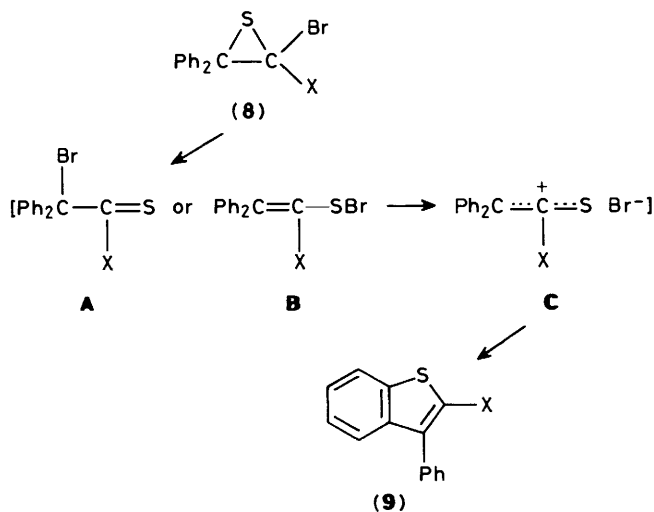


Table 3. Oxidations by (1a)

Substrate [ratio of (1a): substrate]	Conditions	Products (% yield ^a)
Ph ₂ C(OH)C(OH)Ph ₂ (1:1)	R.t., 12 h	Ph ₂ CO (98)
1,2-Epoxy cyclohexane (1:5.5)	R.t., 24 h	2-Hydroxycyclohexanone (59)
1,2-Diphenyloxirane (1:2.5)	R.t., 12 h	PhCHO (41) + Ph ₂ CHCHO (55)
Xylene-4,5-diamine (1:1)	R.t., 12 h	1,1'-Azo-2-amino-4,5-dimethylbenzene (30)
Ph ₂ C=CPh ₂ (1:1)	R.t., 12 h	Ph ₂ CO (6) ^b
PhCH=CH ₂ (1:excess)	hν, 75 min	PhCHO (68) ^b
Ph ₂ C=CH ₂ (1:excess)	hν, 5 h	Ph ₂ CO (81)
PhC≡CPh (1:5.5)	hν, 5 h	PhCOCOPh (30) ^b
1,3-Benzodioxole (1:8)	N ₂ , hν, 5 min	Pyrocatechol (75)

^a Yields of isolated products (except for PhCHO and Ph₂CHCHO), based on (1a). ^b Other products were also produced.⁸

have been reported.^{10,14-17} These reactions are intramolecular aromatic electrophilic substitutions and Seyferth¹⁰ suggested that the thiirane may react through a ring-opened intermediate of type A or B, both of which are subsequently converted into the reactive species C, which eventually cyclises to (9) (Scheme 5).

**Scheme 5.**

The reluctance of the spirothiirane (3b) to undergo the reaction to benzothiophene lends support to Seyferth's intermediate A, because a migration of the SO₂ group to C in (3b) would not be favoured. Among alternative mechanisms, a possibility involves direct attack from the aromatic *p*-methoxyphenyl ring at sulphur of the thiirane, with the intermediate formation of a benzothiete. Whatever the exact mechanism, it appears that strong activation is necessary for the ring closure and one phenyl group of the thiobenzophenone must bear a methoxy group. The reactions of *p*-methyl-*p*'-methoxythiobenzophenone (2c) gave, exclusively, 6-methoxy-3-(*p*-tolyl)benzothiophenes, in accordance with the better electron-donating character of the methoxy group as compared to the methyl group, although by necessity it is carbon from the *meta* position which attacks the electrophilic centre. With *p,p*'-dimethylthiobenzophenone the activation is not sufficient, so that its reaction with (1a) stops at the thiirane.

A reaction of the mixed ylide PhI⁺-C⁻(SO₂Tol)(SO₂Me) with thiobenzophenone (2b) resulted in the isolation of only one benzothiophene, (4b), having a 2-*p*-tolylsulphonyl group, in 5% yield. This selectivity may be related to the higher electronegativity of the MeSO₂ group in comparison to that of the TolSO₂ group (3.1 and 2.9 in Pauling's scale, respectively¹⁸), so

that MeSO₂ constitutes a better leaving group. The low yield of (4b) in this reaction is attributed to the low melting point of the ylide (90 °C) which is lower than the m.p. of (2b) (110 °C), so that extensive decomposition of the ylide took place before the melt was formed.

Formation of the alkene (5) must be the result of thermal desulphurisation of its thiirane precursor. Such transformations are well known¹⁹ and it may be expected that iodonium ylides which cannot be transformed eventually into benzothiophenes in their reaction with thiobenzophenones would give either thiiranes or alkenes (or both) depending on the reaction conditions.

A by-product in all these reactions is benzophenone coming from oxidation of the thiobenzophenone. This side reaction becomes important when the thiobenzophenone bears electron-withdrawing substituents. It is not known how this oxidation is effected but it seems appropriate at this point to examine briefly the oxidative properties of (1a), some of which have already been mentioned.⁷ The ability of (1a) to effect oxidations has been demonstrated to occur either thermally or photochemically. Thermal oxidations were actually performed without heating and in the absence of catalyst. Photochemical oxidations, with one exception, were performed in the presence of air. The results of these reactions have been collected in Table 3. It is noted that several arylalkenes and diarylacetylenes, in addition to products derived from cycloaddition of bis(phenylsulphonyl)methylene to the multiple bond, give also with (1a) oxidation products, both thermally or photochemically.⁸

These exploratory experiments show the potential of (1a) in effecting dehydrogenations, oxygenations, and cleavage of C-C or C-O bonds of various types. The diversity observed can hardly be accounted for by a common route. Since in dehydrogenations, either thermal or photochemical, bis(phenylsulphonyl)methane was always a major product, the possibility of carbene formation⁸ is ruled out; we suggest that a homolytic pathway is available here. The other types of oxidation are more involved and only in some of them was bis(phenylsulphonyl)methane formed. It seems that in addition to homolytic pathways, (1a) can also transfer in some way one of its oxygen atoms to the substrate. The fate of the carbanionic moiety of (1a) in these cases is not presently known.

Despite the lack of more information about these oxidations, some of them might be used to advantage, especially the conversion of 1,3-benzodioxole into pyrocatechol. The latter was obtained in good yield, surpassing an analogous oxidative removal of the methylene group by lead tetra-acetate.²⁰

Experimental

U.v. spectra were recorded with a Shimadzu 210A spectrophotometer, i.r. spectra (in Nujol) with a Perkin-Elmer 257 spectrometer, and ¹H n.m.r. spectra on a Varian A-60A

instrument. Mass spectra were obtained from a Hitachi-Perkin-Elmer RMU-6L single focussing mass spectrometer at 70 eV.

Starting Materials.—Thiobenzophenones and disulphones were known compounds. The preparation of the ylides (**1a–c**) has been described previously.⁸ The iodonium ylides (**1d–e**) have been obtained as follows. A cold solution of KOH (1.16 g, 20.7 mmoles) in MeOH (10 ml) was added to a stirred suspension of (MeSO₂)₂CH₂ (1 g, 5.8 mmol) in MeOH (10 ml) at –10 °C. The mixture was stirred at –10 °C for 60 min after which a solution of PhI(OAc)₂ (1.87 g, 5.8 mmol) in MeOH (10 ml) was added gradually to it, the temperature being kept at –5 °C; stirring was then continued for 60 min. The reaction mixture was then set aside at –10 °C for 12 h after which the precipitate was collected, washed with cold MeOH, and dried *in vacuo*, to afford phenyliodonium bis(methylsulphonyl)methylide (75%), m.p. 109–110 °C; ν_{\max} 1 295 and 1 115 cm⁻¹; δ_{H} (CD₃SOCD₃) 3.02 (s, 6 H), 7.50–7.72 (m, 3 H), and 7.87–8.17 (m, 2 H); m/z 374 (M^+ , 0.1%) (Found: C, 28.6; H, 3.0. C₉H₁₁IO₄S₂ requires C, 28.89; H, 2.96).

Using the disulphone of 1,3-dithiane under similar conditions 2-phenyliodonium-1,3-dithian-2-ide 1,1,3,3-tetraoxide (**1e**) was obtained (92%), m.p. 112–115 °C; ν_{\max} 1 300, 1 270, and 1 110 cm⁻¹; δ_{H} (CD₃SOCD₃) 2.02–2.45 (m, 2 H), 2.73–3.07 (m, 2 H), 3.20–3.67 (m, 2 H), 7.45–7.72 (m, 3 H), and 7.83–8.17 (m, 2 H); m/z no M^+ , 204 (C₆H₅I, 95%), and 184 (28). This ylide was insufficiently stable to provide a satisfactory elemental analysis.

Reactions of Iodonium Ylides (1) with Thiobenzophenones: General Procedure.—An intimate mixture of the ylide (1–2 mmol) with thiobenzophenone (4–5 mmol) containing Cu(acac)₂ (1 mg) was heated under nitrogen in an oil-bath for a few minutes at 110 °C (for details see Table 1). The reaction mixture was dissolved in chloroform and passed through a silica gel chromatographic column (eluant chloroform or methylene dichloride–light petroleum) and after phenyl iodide and unchanged thiobenzophenone the 2-aryl- (or methyl)sulphonyl-3-aryl-6-methoxybenzo[*b*]thiophenes of Table 1 were obtained; their properties appear in Table 2.

Under similar conditions the thiiranes (**3a, b**) and the alkene (**5**) were obtained.

3,3-Bis(phenylsulphonyl)-2,2-di-*p*-tolylthiirane (3a). This compound was obtained after heating (**1a**) and (**2a**) at 120 °C for 20 min. Some *p,p'*-dimethylbenzophenone was also eluted before (**3a**), which was obtained in 27% yield as white crystals, m.p. 251–253 °C (from chloroform–hexane); ν_{\max} 1 325 and 1 160 cm⁻¹; λ_{\max} (EtOH) 320 nm (log ϵ 4.24); δ_{H} (CDCl₃) 2.35 (s, 6 H) and 6.82–8.00 (m, 18 H); m/z 488 ($M - 32$) (Found: C, 64.7; H, 4.8. C₂₈H₂₄O₄S₃ requires C, 64.59; H, 4.65).

2,2-Bis(*p*-methoxyphenyl)-1,4,8-trithiaspiro[2.5]octane 4,4,8,8-tetraoxide (3b). This compound was obtained after heating (**1e**) and (**2c**) at 110 °C for 5 min. Some *p,p'*-dimethoxybenzophenone was eluted before (**3b**); it was obtained as white crystals (26%), m.p. 245–247 °C (from ethyl acetate–hexane); ν_{\max} 1 325 and 1 135 cm⁻¹; δ_{H} (CDCl₃) 2.47 (t, *J* 7 Hz, 2 H), 3.55 (t, *J* 7 Hz, 4 H), 3.83 (s, 6 H), 6.85 (d, *J* 9 Hz, 4 H), 7.30 (d, *J* 9 Hz, 4 H); m/z 408 ($M - 32$) (Found: C, 51.8; H, 4.7. C₁₉H₂₀O₆S₃ requires C, 51.80; H, 4.58).

1,1-Bis(methylsulphonyl)-2-(*p*-methylphenyl)-2-(*p*-methoxyphenyl)ethylene (5). This compound was obtained from the reaction of (**1d**) with (**2e**) (Table 1). It was eluted after (**4f**) as white crystals (20%), m.p. 260–262 °C (from ethyl acetate–hexane); ν_{\max} 1 600, 1 310, and 1 130 cm⁻¹; ν_{\max} (EtOH) 330 nm (log ϵ 4.03); δ_{H} (CDCl₃) 2.42 (s, 3 H), 3.38 (s, 3 H), 3.42 (s, 3 H), 3.87 (s, 3 H), and 6.96–7.33 (m, 8 H); m/z 380 (M^+) (Found: C, 57.1; H, 5.4. C₁₈H₂₀O₄S₂ requires C, 56.82; H, 5.30).

Oxidations.—Reaction conditions are given in Table 3. All thermal reactions were performed in methylene dichloride. The photochemical reactions were performed by irradiating the samples (in 10 ml of acetonitrile) in a Pyrex tube with a Philips 400 W low-pressure lamp. After removal of the solvent and volatiles, residues were subjected to column chromatography (using silica gel and either ethyl acetate–light petroleum or methylene dichloride–light petroleum). Phenyl iodide was always the first to be eluted.

Oxidation of 4,5-dimethylphenylenediamine. The oxidation product, *trans*-2,2'-diamino-4,4',5,5'-tetramethylazobenzene, was obtained as red crystals, m.p. 208–210 °C (from chloroform–hexane); ν_{\max} 3 440 cm⁻¹; m/z 268 (M^+ , 45%) (Found: C, 71.2; H, 7.4; N, 20.85. C₁₆H₂₀N₄ requires C, 71.61; H, 7.51; N, 20.88).

Oxidation of cyclohexene oxide. 2-Hydroxycyclohexanone was obtained, m.p. 108–111 °C (lit.,²¹ m.p. 113 °C).

Oxidation of *trans*-1,2-diphenyloxirane. An inseparable mixture of benzaldehyde and diphenylacetaldehyde was identified; the ratio of compounds was determined by ¹H n.m.r. spectroscopy, using authentic samples as standards.

Oxidation of 1,3-benzodioxole. Pyrocatechol was obtained, m.p. 104–106 °C, identical with an authentic sample.

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