# Reactivity of Vinyl Sulphonic Esters. Part XII.[1] Cyclisation of Arylsulphonylvinyl Sulphonates to Benzo[*b*]thiophen 1,1-Dioxides. A Novel 1,2-Sulphonyl Shift

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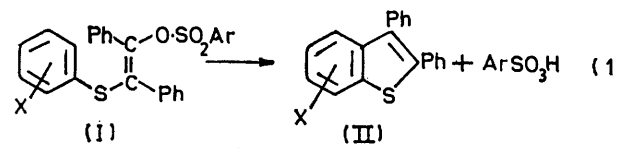
*trans*-2-Arylsulphonyl-1,2-diphenylvinyl *p*-bromobenzenesulphonates containing a methyl or a chloro-substituent in the aryl residue, on treatment with boron trifluoride, gave 2,3-diphenylbenzo[*b*]thiophen 1,1-dioxides. The position of the substituent in the products indicated that a rearrangement had occurred during the cyclisation. The formation of a spirothieten 1,1-dioxide intermediate and a subsequent 1,2-sulphonyl shift are proposed to rationalise the rearrangement.

We have reported[2,3] a study of the rearrangement observed in the cyclisation of *trans*-2-arylthio-1,2-diphenylvinyl arenesulphonates (I) to 2,3-diphenylbenzo[*b*]thiophens (II) [equation (1)]. The rearrangement was strictly related to the directing effect and position of the substituent in the arylthio-residue. We have subsequently shown that no rearrangement occurs in the cyclisations of 2-aryloxy-1,2-diphenylvinyl *p*-bromobenzenesulphonates to 2,3-diphenylbenzo[*b*]furans[4] and of 2-arylamino-1,2-diphenylvinyl *p*-bromobenzenesulphonates to 2,3-diphenylindoles.[1]




(1)

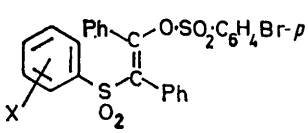
We now report[5] a study of the cyclisation of some *trans*-2-arylsulphonyl-1,2-diphenylvinyl *p*-bromobenzenesulphonates (III). We hoped to discover whether

[1] Part XI, G. Capozzi, G. Modena, and L. Ronzini, *J.C.S. Perkin I*, 1972, 1136.
[2] G. Melloni and G. Modena, *J.C.S. Perkin I*, 1972, 218.
[3] G. Capozzi, G. Melloni, and G. Modena, (*a*) *J. Org. Chem.*, 1970, **35**, 1217; (*b*) *J. Chem. Soc.* (*C*), 1970, 2621; (*c*) *ibid.*, p. 2625.
[4] G. Capozzi and G. Modena, *J.C.S. Perkin I*, 1972, 216.
[5] Preliminary account, G. Melloni and G. Modena, *Internat. J. Sulphur Chem., A*, 1971, **1**, 125.

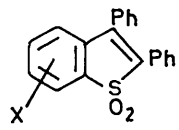
electrophilic ring closure was still possible with a strongly deactivated benzene ring, and whether a concomitant rearrangement took place; we also hoped to ascertain the effect of substituents on the process.

## RESULTS

The *trans*-2-arylsulphonyl-1,2-diphenylvinyl *p*-bromobenzenesulphonates (IIIa—e) were prepared by oxidation with peroxyacetic acid of the corresponding arylthio-derivatives (Ia—e), prepared as already described.[6]



(IIIa-e)



(IVa-f)

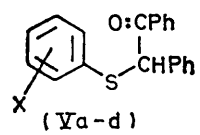
The cyclisation reaction was carried out by saturating dichloromethane solutions of the vinyl sulphonates (III) with gaseous boron trifluoride and keeping the mixtures for 8 days at room temperature. In most cases these conditions were not sufficient for completion of the reaction. They were chosen, however, with the purpose of comparing the yields of the cyclisation products from the variously substituted sulphonates (III). The products in all cases were 2,3-diphenylbenzo[*b*]thiophen 1,1-dioxide derivatives (IV). When reactions were incomplete, appropriate amounts of unchanged sulphonates (III) were recovered. The results are reported in Table 1.

TABLE 1

Cyclisation of vinyl sulphonates (III) to benzo[*b*]thiophen 1,1-dioxides (IV)

| Sulphonate (III) | Product (IV) | Yield (%) |
|---|---|---|
| a; X = H | a; X = H | 81 |
| b; X = *p*-Me | b; X = 6-Me | 95 |
| c; X = *m*-Me | c; X = 5-Me | 15 |
| | d; X = 7-Me | 7 |
| d; X = *p*-Cl | e; X = 6-Cl | 70 |
| e; X = *m*-Cl | f; X = 5-Cl | 9 |
| | g; X = 7-Cl | 0 |

The position of the substituent in the product (IV) was established by comparison with authentic 2,3-diphenylbenzo[*b*]thiophen 1,1-dioxides prepared by oxidation with peroxyacetic acid of the corresponding 2,3-diphenylbenzo[*b*]thiophens (II). For the synthesis of the latter two methods were used: the unsubstituted (IIa) and the 6-substituted (IIb) and (IIe) were prepared by cyclisation of the appropriate arylthiovinyl sulphonates (I) in the presence of boron trifluoride;[3a,b] the 5- and 7-substituted benzo[*b*]thiophens (IIc—d) and (IIf—g)



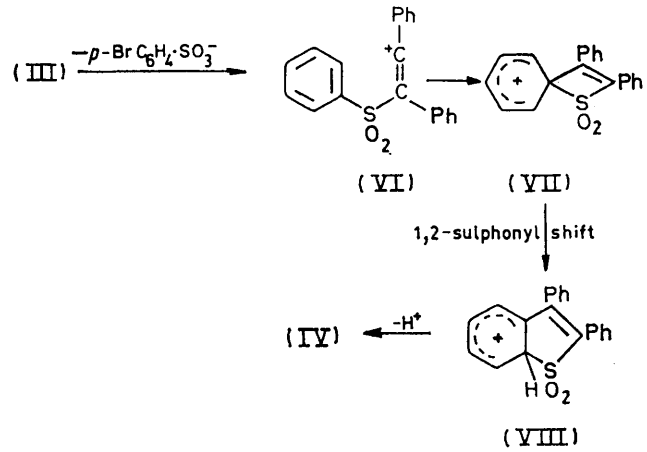
(Va-d)

were prepared by cyclisation of the appropriate 2-arylthio-2-phenylacetophenones (V) in polyphosphoric acid (PPA).[3b]

It was thus ascertained that in all the cyclisation products (IV) the position of the substituent X with respect to the sulphonyl group was different from that in the starting compounds (III).

## DISCUSSION

The results may be rationalised as depicted in the Scheme. Heterolysis of the C–O·$SO_2$Ar bond in (III)



SCHEME

leads to the formation of the vinyl cation (VI), which then attacks the 1-position of the arylsulphonyl residue to give the intermediate spirothieten 1,1-dioxide (VII). Ring expansion of species (VII) by a 1,2-sulphonyl shift leads to (VIII), which then suffers loss of a proton to give the final cyclisation product (IV), in which the substituent, initially *para* or *meta* to the sulphonyl group, is now *para* or *meta* to the newly formed C–C bond.

This mechanism is formally identical to that proposed for the cyclisation with rearrangement of the arylthio-derivatives (I). However, whereas in the case of the latter there was a delicate balance between cyclisation with and without rearrangement, *i.e.* between attack of the positive centre at the 1-position and attack at one of the two *ortho*-positions, in the present case the rearrangement occurred in all cases, regardless of the position and effect of the substituent in the arylsulphonyl residue. Nevertheless, the substituent clearly affects the yields of the cyclisation products.

A rationale of the tendency of the electrophilic centre to attack the 1-position in these cyclisation reactions may be found in the following factors: (*a*) the intramolecular character of the reaction, which makes available for electrophilic attack only the apical positions (1, 2, and 6); (*b*) the balance between the charge density in the 1-position and that in the *ortho*-positions, determined by the combined effects of the sulphur ($-SO_2-$ in the present case) and of the substituent, in the ring on which electrophilic attack occurs; and (*c*) the balance between the reversibility of the attack by the positive centre and the ability of the heteroatom to leave as a positively charged entity and/or to shift to the adjacent position.

In the system studied here the exclusive attack of the positive centre at the 1-position is probably due to the strong deactivating effect of the sulphonyl group on the *ortho*-positions, at which an electrophilic ring closure generally occurs; in the arylthio-system the sulphide sulphur atom has practically no effect in determining the position of attack. Moreover, the ability of an $RSO_2$ group to leave as a positively charged entity is illustrated by the well-known electrophilic desulphonation and desulphonylation reactions.[7] In particular, this work is analogous to the recently reported benzyl-desulphonation of arenesulphonic acids,[8] in which the sulphonic group is lost in consequence of the preferential attack of a carbonium ion at the position carrying this group.

Direct evidences of the intermediacy of the vinyl cation (VI) is lacking, but the course of the reaction and analogy with those previously reported support this hypothesis, which is also consistent with the observed small effect of β-substituents on the rate of formation of vinyl cations,[9] and hence with the fact that a β-sulphonyl group retards the reaction but does not prevent it.

TABLE 2

Physical constants and analytical data of arylthiovinyl *p*-bromobenzenesulphonates (I)

| Compound | X | M.p. (°C) | Found (%) C | H | S | Formula | Calc. (%) C | H | S |
|---|---|---|---|---|---|---|---|---|---|
| (Ia) | H | 132—134 [a,b] | | | | $C_{26}H_{19}BrO_3S_2$ | | | |
| (Ib) | *p*-Me | 146—147 [c] | 60·35 | 3·95 | 11·95 | $C_{27}H_{21}BrO_3S_2$ | 60·3 | 3·95 | 11·95 |
| (Ic) | *m*-Me | 131—132 [b] | 60·05 | 3·95 | 12·05 | $C_{27}H_{21}BrO_3S_2$ | 60·3 | 3·95 | 11·95 |
| (Id) | *p*-Cl | 132—133 [b] | 56·05 | 3·2 | 11·5 | $C_{26}H_{18}BrClO_3S_2$ | 56·0 | 3·25 | 11·5 |
| (Ie) | *m*-Cl | 147—148 [a,b] | | | | $C_{26}H_{18}BrClO_3S_2$ | | | |

[a] Described in ref. 6. [b] From methanol. [c] From hexane.

TABLE 3

Physical constants and analytical data of arylsulphonylvinyl *p*-bromobenzenesulphonates (III)

| Compound | X | M.p. (°C) | Found (%) C | H | S | Formula | Calc. (%) C | H | S |
|---|---|---|---|---|---|---|---|---|---|
| (IIIa) | H | 194—195 [a,b] | | | | $C_{26}H_{19}BrO_5S_2$ | | | |
| (IIIb) | *p*-Me | 165—166 [c] | 57·2 | 3·85 | 11·05 | $C_{27}H_{21}BrO_5S_2$ | 56·95 | 3·7 | 11·25 |
| (IIIc) | *m*-Me | 179—180 [b] | 56·9 | 3·65 | 11·35 | $C_{27}H_{21}BrO_5S_2$ | 56·95 | 3·7 | 11·25 |
| (IIId) | *p*-Cl | 205—206 [d] | 52·95 | 3·10 | 10·8 | $C_{26}H_{18}BrClO_5S_2$ | 52·95 | 3·05 | 10·9 |
| (IIIe) | *m*-Cl | 178—179 [c] | 53·15 | 3·3 | 11·0 | $C_{26}H_{18}BrClO_5S_2$ | 52·95 | 3·05 | 10·9 |

[a] Described in ref. 9. [b] From ethanol–acetone (4 : 1). [c] From methanol. [d] From ethyl acetate.

## EXPERIMENTAL

trans-2-*Arylthio*-1,2-*diphenylvinyl* p-*Bromobenzenesulphonates* (Ia—e).—These compounds were prepared by addition of the appropriate arenesulphenyl *p*-bromobenzenesulphonates to diphenylacetylene in dichloromethane (60—80% yields), as previously described [6,10] (see Table 2).

trans-2-*Arylsulphonyl*-1,2-*diphenylvinyl* p-*Bromobenzenesulphonates* (IIIa—e).—These compounds were prepared by oxidation with peroxyacetic acid of the corresponding arylthio-derivatives (Ia—e) (70—80% yields) (see Table 3).

*Cyclisation of Vinyl Sulphonates* (III) *to* 2,3-*Diphenylbenzo*[b]*thiophen* 1,1-*Dioxides* (IV) (*Table* 1).—A solution of compound (III) (10 mmol) in anhydrous dichloromethane (200 ml) was saturated with gaseous boron trifluoride at room temperature. The flask was stoppered, and the mixture was set aside for 8 days at room temperature. Aqueous 10% potassium fluoride was added, and the organic layer was separated, dried ($CaCl_2$), and evaporated to give a pale yellow residue, which was chromatographed on silica gel. Elution with light petroleum (b.p. 40—70°)–diethyl ether (9 : 1) gave the white crystalline benzo[*b*]-thiophen 1,1-dioxide derivative (IV). Further elution with diethyl ether gave, in the cases of incomplete reaction, unchanged starting material.

The two isomeric benzo[*b*]thiophen 1,1-dioxides formed in the cyclisation of vinyl sulphonate (IIIc) were separated by chromatography on silica gel. Elution with light petroleum (b.p. 40—70°)–diethyl ether (9 : 1) gave first the 7-methyl derivative (IVd) and then the 5-methyl derivative (IVc). Chromatography of the reaction mixture from the cyclisation of vinyl sulphonate (IIIe) afforded only the 5-chloro-derivative (IVf) and none of the expected 7-chloro-derivative (IVg). From this reaction a crystalline compound (60 mg) of unknown structure was also isolated, m.p. 182—183° [from petroleum (b.p. 75—120°)] [Found: C, 72·2; H, 4·25; Cl, 8·0; S, 7·2%; *M* (camphor method), 871. Calc. for $C_{54}H_{36}Cl_2O_5S_2$: C, 72·05; H, 4·05; Cl, 7·9; S, 7·1%; *M*, 899·9].

2,3-*Diphenylbenzo*[b]*thiophens* (IIa—g).—Benzo[*b*]thiophens (IIa, b, and e) were prepared by cyclisation of arylthiovinyl sulphonates (Ia, b, and d) in dichloromethane in the presence of boron trifluoride (50—70% yields), as previously described.[3b] Benzo[*b*]thiophens (IIc and d) were prepared by cyclisation of 2-arylthio-2-phenylacetophenones (Va and b) in polyphosphoric acid for 6—7 h at

[6] G. Capozzi, G. Melloni, and G. Modena, *J. Chem. Soc.* (*C*), 1970, 2617.

[7] H. Cerfontain, 'Mechanistic Aspects in Aromatic Sulfonation and Desulfonation,' Interscience, New York, 1968.

[8] I. Shimao, *Nippon Kagaku Zasshi*, 1967, **88**, 1314 (*Chem. Abs.*, 1968, **69**, 2241c).

[9] G. Capozzi, G. Modena, and U. Tonellato, *J. Chem. Soc.* (*B*), 1971, 1700, and references cited therein.

[10] G. Capozzi, G. Melloni, and G. Modena, *J. Chem. Soc.* (*C*), 1971, 3018.

TABLE 4

Physical constants and analytical data of 2,3-diphenylbenzo[*b*]thiophens (II)

| Compound | X | M.p. (°C) | Found (%) C | H | S | Formula | Calc. (%) C | H | S |
|---|---|---|---|---|---|---|---|---|---|
| (IIa) | H | 113—114 [a] | | | | $C_{20}H_{14}S$ | | | |
| (IIb) | 6-Me | 154 [a] | | | | $C_{21}H_{16}S$ | | | |
| (IIc) | 5-Me | 173—174 | 83·7 | 5·7 | 10·65 | $C_{21}H_{16}S$ | 83·95 | 5·4 | 10·65 |
| (IId) | 7-Me | 108—109 | 84·05 | 5·4 | 10·75 | $C_{21}H_{16}S$ | 83·95 | 5·4 | 10·65 |
| (IIe) | 6-Cl | 175—176 [a] | | | | $C_{20}H_{13}ClS$ | | | |
| (IIf) | 5-Cl | 160—161 | 75·2 | 4·15 | 9·85 | $C_{20}H_{13}ClS$ | 74·9 | 4·1 | 10·0 |
| (IIg) | 7-Cl | 114—116 | 74·75 | 3·9 | 10·1 | $C_{20}H_{13}ClS$ | 74·9 | 4·1 | 10·0 |

[a] Described in ref. 3*b*.

TABLE 5

Physical constants and analytical data of 2,3-diphenylbenzo[*b*]thiophen 1,1-dioxides (IV)

| Compound | X | M.p. (°C) | Found (%) C | H | S | Formula | Calc. (%) C | H | S |
|---|---|---|---|---|---|---|---|---|---|
| (IVa) | H | 174—175 [a] | 75·25 | 4·45 | 10·1 | $C_{20}H_{14}O_2S$ | 75·45 | 4·45 | 10·05 |
| (IVb) | 6-Me | 167 [b] | 76·05 | 5·2 | 9·65 | $C_{21}H_{16}O_2S$ | 75·9 | 4·85 | 9·65 |
| (IVc) | 5-Me | 190—191 [b] | 75·5 | 4·9 | 9·55 | $C_{21}H_{16}O_2S$ | 75·9 | 4·85 | 9·65 |
| (IVd) | 7-Me | 164—165 [c] | 75·85 | 4·85 | 9·7 | $C_{21}H_{16}O_2S$ | 75·9 | 4·85 | 9·65 |
| (IVe) | 6-Cl | 183—184 [a] | 68·2 | 3·7 | 9·2 | $C_{20}H_{13}ClO_2S$ | 68·1 | 3·7 | 9·1 |
| (IVf) | 5-Cl | 190—191 [a] | 67·85 | 3·55 | 9·35 | $C_{20}H_{13}ClO_2S$ | 68·1 | 3·7 | 9·1 |
| (IVg) | 7-Cl | 174—175 [c] | 68·0 | 3·8 | 9·15 | $C_{20}H_{13}ClO_2S$ | 68·1 | 3·7 | 9·1 |

[a] From hexane. [b] From ethanol. [c] From petroleum (b.p. 75—120°).

150—160° (50—60% yields).[3b] Benzo[*b*]thiophens (IIf and g) were prepared in the same way from ketones (Vc and d) (8—10 h at 180—190°; 15—20% yields).

The benzo[*b*]thiophens obtained (Table 4) were all purified by chromatography on silica gel and by recrystallisation from ethanol.

2,3-*Diphenylbenzo*[b]*thiophen* 1,1-*Dioxides* (IVa—g).—These compounds were prepared in 85—95% yields by oxidation with peroxyacetic acid of the corresponding benzo[*b*]thiophens (IIa—g) (see Table 5).

2-*Arylthio*-2-*phenylacetophenones* (Va—d).—These compounds were prepared by the reaction of 2-chloro-2-phenylacetophenone [11] with the sodium salt of the appropriate arenethiol in absolute ethanol (50—70% yields), as previously described [3b] (see Table 6).

TABLE 6

Physical constants and analytical data of 2-arylthio-2-phenylacetophenones (V)

| Compound | X | M.p. (°C) | Found (%) Cl | S | Formula | Calc. (%) Cl | S |
|---|---|---|---|---|---|---|---|
| (Va) | *p*-Me | 92—93 [a,b] | | | $C_{21}H_{18}OS$ | | |
| (Vb) | *o*-Me | 116 [c,d] | | | $C_{21}H_{18}OS$ | | |
| (Vc) | *p*-Cl | 108—109 [d] | 10·55 | 9·3 | $C_{20}H_{15}ClOS$ | 10·45 | 9·45 |
| (Vd) | *o*-Cl | 83 [e] | 10·6 | 9·6 | $C_{20}H_{15}ClOS$ | 10·45 | 9·45 |

[a] Described in ref. 3*b*. [b] From ethanol. [c] Lit., 115° (A. Schönberg, A. K. Fateen, and S. M. A. R. Omran, *J. Amer. Chem. Soc.*, 1956, **78**, 1224). [d] From petroleum (b.p. 75—120°). [e] From methanol.

[1/2263 *Received*, 29*th November*, 1971]

[11] A. M. Ward, *Org. Synth.*, 1943, Coll. Vol. II, p. 159.