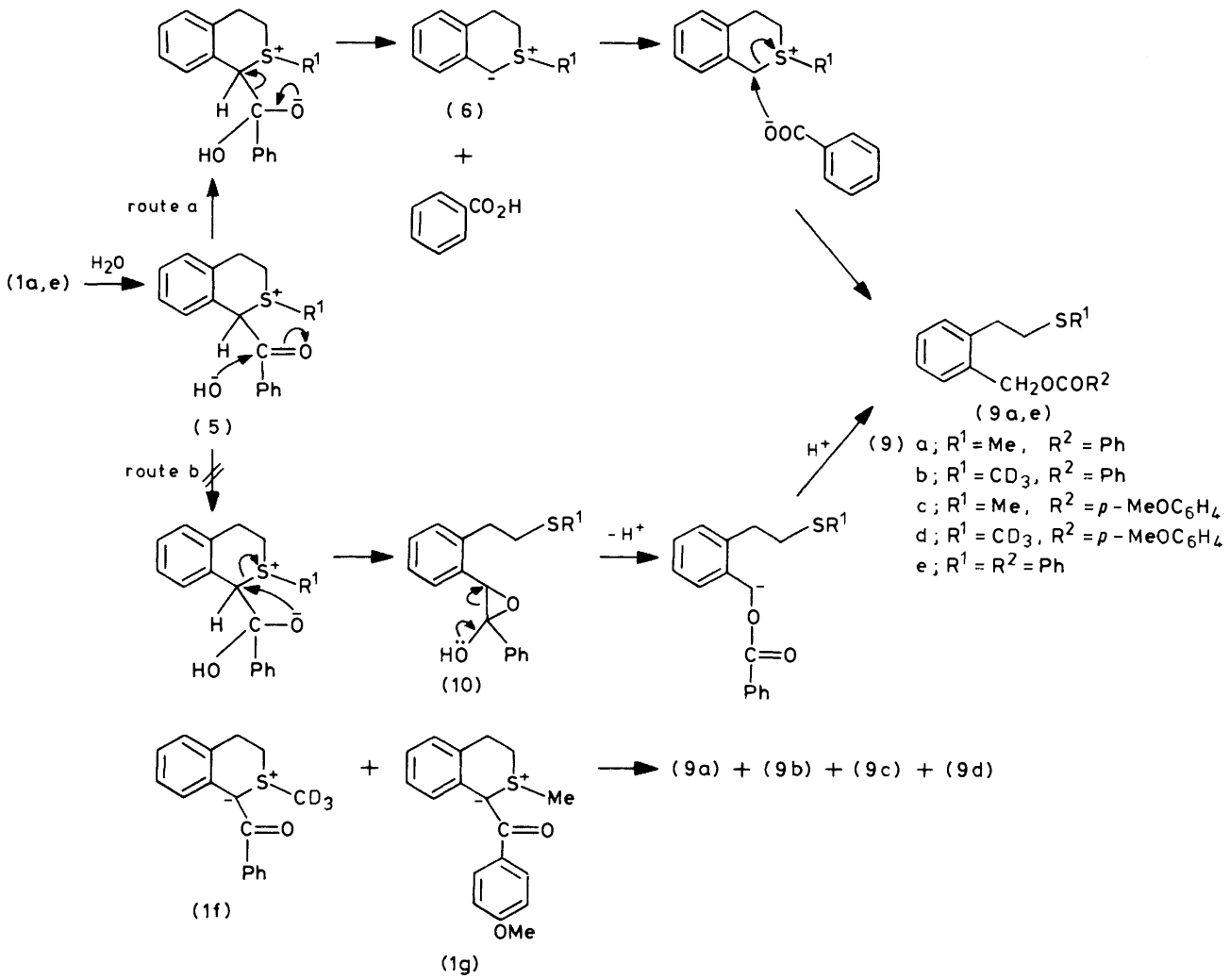
PhOH (molar ratio)	Product (% yield)		
	(19)	(22)	(23)
2	63.9	0	0
10	50.0	12.3	19.8
100	0	27.2	47.6

of the products showed molecular ion peaks at *m*/*z* 286 and 316 for the crossover products, (9a) and (9d), respectively. *S*-Phenyl ylide (1e) similarly reacted with boiling water to give (9e) in 26.0% yield.

The results described above are similar to that of the reaction of 1-isothiochromaniobis(ethoxycarbonyl)methanide in acetic acid. However, the isothiochroman congener did not undergo a similar reaction but underwent [1,2]-migration under the same conditions.[5] As the ylides (1a—e) are the endocyclic isothiochroman sulphonium ylides and do not cause [1,2]-rearrangement,[3] we expected interesting reactions of the ylides with compounds possessing an acidic hydrogen. The ylide (1a) reacted easily with acetic acid in refluxing benzene to afford α-acetoxy-*o*-(methylthioethyl)benzyl phenyl ketone (11) in 89.0% yield. The structure of the product (11) was determined by the spectral data: the ^1H n.m.r. spectrum showed the presence of a methylthio group [δ 2.12 (s)], an acetyl group [δ 2.18 (s)], and a methine proton [δ 7.10 (s)], and the i.r. spectrum exhibited an absorption at 1 745 cm^{-1} due to an ester group. Reaction of the ylide (1a) with benzenethiol gave α-phenylthio-*o*-(methylthioethyl)benzyl phenyl ketone (16) in 95.2% yield. Other carboxylic acids and thiols reacted similarly (Scheme 4). Results are shown in Table 2.

Reactions of the ylides with alcohols, carboxylic acids, and thiols were initiated by protonation followed by nucleophilic attack of the conjugate base at the benzoyl carbon or C(1). If the conjugate bases are poor nucleophiles, new reactions would occur. Reactions of (1a) with imides gave 2-phenyl-6,7-dihydro-3,5-benzoxathionine (19) in high yield. The structure was deduced from the spectral data and confirmed by chemical reactions. The oxathionine (19) was hydrolysed with dilute sulphuric acid to give 2-phenyl-4,5-dihydro-3-benzothiepine (20), which was oxidised with *m*-chloroperbenzoic acid to yield the sulphone (21). The mechanism of formation of the oxathionine (19) is shown in Scheme 5. The first intermediate (5) is deprotonated by the imide anion to form an exocyclic methanide (18). [2,3]-Sigmatropic rearrangement of the ylide (18) then leads to the ring-expansion product (19). The *S*-ethyl ylide (1b) and *S*-phenyl derivative (1e) did not form ring-expansion products. These reactions show that the methanide (18) is the key intermediate for the ring expansion.

Next, we examined the reactions with phenols, whose acidity is between those of carboxylic acids and alcohols, and whose conjugate bases, phenoxide ions, are nucleophilic. Reactions of (1a) with phenol in refluxing benzene gave very



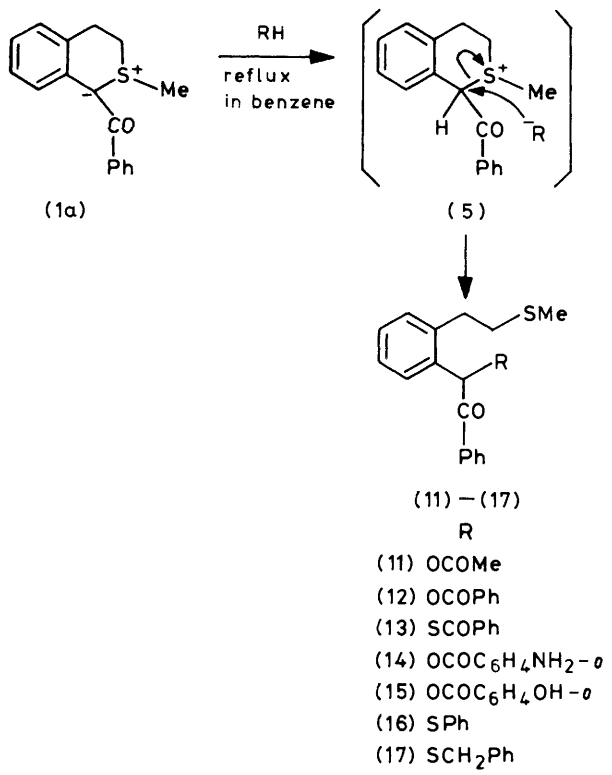
Scheme 3.

interesting results in which the proportions of product (19), (22), and (23) varied with the amount of phenol used. The mechanism of the reaction is shown in Scheme 6. The sulphonium salt (5) is initially formed by protonation with phenol as a common intermediate. If the methyl group is deprotonated by phenoxide ion, the reaction proceeds through (18) to the product (19) (path a). The phenoxide ion may also attack at C(1) of (5) to form the ring-opened product (22) (path b). The third pathway (path c) involves nucleophilic attack of phenoxide ion at the carbonyl carbon followed by debenzoylation *via* phenyl benzoate and formation of an ylide (6; R = Me). The ylide (6) then reacts with phenol to yield a ring-opened product (23). The relation of quantity of phenol to product ratio can be explained by hydrogen bonding between phenoxide ion and phenol. When 2 equiv. of phenol were used, phenoxide ion reacted with the sulphonium salt (5) as a base and the reaction proceeds through path a. The greater the proportion of phenol used, the easier it becomes for phenoxide ion to form hydrogen bonds with the phenol. Consequently, the possibility of hydrogen abstraction becomes less by using 10 or 100 equiv. of phenol; then, phenoxide ion acts as a nucleophile. The reaction thus progresses *via* path b or c. As phenoxide ion nucleophilically attacks the sulphonium salt (5) in the solvated form, phenoxide ion in amounts equal to 100 equiv. of phenol attacks predominantly at the benzoyl carbon, which is a less hindered reaction site than C(1).

In order to examine the substituent effect of phenols on the [2,3]-sigmatropic ring-expansion reaction the ylide (1a) was allowed to react with 2 equiv. of phenols having *o*- or *p*-substituents. The results are shown in Table 4. In the reaction of (1a) with *o*-nitrophenol, hydrogen abstraction was reduced by an electron-withdrawing group (*o*-NO_2) and the intermediate (5) underwent nucleophilic attack by the *o*-nitrophenoxide ion at C(1) (path b) to form [α-(*o*-nitrophenoxy)-*o*-methylthioethyl]benzyl phenyl ketone (24). On the other hand, an electron-releasing group in the *ortho*-position of the phenoxide ion activated the substrate to hydrogen abstraction to afford the ring-expanded product (19) as the sole product. We could not explain clearly the reactions with *o*- and *p*-aminophenols. The reaction may be complicated since *o*- and *p*-aminophenoxide ion can react as ambident nucleophiles.

Experimental

M.p.s were determined on a Yanagimoto micro melting point apparatus and are uncorrected. I.r. spectra of solid (KBr) and liquids (film) were recorded on a JASCO A-1 spectrophotometer. ^{1}H N.m.r. spectra were obtained for solutions in $CDCl_3$ on a Hitachi R-20B spectrometer with tetramethylsilane as internal standard, unless indicated otherwise. ^{13}C Spectra were run on a JEOL FX-90Q spectrometer. Mass spectra were obtained using a JEOL JMS-D 300 spectrometer



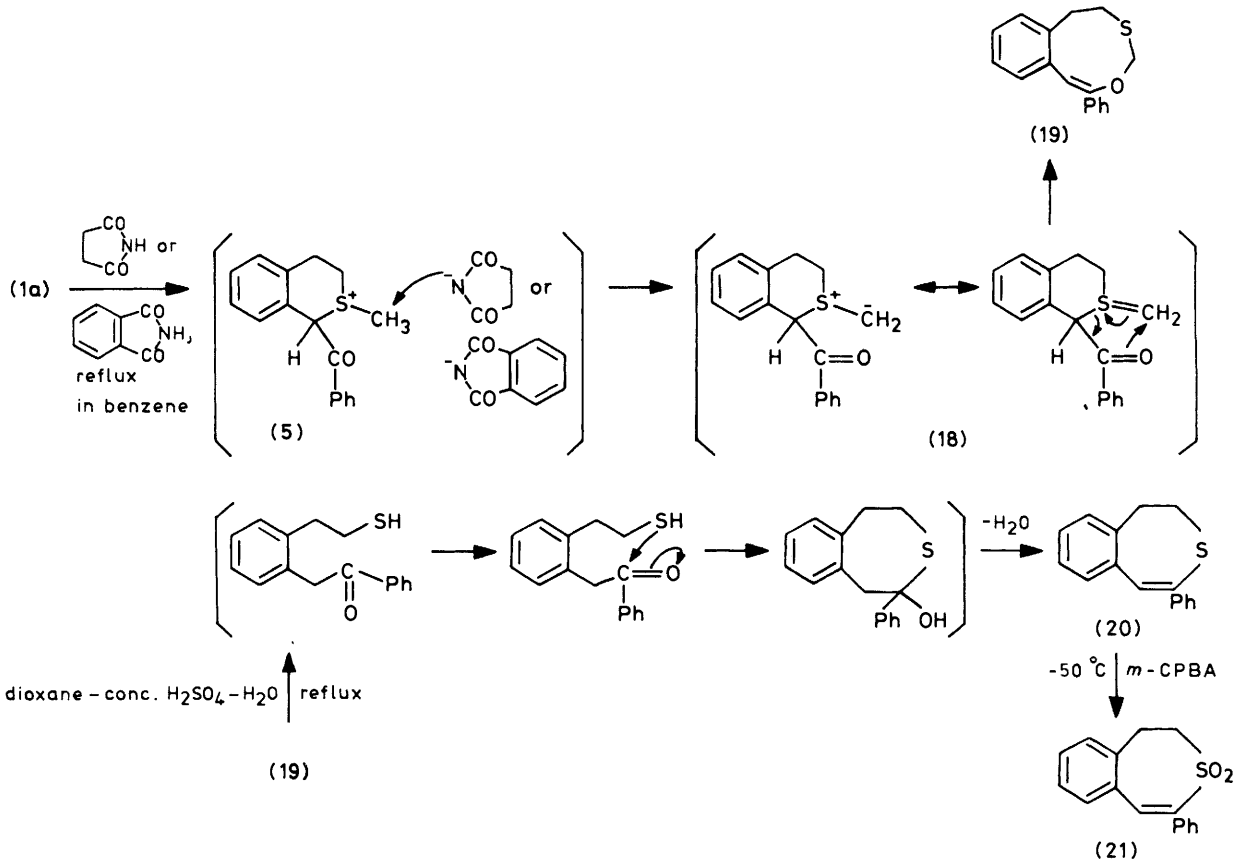
Scheme 4.

with a direct-insertion probe, at 70 eV. All exact mass determinations were obtained on the JMA 2000 on-line system. C.i.m.s. refers to chemical ionisation mass spectrometry.

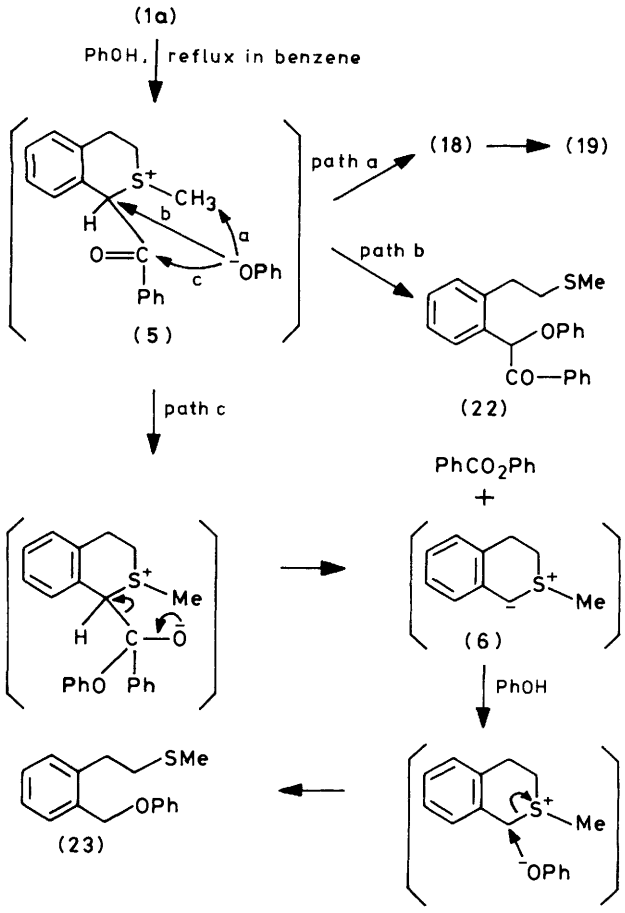
General Procedure for the Thermal Reactions of 2-Alkyl-1-benzoyl-3,4-dihydro-1H-2-thionianaphthalen-1-ides (1a—d) *in Ethanol or Methanol.*—An ylide (1) (0.1 g) was dissolved in ethanol or methanol (20 ml) and refluxed for 3 h under nitrogen. The solvent was removed under reduced pressure. The residual oil was separated by preparative t.l.c. (p.l.c.) on silica gel using hexane–chloroform (1 : 1) as developer to give the corresponding alkyl *o*-vinylbenzyl sulphide (2) as a yellow oil, and ethyl benzoate or methyl benzoate. Yields and spectral data are shown in Tables 1 and 5, respectively.

Thermal Reaction of 1-Benzoyl-2-phenyl-3,4-dihydro-1H-2-thionianaphalen-1-ide (1e) *in Ethanol.*—Ylide (1e) (0.1 g) was dissolved in ethanol (20 ml) and refluxed for 8 h under nitrogen. The solvent was removed under reduced pressure. The residual oil was separated by p.l.c. on silica gel using hexane–ethyl acetate (5 : 1) to give *phenyl o-vinylbenzyl sulphide* (2e) as a yellow oil, ethyl benzoate, and o-(*ethoxymethyl*)*phenethyl phenyl sulphide* (3) as an oil (10 mg, 12.1%), δ 1.19 (3 H, t, *J* 7.2 Hz, CH_3), 2.90—3.25 (4 H, m, $CH_2 \times 2$), 3.49 (2 H, q, *J* 7.2 Hz, CH_2), 4.43 (2 H, s, CH_2), and 7.10—7.53 (9 H, m, ArH) (Found: M^+, 272.1242. $C_{17}H_{20}OS$ requires *M*, 272.1241).

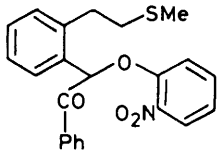
Methyl o-Vinylbenzyl Sulphide (2a).—*o*-Vinylphenylmagnesium chloride was prepared from *o*-chlorostyrene (5.0 g, 36.1 mmol), magnesium (0.88 g, 36.1 mg-atom), and bromoethane (0.3 ml) as an initiator in dry tetrahydrofuran (THF) (20 ml).



Scheme 5.



Scheme 6.



(24)

DMSO (1.41 g, 18.1 mmol) was gradually added to the ice-cooled Grignard reagent. The reaction mixture was stirred for 3 h at 30 °C and then decomposed with 5% aqueous hydrochloric acid (30 ml). The mixture was diluted with water (100 ml) and extracted with diethyl ether. The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was separated by column chromatography and p.l.c. on silica gel using hexane–ethyl acetate (10 : 1) and hexane–chloroform (2 : 1), respectively, to give a yellow oil (240 mg, 8.1%).

Thermal Reaction of S-*Methyl Ylide* (1a) *in t-Butyl Alcohol.*—Ylide (1a) (0.1 g) was dissolved in t-butyl alcohol (15 ml) and the solution was refluxed for 28 h under nitrogen. The solvent was evaporated under reduced pressure. The residue was separated by p.l.c. on silica gel using hexane–chloroform (1 : 1) to give o-(*methylthioethyl*)*benzyl benzoate* (8a) (47 mg, 44.0%) as an oil, $\nu_{max.}$ 1 715 cm^{-1} (CO); δ 2.08 (3 H, s, CH_3), 2.55—3.35 (4 H, m, $CH_2 \times 2$), 5.40 (2 H, s, CH_2), and 7.20—7.60 (7 H, m, ArH) (Found: M^+, 286.1008. $C_{22}H_{20}O_2S$ requires M, 286.1010).

Table 4. Thermal reactions of 1-benzoyl-2-methyl-3,4-dihydro-1*H*-2-thionianaphthalen-1-ide (1a) with substituted phenols

Phenol R	(RC_6H_4OH) (molar ratio)	Time (h)	Product (19) (Yield/%)
o-NO_2	(2)	43	21.3 [a]
o-Me	(2)	68	75.5
p-Me	(2)	37	52.7
o-OMe	(2)	39	83.2
	(10)	41	89.7
p-OMe	(2)	60	49.3
o-NH_2	(2)	24	14.5
p-NH_2	(2)	22	13.1
o,*m*,*p*-Me_3	(2)	65	80.0

[a] A ring-opened product (24) was obtained in 16.5% yield.

Thermal Reaction of S-*Phenyl Ylide* (1e) *in t-Butyl Alcohol.*—A solution of the ylide (1e) (0.102 g, 0.309 mmol) in t-butyl alcohol (15 ml) was refluxed for 45 h under nitrogen and the solvent was evaporated under reduced pressure. The residue was separated by p.l.c. on silica gel using hexane–ethyl acetate (15 : 1) to give o-(*phenylthioethyl*)*benzyl benzoate* (9e) as an oil, $\nu_{max.}$ 1 715 cm^{-1} (CO); δ 2.90—3.40 (4 H, m, $CH_2 \times 2$), 5.35 (2 H, s, CH_2), 7.10—7.65 (12 H, m, ArH), and 7.95—8.28 (2 H, m, ArH) (Found: M^+, 348.1156. $C_{22}H_{20}O_2S$ requires M, 348.1153).

Thermal Reaction of S-*Methyl Ylide* (1a) *in Water.*—A suspension of the ylide (1a) in water was refluxed for 20 min under nitrogen. Water was then evaporated off under reduced pressure. The residue was purified by p.l.c. on silica gel using hexane–ethyl acetate (7 : 1) to give the product (9a) (48 mg, 45.0%) as an oil.

Thermal Reactions of 1-*Benzoyl*-2-*trideuteriomethyl*-3,4-*dihydro*-1H-2-*thionianaphthalen*-1-*ide* (1f) and 1-(p-*Methoxybenzoyl*)-2-*methyl*-3,4-*dihydro*-1H-2-*thionianaphthalen*-1-*ide* (1g) *in Water.*—A mixture of the ylides (1f) (32 mg) and (1g) (30 mg) in water (30 ml) was refluxed for 30 min. After being cooled, the reaction mixture was extracted with dichloromethane. The extracts were dried ($MgSO_4$) and evaporated. The mass spectrum of the residue showed four molecular-ion peaks at *m*/*z* 286, 289, 316, and 319 of (9a), (9b), (9c), and (9d), respectively.

Thermal Reactions of S-*Methyl Ylide* (1a) *with Carboxylic Acids or Thiols.*—To a solution of the ylide (1a) (0.1 g) in dry benzene (20 ml) was added a carboxylic acid or a thiol. The reaction mixture was heated under nitrogen. After being cooled the mixture was washed with 10% aqueous sodium hydroxide to remove an excess of the carboxylic acid or thiol, and then dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was separated by p.l.c. on silica gel using hexane–ethyl acetate (5 : 1). Products (11)—(17) and their yields are shown in Table 2, and their spectral data are listed in Table 6.

Thermal Reactions of S-*Methyl Ylide* (1a) *with Succinimide.*—Succinimide (110 mg, 1.106 mmol) was added to a solution of the ylide (1a) (99 mg, 0.369 mmol) in dry benzene (20 ml). The resulting mixture was refluxed for 67 h and concentrated under reduced pressure. The residue was separated by p.l.c. on silica gel using hexane–ethyl acetate (7 : 1) to give 2-*phenyl*-6,7-*dihydro*-3,5-*benzoxathionine* (19) (74 mg, 74.7%) as prisms (from dichloromethane–hexane), m.p. 107 °C; δ_H 2.74—3.30 (4 H, m, $CH_2 \times 2$), 4.84 (2 H, s, CH_2), 6.45 (1 H, s, CH), and 7.10—7.80 (9 H, m, ArH); δ_C 32.234 [C(7)], 36.668 [C(6)],

Table 5. Spectral data of alkyl (or phenyl) *o*-vinylbenzyl sulphides (2a—e)

Compd.	Formula	High-resolution m.s. Calc.	Found	^{1}H n.m.r. ($CDCl_3$) δ
(2a)	$C_{10}H_{12}S$	164.0637	164.0634	1.94 (3 H, s, CH_3), 3.67 (2 H, s, CH_2), 5.28 (1 H, dd, *J* 1.4, 11.1 Hz, Ar$\diagup\!\!=\!\!\diagdown$H), 5.63 (1 H, dd, *J* 1.4, 17.4 Hz, $_{Ar}\diagup\!\!=\!\!\diagup^{H}$), 7.09 (1 H, dd, *J* 11.1, 17.4 Hz, Ar*H*C=), 7.10—7.60 (4 H, m, ArH)
(2b)	$C_{11}H_{14}S$	178.0789	178.0786	1.23 (3 H, t, *J* 7.2 Hz, CH_3), 2.48 (2 H, q, *J* 7.2 Hz, CH_2), 3.77 (2 H, s, CH_2), 5.31 (1 H, dd, *J* 1.4, 11.1 Hz, Ar$\diagup\!\!=\!\!\diagdown$H), 5.66 (1 H, dd, *J* 1.4, 17.4 Hz, $_{Ar}\diagup\!\!=\!\!\diagup^{H}$), 7.09 (1 H, dd, *J* 11.1, 17.4 Hz, Ar*H*C=), 7.16—7.70 (4 H, m, ArH)
(2c)	$C_{12}H_{16}S$	192.0976	192.0976	0.95 (3 H, t, *J* 7.2 Hz, CH_3), 1.25—1.95 (2 H, m, CH_2), 2.45 (2 H, t, *J* 7.8 Hz, CH_2), 5.32 (1 H, dd, *J* 1.4, 11.1 Hz, Ar$\diagup\!\!=\!\!\diagdown$H), 5.66 (1 H, dd, *J* 1.4, 17.4 Hz, $_{Ar}\diagup\!\!=\!\!\diagup^{H}$), 7.09 (1 H, dd, *J* 11.1, 17.4 Hz, Ar*H*C=), 7.16—7.70 (4 H, m, ArH)
(2d)	$C_{12}H_{16}S$	192.0967	192.0966	1.27 (6 H, d, *J* 6.0 Hz, CH_3 × 2), 2.65—3.15 (1 H, m, CH), 3.79 (2 H, s, CH_2), 5.31 (1 H, dd, *J* 1.4, 11.1 Hz, Ar$\diagup\!\!=\!\!\diagdown$H), 5.67 (1 H, dd, *J* 1.4, 17.4 Hz, $_{Ar}\diagup\!\!=\!\!\diagup^{H}$), 7.09 (1 H, dd, *J* 11.1, 17.4 Hz, Ar*H*C=), 7.13—7.68 (4 H, m, ArH)
(2e)	$C_{15}H_{14}S$	226.0815	226.0815	4.14 (2 H, s, CH_2), 5.32 (1 H, dd, *J* 1.4, 11.1 Hz, Ar$\diagup\!\!=\!\!\diagdown$H), 5.66 (1 H, dd, *J* 1.4, 17.4 Hz, $_{Ar}\diagup\!\!=\!\!\diagup^{H}$), 7.09 (1 H, dd, *J* 11.1, 17.4 Hz, Ar*H*C=), 7.12—7.70 (4 H, m, ArH)

Table 6. Spectral data of products (11)—(17)

Compd.	Formula	High-resolution m.s. Calc.	Found	$\nu_{max.}$/cm^{-1} (neat)	^{1}H n.m.r. ($CDCl_3$) δ
(11)	$C_{19}H_{20}O_3S$	328.1118	328.1117	1 700 (PhCOC) 1 745 ($MeCO_2$)	2.12 (3 H, s, CH_3), 2.18 (3 H, s, $COCH_3$), 2.50—3.30 (4 H, m, CH_2 × 2), 7.10 (1 H, s, CH), 7.15—7.55 (7 H, m, ArH), 7.77—7.98 (2 H, m, ArH)
(12)	$C_{24}H_{22}O_3S$	390.1268	390.1266	1 700 (PhCOC) 1 725 ($PhCO_2$)	2.03 (3 H, s, CH_3), 2.45—3.35 (4 H, m, CH_2 × 2), 7.15—7.60 (11 H, m, CH, ArH), 7.82—8.20 (4 H, m, ArH)
(13)	$C_{24}H_{22}O_2S_2$	406.1076	406.1078	1 655 (PhCOS) 1 695 (PhCOC)	2.08 (3 H, s, CH_3), 2.57—3.40 (4 H, m, CH_2 × 2), 6.75 (1 H, s, CH), 7.10—7.70 (10 H, m, ArH), 7.85—8.20 (4 H, m, ArH)
(14)	$C_{24}H_{23}NO_3S$	405.1411	405.1413	1 690 (PhCOC) 1 710sh ($ArCO_2$) 3 380, 3 500 (NH_2)	2.02 (3 H, s, CH_3), 2.50—3.40 (4 H, m, CH_2 × 2), 5.63 (2 H, br s, NH_2), 6.35—6.70 (2 H, m, ArH), 7.00—7.60 (9 H, m, CH and ArH), 7.75—8.00 (3 H, m, ArH)
(15)	$C_{24}H_{22}O_4S$	406.1211	406.1208	1 700 (PhCOC) 1 720 ($ArCO_2$) 3 200 (OH)	2.05 (3 H, s, CH_3), 2.56—3.41 (4 H, m, CH_2 × 2), 6.68—7.81 (10 H, m, ArH), 7.81—8.20 (3 H, m, ArH), 10.42 (1 H, br s, OH)
(16)	$C_{23}H_{22}OS_2$	378.1099	378.1098	1 690 (PhCOC)	2.01 (3 H, s, CH_3), 1.98—3.20 (4 H, m, CH_2 × 2), 6.09 (1 H, s, CH), 7.10—7.60 (12 H, m, ArH), 7.75—8.00 (2 H, m, ArH)
(17)	$C_{24}H_{24}OS_2$	392.1257	392.1258	1 680 (PhCOC)	1.97 (3 H, s, CH_3), 2.49—2.95 (4 H, m, CH_2 × 2), 3.74 (2 H, d, *J* 1.5 Hz, CH_2), 5.44 (1 H, s, CH), 7.10—7.80 (14 H, m, ArH)

72.316 [C(4)], 113.904 [C(1)], 158.082 [C(2)], 126.356, 126.722, 127.307, 128.500, 128.695, 129.233, 129.397 (ArC), 135.439, 136.102, and 139.611 p.p.m. [C(7a, 11a, and 1')] (Found: C, 76.05; H, 5.95. $C_{17}H_{16}OS$ requires C, 76.08; H, 6.01%); *m*/*z* 268 (M^+).

Thermal Reactions of S-*Methyl Ylide* (1a) *with Phthalimide.*—Phthalimide (169 mg, 1.15 mmol) was added to a solution of the ylide (1a) (103 mg, 0.384 mmol) in dry benzene (20 ml). The reaction mixture was refluxed for 72 h under nitrogen and the solvent was removed under reduced pressure. The residue was separated by p.l.c. on silica gel using hexane–ethyl acetate (7 : 1) to give the benzoxothionine (19) (72 mg, 69.9%).

Hydrolysis of the Benzoxathionine (19).—Water (2.2 ml) and conc. sulphuric acid (0.6 ml) were added to a solution of compound (19) (240 mg, 0.894 mmol) in dioxane (20 ml). The mixture was refluxed for 26 h under nitrogen. After being cooled the mixture was diluted with water (50 ml) and extracted with chloroform. The extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by p.l.c. on silica gel using hexane–ethyl acetate (35 : 1) to give *2-phenyl-4,5-dihydro-3-benzothiepine* (20) (56 mg, 26.3%) as a yellow oil, δ 3.28 (4 H, s, CH_2 × 2), 6.82 (1 H, s, CH), and 7.02—7.70 (9 H, m, ArH) (Found: M^+, 238.0834. $C_{16}H_{14}S$ requires *M*, 238.0832).

2-Phenyl-4,5-dihydro-3-benzothiepine 3,3-Dioxide (21).—A solution of the benzothiepine (20) (55 mg, 0.231 mmol) in dry dichloromethane (10 ml) was cooled to −50 °C. *m*-Chloroperbenzoic acid (119 mg, 0.692 mmol) was added to the mixture which was then stirred at −50 °C. 10% Aqueous sodium hydrogen carbonate (30 ml) was added to the mixture. The organic layer was separated and the aqueous layer was extrac-

ted with dichloromethane. The combined extracts and mother liquor were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was recrystallised from ethanol to give the *dioxide* (21) as prisms (38 mg, 60.9%), m.p. 99—100 °C, $\nu_{max.}$ 1 120 and 1 289 cm^{-1} (SO_2); δ 3.25—3.70 (4 H, m, $CH_2 \times 2$), 6.87 (1 H, s, CH), and 7.15—8.00 (9 H, m, ArH) (Found: C, 71.0; H, 5.1. $C_{16}H_{14}O_2S$ requires C, 71.08; H, 5.22%); *m/z* 270 (M^+).

Reactions of S-*Methyl Ylide* (1a) *with Phenol.*—(a) Phenol (76 mg, 0.804 mmol) was added to a solution of the ylide (1a) (108 mg, 0.402 mmol) in dry benzene (20 ml) and the mixture was refluxed for 60 h under nitrogen. After being cooled the mixture was washed with 10% aqueous sodium hydroxide and dried ($MgSO_4$). The solvent was then evaporated under reduced pressure. The residue was purified by p.l.c. on silica gel using hexane–ethyl acetate (7 : 1) to give the benzoxathionine (19).

(b) Phenol (386 mg, 4.10 mmol) was added to a solution of the ylide (1a) (110 mg, 0.41 mmol) in benzene and the mixture was refluxed for 86 h. After being cooled the reaction mixture was washed with 10% aqueous sodium hydroxide, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was separated by p.l.c. on silica gel using hexane–ethyl acetate (15 : 1) to give *methyl* o-(α-*phenoxyphenacyl*)*phenethyl sulphide* (22) and a mixture of the benzoxathionine (19) and the ether (23).The product ratio of (19) to (23) [(19) : (23), 5 : 2] was determined by the intensities of the two singlet peaks of the methylene groups at δ 4.84 (OCH_2S) of (19) and at δ 5.03 ($ArCH_2O$) of (23). Compound (22) gave prisms (from dichloromethane–hexane), m.p. 75 °C; $\nu_{max.}$ 1 700 cm^{-1} (CO); δ 2.00 (3 H, s, CH_3), 2.50—3.30 (4 H, m, $CH_2 \times 2$), 6.63 (1 H, s, CH), 6.80—7.55 (12 H, m, ArH), and 7.90—8.15 (2 H, m, ArH) (Found: C, 76.95; H, 6.1. $C_{23}H_{22}O_2S$ requires C, 76.21; H, 6.12%); *m/z* 362 (M^+).

(c) A mixture of phenol (3.82 g, 40.6 mmol) and the ylide (1a) (109 mg, 0.41 mmol) in dry benzene (20 ml) was refluxed for 42 h under nitrogen. After being cooled the reaction mixture was washed with 10% aqueous sodium hydroxide, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was separated by p.l.c. on silica gel using hexane–ethyl acetate (7 : 1) to give compounds (22) and (23). Compound (23) was an oil, δ 2.02 (3 H, s, CH_3), 2.60—3.20 (4 H, m, $CH_2 \times 2$), 5.03 (2 H, s, CH_2), and 6.80—7.67 (9 H, m, ArH); c.i.m.s. *m/z* 259 (MH^+).

Reactions of S-*Methyl Ylide* (1a) *with* o- *or* p-*Substituted Phenols.*—An *o*- or *p*-substituted phenol was added to a solution of the ylide (1a) (0.1 g) in dry benzene and the reaction mixture was refluxed under nitrogen. The solvent was removed under reduced pressure and the residue was purified by p.l.c. on silica gel using hexane–ethyl acetate (7 : 1—10 : 1) to give the benzoxathionine (19). Reaction conditions and yields are shown in Table 4. Compound (24) was obtained from the reaction of the ylide (1a) with *o*-nitrophenol, and was obtained as needles (from diethyl ether–hexane), m.p. 60 °C; $\nu_{max.}$ 1 360, 1 530 (NO_2), and 1 700 cm^{-1} (CO); δ 2.03 (3 H, s, CH_3), 2.52—3.30 (4 H, m, $CH_2 \times 2$), 6.66 (1 H, s, CH), and 6.85—8.85 (13 H, m, ArH) (Found: C, 68.0; H, 5.15; N, 3.45. $C_{23}H_{21}NO_4S$ requires C, 67.79; H, 5.19; N, 3.44%).

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