Reactivity of Vinyl Sulphonic Esters. Part X.[1] Effect of the Substituents on the Cyclisation of Arylthiovinyl Sulphonates to Benzo[*b*]thiophens

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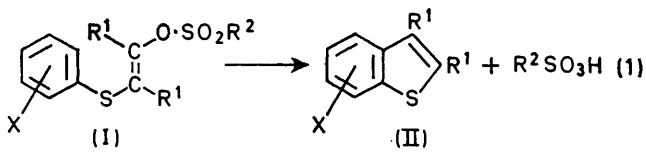
Cyclisation of either *meta*- and *para*-phenylsulphonyl-substituted 2-arylthio-1,2-diphenylvinyl 2,4,6-trinitrobenzenesulphonate in dichloromethane with boron trifluoride as catalyst affords 2,3-diphenyl-5-phenylsulphonylbenzo[*b*]thiophen. The position of the substituent in the product indicates that a rearrangement occurs in the cyclisation of the *meta*-substituted derivative, whereas with the *para*-derivative the position of the substituent in respect to the sulphur atom is retained. The results are discussed in terms of the *meta*-directing effect of the phenylsulphonyl-group. A close connection is found with the cyclisation of vinyl sulphonates having *ortho,para*-directing substituents in the arylthio-residue.

In previous papers [2] we have reported that 2-arylthio-1,2-diarylvinyl arenesulphonates [I; R^1 = Ph or *p*-MeC_6H_4; R^2 = 2,4,6-$(NO_2)_3C_6H_2$, 2,4-$(NO_2)_2C_6H_3$, *p*-$NO_2{\cdot}C_6H_4$, or *p*-BrC_6H_4] may cyclise to 2,3-diarylbenzo[*b*]thiophens (II) [equation (1)].



	R^1	R^2	X
a;	Ph	2,4,6-$(NO_2)_3C_6H_2$	*p*-$PhSO_2$
b;	Ph	2,4,6-$(NO_2)_3C_6H_2$	*m*-$PhSO_2$

In this cyclisation, wherever a substituent, such as Me, MeO, Cl, or Br, was *para* to the sulphur atom in the arylthio-residue, an unusual 1,2-sulphur shift was observed, leading to a rearranged benzo[*b*]thiophen. No rearrangement occurred where a substituent of the same type was *meta* to the sulphur in (I). This behaviour was tentatively interpreted in terms of the directing effect of the substituents. Such an interpretation was confirmed by deuterium-labelling experiments,[3] which showed that the cyclisation of the unsubstituted derivative (I; X = H) gave almost equal amounts of both rearranged and unrearranged benzo[*b*]thiophen (II; X = H).

In order to obtain further information on the effect of the substituents on this reaction, we have studied the cyclisation of two vinyl sulphonic esters (I), *para*- and respectively *meta*-substituted in the arylthio-residue with a typical electron-withdrawing, *meta*-directing substituent, namely the phenylsulphonyl-group.

RESULTS

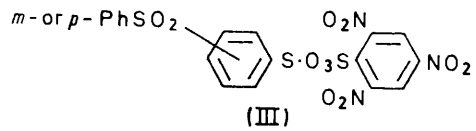
The 1,2-diphenyl-2-(*p*-phenylsulphonyl)phenylthiovinyl 2,4,6-trinitrobenzenesulphonate (Ia) and the corresponding *m*-phenylsulphonyl-substituted derivative (Ib) were prepared following the method previously described,[2a] *i.e.* by addition of *p*- and *m*-phenylsulphonylbenzenesulphenyl 2,4,6-trinitrobenzenesulphonate (IIIa) and (IIIb) respectively to diphenylacetylene in dichloromethane at room temperature. The unstable sulphenyl sulphonates (III)

[1] Part IX, G. Capozzi, and G. Modena, preceding paper.

[2] (*a*) G. Capozzi, G. Melloni, and G. Modena, *J. Chem. Soc.* (*C*), 1970, 2617; (*b*) *ibid.*, p. 2621; (*c*) *ibid.*, p. 2625.

[3] G. Capozzi, G. Melloni, and G. Modena, *J. Org. Chem.*, 1970, **35**, 1217.

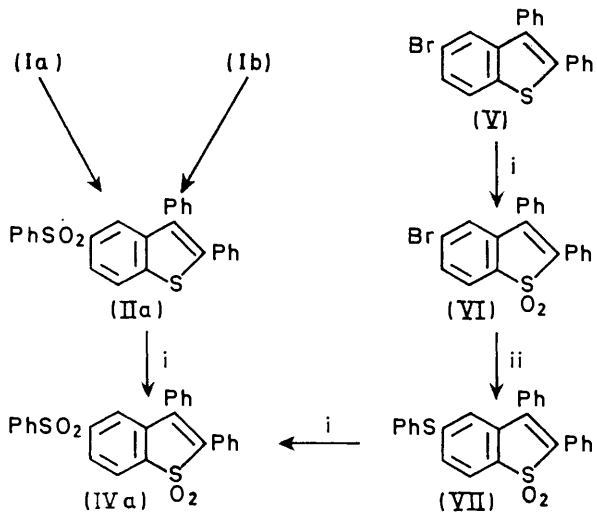
were not isolated. They were prepared *in situ* by the exchange reaction between the corresponding sulphenyl chlorides and silver 2,4,6-trinitrobenzenesulphonate.



(III)

The vinyl sulphonates (Ia) and (Ib) were allowed to react for 48 h in dichloromethane saturated with gaseous boron trifluoride. Chromatography of the reaction mixtures on silica gel afforded in both cases, in low yield (10—12%), only one product which was identified as a 2,3-diphenylbenzo[*b*]thiophen on the basis of its characteristic u.v. spectrum,[2b] together with intractable tarry materials, and small amounts of benzil.

After careful purification and characterisation (elemental analysis, i.r., u.v., and mass spectra) the reaction product was found to be the same from the two different starting compounds, and was identified as 2,3-diphenyl-5-phenylsulphonylbenzo[*b*]thiophen (IIa) by comparison of its oxidation product, the 2,3-diphenyl-5-phenylsulphonylbenzo[*b*]thiophen 1,1-dioxide (IVa), with an authentic sample (see Scheme 1). The synthesis of an authentic



SCHEME 1

Reagents: i, H_2O_2–acetic acid; ii, PhSCu in quinoline–pyridine (10 : 1).

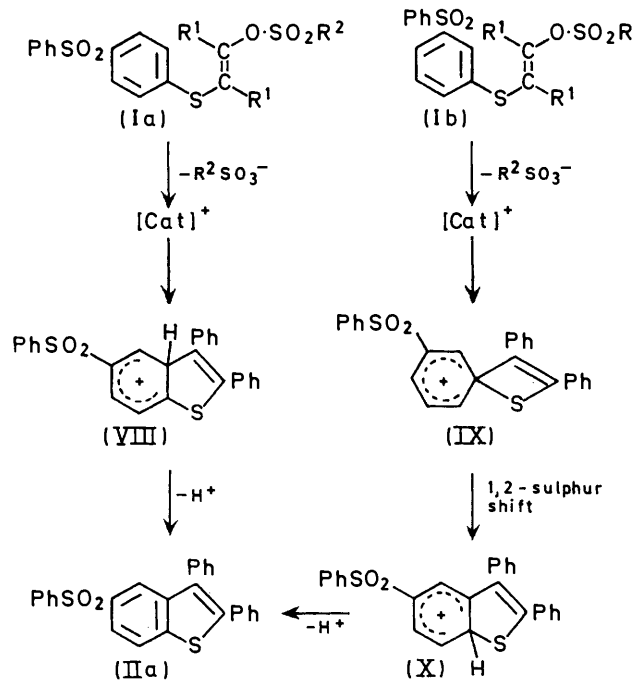
sample of (IVa) was accomplished by oxidation of 2,3-diphenyl-5-phenylthiobenzo[*b*]thiophen 1,1-dioxide (VII), obtained by reaction of cuprous benzenethiolate with 5-bromo-2,3-diphenylbenzo[*b*]thiophen 1,1-dioxide (VI). For comparison purposes the isomeric 2,3-diphenyl-6-phenylsulphonylbenzo[*b*]thiophen 1,1-dioxide (IVb) was also prepared following the same route.

DISCUSSION

The results reported herein indicate that in the cyclisation of the *meta*-substituted vinyl sulphonate (Ib) the position of the substituent in respect to the sulphur is changed, whereas it is retained in the case of the *para*-derivative (Ia). The cyclisation of the vinyl sulphonates (Ia) and (Ib) differs then from that of the vinyl sulphonates (I) previously studied [2b] in two respects: (i) in the very low yield of the cyclisation product and (ii) in the inversion of the regioselectivity of the cyclisation (rearrangement in the case of the *meta*-substituted derivative, and no rearrangement in the case of the *para*-substituted).

The low yield of the cyclisation product is due to the strong deactivating effect of the phenylsulphonyl-group. In other words, the cationic intermediate formed by heterolysis of the C–O·SO_2R^2 bond,[2,4] is almost completely destroyed by side reactions (even in the presence of boron trifluoride) before attack on the arylthio-residue to give the benzo[*b*]thiophen (II) can occur. This is related to our previous observation [2b] that the non-catalysed solvolysis of vinyl sulphonates (I) in inert solvents gave high yields of benzo[*b*]thiophens (II) when the arylthio-residue was activated by electron-donor substituents, but very low yields with mildly electron-withdrawing substituents.

More interesting is the effect of the phenylsulphonyl-group in directing the attack of the cationic centre at the arylthio-residue. As already said, both vinyl sulphonates (Ia) and (Ib) gave the same benzo[*b*]thiophen derivative, namely the 5-substituted compound, (IIa). This means that the *para*-substituted compound (Ia) cyclises *via* attack of the cationic intermediate at the positions *meta* to the phenylsulphonyl group, *i.e. ortho* to the sulphur, giving a straightforward cyclisation, while the *meta*-substituted compound (Ib) cyclises *via*



SCHEME 2

attack at the position occupied by the sulphur, followed by 1,2-sulphur shift. These two cyclisation patterns are depicted in Scheme 2.

[4] G. Modena and U. Tonellato, *J. Chem. Soc.* (*B*), 1971, 374.

It should be noted that two isomers could be formed following the 1,2-sulphur shift, namely the 5- and the 7-phenylsulphonylbenzo[*b*]thiophens (II), arising from the shift of the sulphur to the positions *para* and *ortho* respectively to the substituent. The latter is probably hindered by the bulky phenylsulphonyl-group, as indicated by the almost exclusive * formation of the 5-substituted isomer.

The results herein reported complete the picture of the effect of the substituents on the regioselectivity of the cyclisation reaction briefly described in our previous papers;[2,3] they support the hypothesis[2b] that the substituent in the arylthio-residue is mainly responsible for the course of the reaction. Thus, *ortho, para*-directing substituents, both activating (Me, MeO) and deactivating (Cl, Br) direct the attack at the positions *ortho,para* to them independently of the presence of the sulphur; the latter if present shifts to the adjacent position. Similarly, *meta*-directing, deactivating substituents ($PhSO_2$) direct the attack only at the *meta*-positions.

The ease of the attack of the electrophilic centre at the position bonded to the sulphur and the subsequent rearrangement, not previously observed in the syntheses of heterocycles,[2b] raises the question as to whether the reactivity observed is unique for the system we have investigated or is effective, perhaps, as a side reaction, and as yet overlooked, in other related systems.

EXPERIMENTAL

m-Chloronitrobenzene and diphenylacetylene were purchased and purified by standard methods. 4-Chlorodiphenyl sulphone,[5] silver 2,4,6-trinitrobenzenesulphonate,[6] 3-nitrodiphenyl sulphone,[7] and cuprous benzenethiolate [7] were prepared by literature methods.

p-*Phenylsulphonylbenzenethiol*.—To a mixture of sodium sulphide nonahydrate (3·35 g, 14 mmol), sulphur (0·45 g, 14 g-atom), and sodium hydroxide (0·8 g, 20 mmol) in purified dimethylformamide (15 ml) was added dropwise, with vigorous stirring, at room temperature a solution of 4-chlorodiphenyl sulphone (5·05 g, 20 mmol) in dimethyl formamide (10 ml); the mixture was then refluxed for 1 h. The cool reaction mixture was poured in ice-water and filtered. The filtrate was saturated with sodium chloride and acidified with concentrated hydrochloric acid with cooling. The p-*phenylsulphonylbenzenethiol* which was precipitated was filtered off and thoroughly washed with cold water. The crude product was dissolved in the minimum amount of 20% aqueous sodium hydroxide, and the mixture was filtered; the product was reprecipitated by addition of concentrated hydrochloric acid to the filtrate with cooling. There were obtained 2·35 g (47%) of *p*-phenylsulphonylbenzenethiol, m.p. 117—118° (Found: C, 57·2; H, 3·9; S, 25·6. $C_{12}H_{10}O_2S_2$ requires C, 57·6; H, 4·0; S, 25·6%).

The alkali-insoluble material was identified as *di*-(p-*phenylsulphonyl*)*phenyl disulphide*, m.p. 170—172° [from chloroform–light petroleum (b.p. 40—70°)] (Found: S, 25·85. $C_{24}H_{18}O_4S_4$ requires S, 25·7%).

p-*Phenylsulphonylbenzenesulphenyl Chloride*.—Dry chlorine was passed into a boiling solution of *p*-phenylsulphonylbenzenethiol (1·25 g, 5 mmol) in dry carbon tetrachloride (15 ml), or, alternatively, into a suspension of the corresponding disulphide in the same solvent, until all the di(*p*-phenylsulphonyl)phenyl disulphide, formed at first, had gone into solution (*ca.* 5 h). The orange-coloured solution was cooled, and the p-*phenylsulphonylbenzenesulphenyl chloride* was precipitated by addition of light petroleum (b.p. 40—70°) (*ca.* 200 ml), with careful exclusion of moisture. There were obtained 0·7 g (50%) of the sulphenyl chloride, m.p. 89—91° (decomp.) (yellow crystals from dichloromethane–pentane). The compound was very sensitive to heat and moisture. Since satisfactory analyses could not be obtained, the purity of the compound was checked by iodometric titration on freshly prepared samples. The values obtained were in all cases quite high 92—96%).

1,2-*Diphenyl*-2-(p-*phenylsulphonyl*)*phenylthiovinyl* 2,4,6-*Trinitrobenzenesulphonate* (Ia).—Diphenylacetylene (0·98 g), 5·5 mmol) was dissolved in anhydrous dichloromethane (15 ml), silver 2,4,6-trinitrobenzenesulphonate (acetonitrile complex,[6] 2·76 g, 6 mmol) was added, and the suspension was stirred for a few min. A solution of *p*-phenylsulphonylbenzenesulphenyl chloride (1·5 g, 5 mmol) in dichloromethane (10 ml) was added dropwise at room temperature to the reaction mixture which was then stirred for 1 h. The silver chloride was filtered off and pentane was added to the clear solution to precipitate the 1,2-*diphenyl*-2-(p-*phenylsulphonyl*)*phenylthiovinyl* 2,4,6-*trinitrobenzenesulphonate* (Ia) (1·55 g, 40%) m.p. 127—130° (decomp.) (yellow crystals from dichloromethane–pentane) (Found: C, 53·25; H, 3·0; N, 6·05; S, 13·4. $C_{32}H_{21}N_3O_{11}S_3$ requires C, 53·4; H, 2·95; N, 5·85; S, 13·35%).

3-*Aminodiphenyl Sulphone*.—10% Palladium on carbon (1 g) was added to a solution of 3-nitrodiphenyl sulphone (4 g, 15 mmol) in glacial acetic acid (50 ml), and the mixture was hydrogenated at atmospheric pressure. The required amount of hydrogen was adsorbed in *ca.* 2 h. The mixture was filtered and poured into ice–water. The (3·2 g, 92%) precipitated 3-*aminodiphenyl sulphone* was collected and thoroughly washed with water, m.p. 114° (from benzene) (Found: S, 13·65. $C_{12}H_{11}NO_2S$ requires S, 13·75%).

m-*Phenylsulphonylbenzenethiol*.—The 3-aminodiphenyl sulphone (23·3 g, 0·1 mol) was diazotised and slowly added to a vigorously stirred solution of potassium ethyl dithiocarbonate (29·6 g, 0·2 mol) and potassium carbonate (55·3 g, 0·4 mol) in water (120 ml), maintained at 70—80° during the addition. Stirring and heating were continued for 3 h after the completion of the addition; the reaction mixture was then cooled and extracted with ethyl acetate. The organic layer was washed with 10% aqueous sodium hydroxide and the solvent was removed. The red oily residue was dissolved in boiling ethanol (60 ml), and sodium hydroxide (16·0 g, 0·4 mol) was added portionwise to it; the mixture was refluxed for 3 h. Most of the solvent was distilled off from the cool mixture, and the residue was

* The crude (IIa) obtained from the cyclisation of (Ib) could contain a very small amount of an isomer, since it was difficult to obtain a sample of it with a sharp melting point, although the analytical data were consistent with the assigned formula.

[5] J. Weijlard and E. Swanezy, *J. Amer. Chem. Soc.*, 1949, **71**, 4134.

[6] D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, 1964, **29**, 2702.

[7] R. Adams, W. Reifschneider, and M. D. Nair, *Croat. Chem. Acta*, 1957, **29**, 277.

poured into ice–water. The mixture was extracted with ether and the ether extracts were discarded. The aqueous layer was saturated with sodium chloride and acidified with concentrated hydrochloric acid with cooling. The mixture was extracted with ether, the solvent was evaporated, and the residue was repeatedly extracted with boiling ligroin (b.p. 75—120°). From the ligroin extracts there were obtained 6·5 g (26%) of m-*phenylsulphonylbenzenethiol*, m.p. 80—81° (white crystals from ethanol) (Found: C, 57·7; H, 4·0; S, 25·3. $C_{12}H_{10}O_2S_2$ requires C, 57·6; H, 4·0; S, 25·6%).

m-*Phenylsulphonylbenzenesulphenyl Chloride*.—This compound was prepared following the procedure described for the corresponding *para*-derivative. The m-*phenylsulphonylbenzenesulphenyl chloride* was a very unstable, low-melting compound, which could not be satisfactorily characterised and analysed. It was kept in dichloromethane solution, and allowed to react immediately after its preparation.

1,2-*Diphenyl*-2-(m-*phenylsulphonyl*)*phenylthiovinyl* 2,4,6-*Trinitrobenzenesulphonate* (Ib).—This compound was prepared in 55% yield following the procedure described for the corresponding *para*-derivative, m.p. 128—130° (decomp.) (orange-red crystals from dichloromethane–pentane) (Found: C, 53·1; H, 2·95; N, 5·8; S, 13·5. $C_{32}H_{21}N_3O_{11}S_3$ requires C, 53·4; H, 2·95; N, 5·85; S, 13·35%).

Treatment of the Vinyl Sulphonate (Ia) *with Boron Trifluoride*.—A solution of compound (Ia) (7·2 g, 10 mmol) in anhydrous dichloromethane (120 ml) was saturated with gaseous boron trifluoride at room temperature. The flask was stoppered, and the reaction mixture was set aside for 48 h at room temperature. 10% Aqueous potassium fluoride was added to it, and the organic layer was separated, dried ($CaCl_2$), and evaporated to give a reddish residue, which was chromatographed on silica gel. Elution with light petroleum (b.p. 40—70°)–ethyl ether (9 : 1) gave benzil (0·25 g, 12%) and a white crystalline compound (0·43 g), m.p. 178—179° (from methanol), together with a large amount of intractable tarry material. The crystalline material was identified as 2,3-*diphenyl*-5-*phenylsulphonylbenzo*[b]*thiophen* (IIa) (10% yield) (Found: S, 14·75. $C_{26}H_{18}O_2S_2$ requires S, 15·0%); $\lambda_{max.}$ (cyclohexane) 302 nm (log ε 3·85); molecular weight 426 (mass spectrum).

Treatment of Vinyl Sulphonate (Ib) *with Boron Trifluoride*.—This reaction was carried out as described for the corresponding reaction of the vinyl sulphonate (Ia), using 3·6 g (5 mmol) of (Ib). Chromatography of the reaction mixture on silica gel, with light petroleum (b.p. 40—70°)–ethyl ether (9 : 1) as eluant, gave benzil (0·08 g, 8%) and a white crystalline compound (0·26 g), m.p. 174—178° (from methanol). Purification of the latter to obtain a sharp melting point (178—179°) required repeated fractional recrystallisations. This compound was identical in all respects (m.p., mixture m.p., i.r., and u.v. spectrum) to the 2,3-diphenyl-5-phenylsulphonylbenzo[*b*]thiophen (IIa) (12% yield) isolated in the corresponding reaction of the isomeric vinyl sulphonate (Ia).

Oxidation of 2,3-*Diphenyl*-5-*phenylsulphonylbenzo*[b]*thiophen* (IIa).—This compound (0·43 g, 1 mmol) was oxidised with peroxyacetic acid to the corresponding 2,3-*diphenyl*-5-*phenylsulphonylbenzo*[b]*thiophen* 1,1-*dioxide* (IVa) (0·38 g, 84%), m.p. 264—265° [from benzene–ligroin (b.p. 75—120°)], which was identical (m.p., i.r. spectrum) to an authentic sample of (IVa), prepared as described below.

5-*Bromo*-2,3-*diphenylbenzo*[b]*thiophen* 1,1-*Dioxide* (VI).—This compound was prepared by oxidation with peroxyacetic acid of the corresponding 5-bromo-2,3-diphenylbenzo[*b*]thiophen (V) (1·1 g, 3 mmol), prepared as previously described.[3] The yield of product was 1·1 g (92%) of (VI), m.p. 200—201° (from methanol) (Found: C, 60·2; H, 3·2; S, 8·05. $C_{20}H_{13}BrO_2S$ requires C, 60·45; H, 3·3; S, 8·05%).

2,3-*Diphenyl*-5-*phenylthiobenzo*[b]*thiophen* 1,1-*Dioxide* (VII).—A mixture of compound (VI) (0·79 g, 2 mmol), cuprous benzenethiolate (0·39 g, 2·2 mmol), quinoline (12 ml), and pyridine (1·2 ml) was heated to reflux (200—210°) until a homogeneous solution was obtained (*ca.* 7 h). The hot solution was poured into concentrated hydrochloric acid containing cracked ice, and the mixture was set aside for 2 h. The gummy solid formed was collected by decantation and extracted several times with ether; the ethereal layer was washed with water and dried ($CaCl_2$). Evaporation of the solvent gave 2,3-*diphenyl*-5-*phenylthiobenzo*[b]*thiophen* 1,1-*dioxide* (VII) (0·64 g, 75%), m.p. 210—212° [pale yellow crystals from benzene–ligroin (b.p. 75—120°)] (Found: C, 73·3; H, 4·4; S, 15·05. $C_{26}H_{18}O_2S_2$ requires C, 73·2; H, 4·25; S, 15·0%).

2,3-*Diphenyl*-5-*phenylsulphonylbenzo*[b]*thiophen* 1,1-*Dioxide* (IVa).—This compound was prepared by oxidation with peroxyacetic acid of the 5-phenylthio-derivative (VII) (0·42 g, 1 mmol). The yield of product was 0·38 g (84%) m.p. 264—265° [white crystals from benzene–ligroin (b.p. 75—120°)] (Found: C, 67·7; H, 3·9; S, 13·8. $C_{26}H_{18}O_4S_2$ requires C, 68·1; H, 3·95; S, 14·0%).

2,3-*Diphenyl*-6-*phenylsulphonylbenzo*[b]*thiophen* 1,1-*Dioxide* (IVb).—The title compound was prepared from 6-bromo-2,3-diphenylbenzo[*b*]thiophen,[3] following the procedure described for the preparation of the 5-substituted isomer (IVa). The compound (IVb) had m.p. 282—283°, [white crystals from benzene–ligroin (b.p. 75—120°)] (Found: C, 68·2; H, 3·95; S, 13·7. $C_{26}H_{18}O_4S_2$ requires C, 68·1; H, 3·95; S, 14·0%).

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