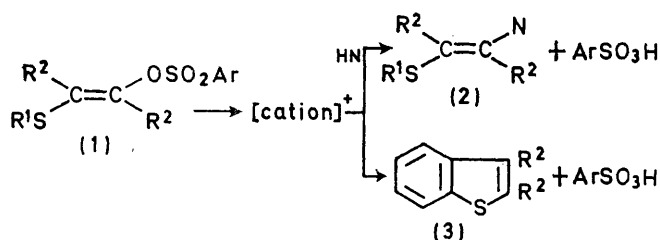


Reactivity of Vinyl Sulphonic Esters. Part IX.¹ Cyclisation of Aryloxyvinyl *p*-Bromobenzenesulphonates to Benzo[*b*]furans

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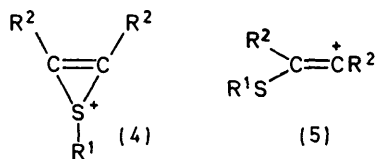
1,2-Diaryl-2-aryloxyvinyl *p*-bromobenzenesulphonates (7) have been prepared by reaction of 2-aryl-2-aryloxyacetophenone (6) with *p*-bromobenzenesulphonyl chloride in the presence of sodium hydride. Compounds (7) give upon reaction with BF₃ in dichloromethane 2,3-diarylbenzo[*b*]furans (8) and *p*-bromobenzenesulphonic acid. Evidence is presented that the β-oxygen, in contrast to the corresponding sulphur atom in analogous reactions of thiovinylsulphonates (1), does not participate at any significant extent in the reaction.

In previous papers of this series we have reported that 1,2-diaryl-2-arylthiovinylarenesulphonates (1) may undergo S_N1-like substitution in the presence of weak nucleophiles or cyclisation to benzo[*b*]thiophen derivatives (3) in inert media.² These reactions, discussed in previous papers,^{2,3} follow the general pattern indicated in Scheme 1.



SCHEME 1

Evidence in favour of the participation of the β-sulphur has been offered and the hypothesis advanced^{1,3,4} that the cationic intermediate may have the thiirenium structure (4) rather than the vinyl cationic structure (5).



The participation of the sulphur atom in the above system raises the question as to whether oxygen and

furans are now reported. They indicate that oxygen is reluctant to give bridged ions in these systems.

RESULTS AND DISCUSSION

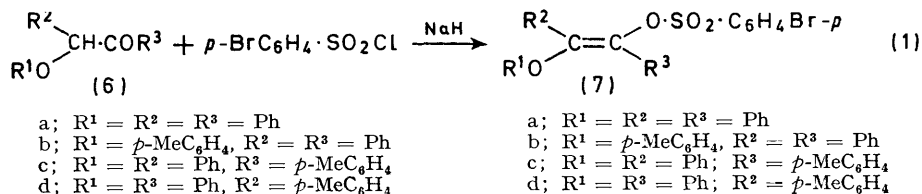
1,2-Diaryl-2-aryloxyvinyl *p*-bromobenzenesulphonates (7a—d) were obtained in moderate yields (25—30% after purification) by sulphonylation of the corresponding 2-aryl-2-aryloxyacetophenones (6) with *p*-bromobenzenesulphonyl chloride following the procedure described for the corresponding sulphur derivatives (1)^{1,5} [equation (1)].

The sulphonic esters (7) are assumed to be the *trans*-isomers (with respect to R¹O and O·SO₂·C₆H₄Br-*p*) by analogy¹ with the corresponding sulphur derivatives (1). The physical and analytical data for the vinyl sulphonates (7) are collected in Table 1.

The aryloxyvinyl sulphonates (7) undergo solvolytic reaction in 80% ethanol at 150° at rates similar to that of triphenylvinyl sulphonates.⁴ However the solvolysis appears to be complicated by side reactions and it deserves further investigation.

Anhydrous boron trifluoride in an inert solvent (CHCl₃, CH₂Cl₂) causes cyclisation [equation (2)] of (7a—d) to the four unrearranged benzo[*b*]furans (8a—d) in moderate yields (see Table 2). The structures of compounds (8a—d) were assigned on the basis of a comparison with authentic samples prepared by cyclisation of the appropriate aryloxyacetophenones (6a—d) in polyphosphoric acid.⁶

Confirming the Perrot and Cerutti's findings⁷ we



nitrogen could play a similar role in the reaction of vinyl sulphonates. The results of a study on the cyclisation of aryloxyvinyl sulphonates to benzo[*b*]-

also observed that compound (6c) yields compound (8d) and not the expected compound (8c) [equation

¹ Part VIII, G. Capozzi, G. Melloni, and G. Modena, *J. Chem. Soc. (C)*, 1971, 3018.

² G. Modena and U. Tonellato, *J. Chem. Soc. (B)*, 1971, 374 and preceding papers of the series.

³ G. Capozzi, G. Melloni, G. Modena, and U. Tonellato, *Chem. Comm.*, 1969, 1520; G. Modena and U. Tonellato, *J. Chem. Soc. (B)*, 1971, 381.

⁴ G. Modena and U. Tonellato, *J. Chem. Soc. (B)*, 1971, 1569; G. Capozzi, G. Modena, and U. Tonellato, *J. Chem. Soc. (B)*, 1971, 1700.

⁵ J. D. Brown and J. Harley-Mason, *J. Chem. Soc. (C)*, 1966, 1390.

⁶ A. Wacek and H. Daubner-Rottenbacher, *Monatsh.*, 1948, **81**, 266.

⁷ C. Perrot and E. Cerutti, *Compt. rend.*, (C), 1967, **265**, 320.

(3)]. The latter could, in fact, be obtained from compound (6d) (see Experimental section). This unexplained rearrangement deserves further discussion which, however, is outside the scope of this paper.

oxygen is somewhat unexpected although it is well known that sulphur is a better neighbouring group than oxygen.⁸

It may be that where less-stable vinyl cations are involved, *i.e.* not assisted by resonance with an adjacent

TABLE 1
Analytical data for 1,2-diphenyl-2-aryloxyvinyl *p*-bromobenzenesulphonates (7)

	M.p.	Found				Formula	Calc.			
		C	H	Br	S		C	H	Br	S
(7a)	143—145°	61.65	3.9	15.85	6.4	C ₂₆ H ₁₉ BrO ₄ S	61.55	3.75	15.75	6.3
(7b)	143—145	62.0	3.95	15.0	6.1	C ₂₇ H ₂₁ BrO ₄ S	62.2	4.05	15.3	6.15
(7c)	132—139	61.9	4.0	16.2	6.35	C ₂₇ H ₂₁ BrO ₄ S	62.2	4.05	15.3	6.15
(7d)	139—140	62.40	4.15	15.65	6.45	C ₂₇ H ₂₁ BrO ₄ S	62.2	4.05	15.3	6.15

The cyclisation of compounds (7a—d) to benzo[b]furans parallels the reactions under similar conditions of the thiovinyl sulphonates (1) (see Scheme 1). It is likely that the reactions also proceed *via* a vinyl cation intermediate, although direct evidence is, so far, lacking and a concerted mechanism, similar to that accepted for other heterocyclic syntheses, cannot be excluded.

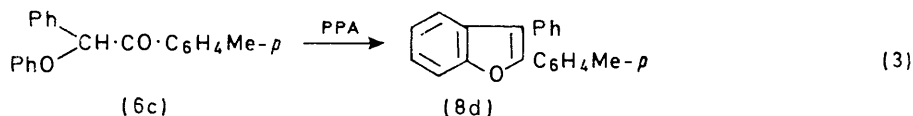
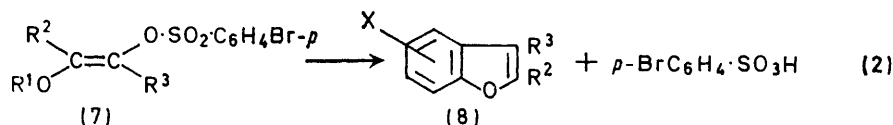
Our results rule out any significant participation of the ethereal oxygen in the reaction. The intervention of bridged species of type (4) would yield a mixture of (8c) and (8d) from (7c) and (7d) or at least some (8c) from (7d) since in this case the migration of the oxygen

aromatic system, some degree of oxygen participation could occur. This would parallel the behaviour of aliphatic substituted vinyl cations which undergo rearrangement in contrast to those α -substituted with strong electron-donor groups which do not.⁹

EXPERIMENTAL

The ¹H n.m.r. spectra were recorded with a Bruker HFX high-resolution spectrometer operating at 90 MHz, and with tetramethylsilane as internal standard in deuteriochloroform solution.

2-Aryl-2-aryloxyacetophenones (6a—d).—These compounds were prepared following the procedure described by Richard:¹⁰ (6a), m.p. 85° (lit.,¹⁰ m.p. 85.5°); (6b),



would have given a more stable vinyl cation. Bearing in mind¹⁻⁴ that the migration of the arylthio-group of (1) from one ethylenic carbon to the next is very easy

m.p. 89—90° (lit.,¹¹ m.p. 91°); (6c), m.p. 98—100° (lit.,⁷ m.p. 100°). *2-Phenyl-2-p-tolylacetophenone* (6d) was prepared in a similar way in 87% yield, m.p. 106—108° (Found: C, 83.9; H, 6.1. C₂₁H₁₈O₂ requires C, 83.5; H, 6.0%).

1,2-Diaryl-2-aryloxyvinyl p-bromobenzenesulphonates (7a—d).—Sodium hydride (50% dispersion in oil, 0.02 mol) was added in small portions to a well stirred solution of 2-aryl-2-aryloxyacetophenone (6) (0.01 mol) in dry acetone (20 ml), with ice cooling. After 15 min *p*-bromobenzenesulphonyl chloride (0.01 mol) in dry acetone (30 ml) was added to the mixture, the temperature of which was then allowed to rise gradually to room temperature. After 30 min, addition of water to the mixture gave an oil which solidified when treated with a little methanol. The solid was filtered off and recrystallised from methanol (25—30% yield).

Analytical data of the sulphonates (7) are reported in Table 1.

TABLE 2

Cyclisation of the sulphonates (7) to 2,3-diarylbenzo[b]furans (8)

(7)	(8)	R ²	R ³	X	M.p.	Yield (%)
(7a)	(8a)	Ph	Ph	H	124° ^a	33
(7b)	(8b)	Ph	Ph	5-Me	112—114° ^b	46
(7c)	(8c)	Ph	<i>p</i> -MeC ₆ H ₄	H	74—75° ^c	37
(7d)	(8d)	<i>p</i> -MeC ₆ H ₄	Ph	H	96° ^d	28

^a Lit.⁶ m.p. 122—124°. ^b Lit.¹¹ m.p. 114°. ^c This work. ^d Lit.⁷ m.p. 96°.

and that the β -sulphur anchimerically assists the formation of vinyl cations, the intermediate probably has the bridged structure (4).

This difference in behaviour between sulphur and

⁸ A. Streitwieser, 'Solvolytic Displacement Reactions,' McGraw-Hill, London, 1962.

⁹ M. Hanack, *Accounts Chem. Res.*, 1970, **3**, 209.

¹⁰ M. G. Richard, *Compt. rend.*, 1934, **198**, 1242.

¹¹ C. Perrot and E. Cerutti, *Compt. rend.*, (C), 1967, **264**, 1301.

Cyclisation of the Sulphonates (7a—d) to 2,3-Diarylbenzo[b]furans (8).—A solution of compound (7) (2 mmol) in anhydrous dichloromethane or chloroform (120 ml) was saturated with gaseous boron trifluoride. The flask was stoppered and left at room temperature for 2 days. A 10% aqueous potassium fluoride was added to the mixture and the organic layer was separated, dried (CaCl₂), and evaporated. The tarry residue was chromatographed on silica gel with light petroleum (40—70°) as eluant, to give the benzo[b]furan derivatives as white crystalline products; these were recrystallised from ethanol (30—45% yields). Among the other products eluted the only one in significant amount (20—25% yields) was identified as benzil, in the case of compounds (7a) and (7b), and *p*-methylbenzil, m.p. 30—31° (lit.,¹² m.p. 31°), from the cyclisation of compounds (7c) and (7d). The ¹H n.m.r. spectra of the crude cyclisation products of (7c) and (7d) show a singlet for the methyl group at τ 7.57 and 7.68 respectively.

2,3-Diphenylbenzo[b]furan (8a), m.p. 124° from ethanol (lit.,⁶ m.p. 122—124°), and 5-methyl-2,3-diphenylbenzo[b]furan (8b) m.p. 112—114° from ethanol (lit.,¹¹ m.p.

114°), were prepared as reported by A. Wacek *et al.*⁶ (*i.e.* reaction of benzoin and the appropriate phenol) and purified by chromatography on silica gel. 3-Phenyl-2-*p*-tolylbenzo[b]furan (8d) was prepared as reported by Perrot and Cerutti⁷ by cyclisation of 4'-methyl-2-phenoxy-2-phenylacetophenone in polyphosphoric acid at 100°, m.p. 96° from ethanol (lit.,⁷ 96°). The ¹H n.m.r. spectrum shows signals at τ 2.00—3.00 (m, 13H) and 7.68 (s, 3H).

The u.v. spectrum in cyclohexane shows a maximum at 305 nm.

2-Phenyl-3-*p*-tolylbenzo[b]furan (8c).—This compound was prepared as reported above from 2-phenyloxy-2-*p*-tolylacetophenone (6d) in 67% yield, m.p. 74—75° (Found: C, 88.8; H, 5.75. C₂₁H₁₆O requires C, 88.7; H, 5.65%). The ¹H n.m.r. spectrum of (8c) shows bands at τ 2.00—2.89 (m, 13H) and 7.57 (s, 3 H). The u.v. spectrum in cyclohexane shows a maximum at 305 nm.

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¹² H. H. Hatt, A. Pilgrim, and J. Hurran, *J. Chem. Soc.*, 1936, 93.