Organic Synthesis with Sulphones. Part 14.[1] Nucleophilic Substitution on Styryl Sulphones; a New Route to Arylacetaldehydes

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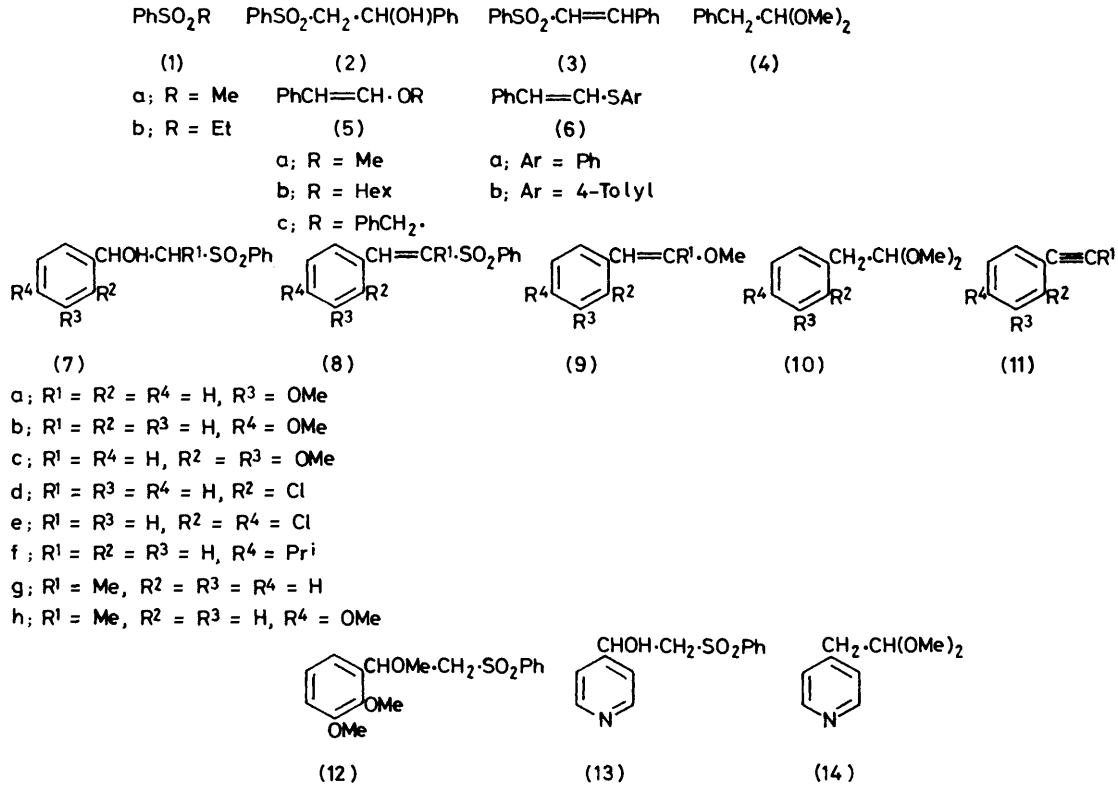
Condensation of sulphones with aromatic aldehydes in an alkaline medium readily gives β-hydroxy-sulphones which can be dehydrated to β-styrylsulphones. When these are treated with one molar equivalent of sodium alkoxides in dimethyl sulphoxide at room temperature, β-alkoxystyrenes are formed by ready nucleophilic substitution. Treatment of the hydroxy-sulphones directly with an excess of sodium methoxide leads to the corresponding dimethyl acetals. This is a new and potentially useful way to prepare arylacetaldehyde derivatives.

β-Oxystyrene derivatives are equivalent to arylacetaldehydes. These compounds are not so very easily prepared; on the other hand, they are interesting starting materials for a variety of reactions, particularly in the heterocyclic series. In the course of other work, it had been found that benzyl alcohol gives a high yield of *trans*-β-benzyloxystyrene (5c) when submitted to strongly basic, mildly oxidising conditions,[2] a reaction thought to involve first oxidation to benzaldehyde and then crotonisation with dimethyl sulphoxide to give β-methylsulphinylstyrene; addition of benzyl oxide anion followed by elimination of methyl sulphenate anion would then account for the result. This has been shown to be a possible route to (5).[3]

It seemed possible to write a similar sequence of reactions with sulphones instead of sulphoxides. In the present work, a route leading from benzaldehydes to the enol ethers (9) is described.



The first two steps (1) and (2) are well documented. Sulphones and aldehydes can be condensed under a variety of basic conditions to hydroxy-sulphones which can be dehydrated to styryl sulphones under acidic or basic conditions. In some cases, the two reaction steps can be carried out in one flask under the influence of a phase-transfer catalyst.[4,5]

Reactions (3) and (4), equivalent to nucleophilic substitution at a vinylic centre [6] with sulphinate anion

[1] Part 13, M. Julia and D. Deprez, *Tetrahedron Letters*, 1976, 279.
[2] H. Langhals, M. Julia, and D. Mansuy, *Tetrahedron Letters*, 1976, 3516,
[3] Unpublished work.
[4] G. Cardillo, D. Savoia, and A. Umani-Ronchi, *Synthesis*, 1975, 453.
[5] (*a*) W. E. Truce and V. V. Badiger, *J. Amer. Chem. Soc.*, 1964, **86**, 3277; (*b*) W. E. Truce and C. T. Goralski, *J. Org. Chem.*, 1971, **36**, 2536; (*c*) L. Field, *J. Amer. Chem. Soc.*, 1952, **74**, 3919.
[6] G. Modena, *Accounts Chem. Res.*, 1971, **4**, 73.

as leaving group would be, of course, the crucial part. The chemistry of vinyl sulphones, including nucleophilic displacement of other leaving groups, has been

$$PhCHO + CH_3{-}SO_2Ph \rightleftharpoons \underset{(2)}{PhCH(OH)\cdot CH_2\cdot SO_2Ph} \quad (1)$$

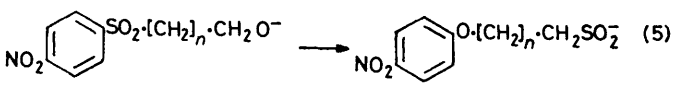
$$PhCH(OH)\cdot CH_2\cdot SO_2Ph \rightleftharpoons \underset{(3)}{PhCH{=}CH\cdot SO_2Ph} \quad (2)$$

$$PhCH{=}CH\cdot SO_2Ph + RO^- \rightleftharpoons \underset{(5)}{PhC(OR)H\cdot CH\cdot SO_2Ph} \quad (3)$$

$$PhC(OR)H\cdot CH\cdot SO_2Ph \rightleftharpoons PhCH{=}CH\cdot OR + PhSO_2^- \quad (4)$$

thoroughly investigated by Stirling and his group [7] but displacement of the sulphinate anion is not very common.

The corresponding aromatic nucleophilic substitution is involved in the Smiles rearrangement [see equation (5)].[8,9]

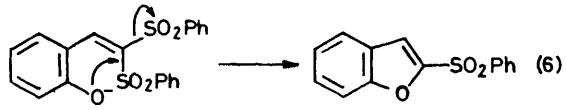


(5)

The addition of alkoxide ion in reaction (3) would, of course, be expected to take place in the reverse direction leading to the more stable α-sulphonyl carbanion. This has been shown [10] to be the case in the base-catalysed addition of thiols to benzothiophen dioxide while the free-radical initiated addition takes place in the reverse direction. The sulphinic acids are prepared efficiently by nucleophilic displacement in some vinyl sulphones; [11] the desired direction of addition being facilitated by an ester group. A remarkable reaction of the type under discussion has been described [see equation (6)].[12a] In this case, however, an addition–elimination mechanism

$$RS^- + R\cdot SO_2\cdot CH{=}CH\cdot CO_2Et \longrightarrow RS\cdot CH{=}CH\cdot CO_2Et + RSO_2^-$$

cannot be expected to operate.[12a,b] Trialkylboranes bring about the displacement of a vinylic sulphonyl group



(6)

by an alkyl group; [13] the mechanism of this reaction is thought, however, to be a free-radical one.

Considering that the addition of alkoxide ion β to the sulphonyl group would be reversible, it was hoped that occasionally the addition would occur in the reverse direction (3) the irreversible formation of phenyl sulphinate ion so formed then ensuring that the reaction went to completion.

TABLE 1

Preparation of styryl sulphones and β-hydroxyphenylethyl sulphones

Starting material	Procedure	Styryl sulphone	Yield (%)	M.p. (°C)	Lit. m.p. (°C)	Ref.	Formula	Found (%)	Required (%)
(1a)	A	*E*-(3)	74	74	73.5—75	5*a*			
Z-(6a)	C	*Z*-(3)	75	63	64—65	5*a*			
(1a)	B	(8a)	64	120.5			$C_{15}H_{14}O_3S$	S11.63	S11.66
(1a)	B	(8b)	76	120			$C_{15}H_{14}O_3S$	S11.7	S11.66
(1a)	B	(8d)	71	106			$C_{14}H_{11}ClO_2S$	S11.37	S11.50
(1a)	B	(8f)	88	103			$C_{17}H_{18}O_2S$	S10.77	S11.18
(1b)	B	(8g)	72	94.5	94.5—95.5	5*b*			
(1b)	B	(8h)	78	90			$C_{16}H_{16}O_3S$	S10.73	S11.10
		β-Hydroxy-sulphone							
(1a)	B	(2)	90.5	94	92—94	5*c*			
(1a)	B	(7e)	76	107			$C_{14}H_{12}Cl_2O_3S$	S10.02	S9.68
(1a)	B	(13)	83	102			$C_{13}H_{13}NO_3S$	S11.98	S12.15

β-Styryl sulphones (3) and a series of substituted derivatives were prepared (Table 1) according to literature procedures, starting with aromatic aldehydes and phenyl methyl (1a) or phenyl ethyl (1b) sulphones; the *E*-configuration about the double bond was ascertained by n.m.r. The *Z*-isomer of β-styryl sulphone (3) was prepared by oxidation of the corresponding sulphide. The olefinic sulphones were then submitted to the original [2] two sets of reaction conditions: when treated with benzyl alcohol and solid potassium hydroxide in dimethyl sulphoxide, the *E*-styryl phenyl sulphone *E*-(3) did not give the corresponding vinyl ether (5a) but phenyl methyl sulphone (1a) which, instead, could be isolated in 18% yield; apparently reactions (2) and (1) had taken place in the reverse direction. However, in the presence of dry sodium benzyl oxide in dimethyl

[7] See for instance N. K. Barlow, D. R. Marshall, and C. J. M. Stirling, *J.C.S. Perkin II*, 1977, 1920 and previous papers in this series, particularly C. J. M. Stirling, *J. Chem. Soc.*, 1964, Suppl. I, 5875; M. J. v. d. Sluijs and C. J. M. Stirling, *J.C.S. Perkin II*, 1974, 1268.

[8] W. E. Truce, E. M. Kreider, and W. W. Brand, 'Organic Reactions,' Wiley, New York, 1970, vol. 18, p. 99.

[9] K. B. Tomer and A. Weisz, *Tetrahedron Letters*, 1976, 231.

[10] F. G. Bordwell and W. H. McKellin, *J. Amer. Chem. Soc.*, 1950, **72**, 1985; F. G. Bordwell, R. D. Chapman, and W. H. McKellin, *ibid.*, 1954, **76**, 3637.

[11] W. E. Truce and F. E. Roberts, jun., *J. Org. Chem.*, 1963, **28**, 593.

[12] (*a*) M. L. Oftedahl, J. W. Baker, and M. W. Dietrich, *J. Org. Chem.*, 1965, **30**, 296; (*b*) J. E. Baldwin, J. Critting, W. Dupont, L. Cruse, L. Silberman, and R. C. Thomas, *J.C.S. Chem. Comm.*, 1976, 736.

[13] H. Nozaki, *Bull. Chem. Soc. Japan*, 1974, **47**, 503.

sulphoxide for a few hours at room temperature, the sulphone *E*-(3) was converted (65%) into the *E*-β-benzyloxystyrene *E*-(5c). It should be pointed out that only the *E*-isomer of β-benzyloxystyrene was formed as in the original work.[2] When the isomeric sulphone *Z*-(3) was submitted to the same reaction conditions the same *E*-ether was obtained in a similar yield. This is not really surprising; although nucleophilic substitution of vinylic halides usually occurs with retention of configuration,[6] displacement of MeO by PhO in *E*- and *Z*-phenoxyvinyl sulphones has been shown to lead to the same *E*-methoxyvinyl sulphone.[7] The sulphone *E*-(3) was then treated with sodium methoxide or sodium n-hexoxide in dimethyl sulphoxide: the corresponding vinyl ethers (5a) and (5b) were isolated in a similar yield. Again only *E*-isomers were formed.

A number of substituted styryl sulphones (8) were then treated with sodium methoxide in dimethyl sulphoxide (Table 2) when the corresponding styryl methyl ethers (9) were formed.

In some cases it proved advantageous to treat the hydroxy-sulphone itself with an excess of sodium methoxide in dimethyl sulphoxide, the dimethyl acetals of the corresponding arylacetaldehydes being obtained in good yields. This latter procedure is one step shorter and the acetals are more stable than the vinyl ethers. Acetal formation is not surprising in view of the known ability of vinyl ethers to add alkoxides.[18] This must be greatly facilitated when the aromatic moiety is particularly apt to stabilise a negative charge on the α carbon atom.

The difficulty associated with dehydration of the hydroxy-sulphones (8) bearing an *ortho*-methoxy-substituent could be avoided by methylation (see Experimental section). Hence with an excess of sodium methoxide the β-methoxy-sulphone (12) gave the corresponding methyl vinyl ether (9c). The sulphones bearing an α-methyl substituent in the styrene moiety (8g and h) gave variable amounts of the corresponding acetylene derivatives (11g and h). The question arises as to whether the styryl ethers (9) could have been formed from the sulphones (8) by a path involving elimination to give the arylpropynes (11) followed by addition of methanol. It is known [19] that addition of alcohols to acetylenes readily occurs in the presence of base. The stereochemistry of the adducts is however *Z* whereas the vinyl ethers obtained from the vinylic sulphones (8) have consistently the *E*-configuration. Moreover, methanol and hexanol add smoothly to phenylacetylene (see Experimental section) whereas benzyl alcohol fails to add under the same reaction conditions.

Other nucleophiles were tried in the nucleophilic substitution of the sulphonyl group of the styryl phenyl sulphone (3). Benzene and toluene-*p*-thiolates led to the corresponding thioethers (6) in *ca.* 30% yield. Addition of a catalytic amounts of cuprous iodide–tributylphosphine doubled the yield. Under free radical initiation thiols also gave the thioether (6) (25% yield).

Attempts to use other nucleophiles have been unsuccessful, so far: potassium phthalimidate, sodium *N*-methyl *N*-phenylamide, and potassium acetate failed to give substitution products.

Nucleophilic substitution by methoxide of the sul-

TABLE 2

Reactions of various sulphones with sodium alkoxides in dimethyl sulphoxide

Starting material	Sodium alkoxide	β-styryl ether: Compound	Yield (%)	Phys. consts.	Arylacetaldehyde acetal: Compound	Yield (%)	Phys. consts.	Arylacetylenic compound: Compound	Yield (%)	Phys. consts.
E-(3)	NaOMe	*E*-(5a)	65 *	B.p. 38—41 °C at 0.2 T (lit.[14] 208—209 °C at 99 T)						
E-(3)	NaOHex n	*E*-(5b)	60—62	B.p. 90 °C at 0.7 T						
E-(3)	$NaOCH_2Ph$	*E*-(5c)	63—65	M.p. and m.m.p. 43 °C (lit.[2] 43 °C)						
Z-(3)	$NaOCH_2Ph$	*E*-(5c)	65	M.p. and m.m.p. 43 °C (lit.[2] 43 °C)						
(8a)	NaOMe	*E*-(9a)	68	B.p. 88 °C at 0.5 T						
(8b)	NaOMe	*E*-(9b)	10 †	B.p. 67—72 °C at 0.2 T				(11b) ‡	1	
(8d)	NaOMe	*E*-(9d)	63	B.p. 66—68 °C at 0.2 T						
(8f)	NaOMe	(9f) §	22	B.p. 100—110 °C at 0·2 T						
(8g)	NaOMe	(9g) §	22	B.p. 80—85 °C at 0.2 T (lit.[14] 86—92 °C at 1 T)				(11g)	11	B.p. 53—55 °C at 10 T (lit.,[15] 90 °C at 20 T)
(8h)	NaOMe							(11h)	70 *	B.p. 66 °C at 0.3 T (lit.,[14] 115—117 °C at 3 T)
β-Hydroxysulphone										
(2)	NaOMe ¶	*E*-(5a)	31 ¶		(4)	12 ‖				
(7c)	NaOMe ¶				(10e)	70 *	B.p. 98 °C at 0.8 T			
(13)	NaOMe ¶				(14)	68	B.p. 80 °C at 0.2 T			
β-Methoxysulphone										
(12)	NaOMe ¶	*E*-(9c)	70 *	B.p. 100—101 °C at 0.2 T						

* N.m.r. showed the crude product to be practically pure. † Purification by column chromatography (silica gel–pentane) prior to distillation. ‡ Not isolated but characterised by comparison of mass spectra with literature data.[17] § Stereochemistry not determined. ‖ Same retention in g.l.c. (SE30, DC550) as an authentic sample. ¶ A three-fold excess of sodium methoxide was used.

[14] E. Taskinen and P. Ylivainio, *Acta Chem. Scand.*, 1975, 329, 1.
[15] C. D. Hurd and A. Tockman, *J. Org. Chem.*, 1958, **23**, 1087.
[16] G. I. Hobday and W. F. Short, *J. Chem. Soc.*, 1943, 609.
[17] S. Safe, *J. Chem. Soc.*, (*B*), 1971, 962.
[18] H. Tsuruta, K. Tomisawa, and T. Mukai, *Bull. Chem. Soc. Japan*, 1972, **45**, 1584.
[19] W. Reppe, *Annalen*, 1956, **601**, 81; see also S. Miller, *J. Amer. Chem. Soc.*, 1956, **78**, 6091.

phonyl group in the readily available sulphones (7) or (8) thus represents a simple procedure to produce aryl acetaldehyde derivatives from benzaldehydes. This compares favourably with known procedures including a recently published route [20] using methylthiomethyl sulphoxide. It should be pointed out that in the sulphone route the elimination step gives a sulphinate salt back which can be recycled.[21]

EXPERIMENTAL

All the reactions were run under an atmosphere of dried argon. Melting and boiling points are uncorrected. N.m.r. spectra were obtained using a Varian A 60 spectrometer in $CDCl_3$ solution with $SiMe_4$ as an internal standard; their descriptions (δ, J/Hz) use the following abbreviations: s = singlet, d = doublet, m = multiplet, b = broad. U.v. spectra were recorded on a Beckman DK 2A apparatus and i.r. spectra on a Perkin-Elmer 257 spectrophotometer. Mass spectra were obtained for solids on a Varian Mat CH7 apparatus and for liquids on a Mat III coupled with g.l.c. (OV 17). G.l.c. analyses were run on a Intersmat GC 120 SL chromatograph. T.l.c. analyses or preparative separations (p.l.c.) were performed on silica gel [PF 254; solvent: CH_2Cl_2–cyclohexane–ethyl acetate (50 : 50 : 10; v/v)]. Solvents were dried by conventional methods: dimethyl sulphoxide (DMSO) and methylene chloride were distilled from calcium hydride, tetrahydrofuran (THF), and ether from benzophenone–sodium, dimethylformamide (DMF), pentane, cyclohexane, and benzene from P_2O_5.

2,4-Dinitrophenylhydrazones (DNP) of both enol-ethers and acetals were obtained by treatment with a molar equivalent of 2,4-dinitrophenylhydrazine in ethanolic perchloric acid solution. After 24 h at room temperature the coloured precipitates were filtered off and washed with water until neutral. T.l.c. analysis of the crude compound so obtained showed their homogeneity; purification for analysis was effected by recrystallisation from ethanol–methylene chloride and drying *in vacuo*.

Phenyl methyl sulphone (1a) and phenyl ethyl sulphone (1b) were prepared by published procedures.[22]

Synthesis of αβ-Unsaturated Sulphones.—Three general procedures were used.

Procedure A. Condensation of an alkyl phenyl sulphone with an aromatic aldehyde with phase-transfer catalysis according to the procedure of Umani-Ronchi.[4]

At the end of reaction (controlled by t.l.c.), the necessary excess of aldehyde was removed by distillation under reduced pressure. The crude product crystallised on trituration in ether. Filtration on silica gel (methylene chloride), followed by recrystallisation from carbon tetrachloride, gave a pure product.

Procedure B. Condensation of the lithiated sulphone with the carbonyl derivative according to published procedures [23a,b] followed by dehydration of the intermediate hydroxy-sulphone by means of 85% H_3PO_4.[5c] After hydrolysis (ice–water), the unsaturated sulphones (generally crystalline at this stage) were filtered off, washed with water, recrystallised twice from MeOH, and dried *in vacuo*; yields were not optimised.

Procedure C. Oxidation by H_2O_2–AcOH of the corresponding sulphide.[5a,*]

β-Hydroxy Sulphones.—In some cases, the hydroxy sulphones (procedure B, see above) were purified by chromatography (see Table 1) (silica gel, solvent dichloromethane) and then crystallised.

TABLE 3

N.m.r. and mass spectra data of styryl and β-hydroxy-sulphones

Sulphone	δ Values (J in Hz)	m/e *
(8a) †	6.7—8.15 (11 H, m), 3.82 (3 H, s)	132, 274 (M^+), 77, 209, 179
(8b)	6.67—8.15 (11 H, m in which d, J 16.5 at 6.8) 3.82 (3 H, s)	
(8d)	7.15—8.2 (10 H, m); 6.9 (1 H, d, J 15.5)	125, 243, 101, 75, 278 (M^+)
(8f)	6.6—8.2 (11 H, m), 2.9 (1 H, sept., J 7); 1.25 (6 H, d, J 7)	144, 129, 286 (M^+), 271
(8h)	6.83—8.15 (10 H, m); 3.84 (3 H, s); 2.14 (3 H, s)	146, 77, 288 (M^+), 103, 131, 115
(7e)	7.18—8.15 (8 H, m), 5.43 (1 H, dd), 3.38 (3 H, b d–bs)	330 (M^+), 312
(13)	7—8.7 (9 H, m), 6.3 (1 H, bs, OH), 5.2—5.5 (1 H, m); 3.3—3.8 (2 H, m)	

* Mass spectra peaks in order of decreasing intensity. † $\nu_{max.}$ 962 cm^{-1}.

O-Methyl Ether of 1-(2,3-Dimethoxyphenyl)-2-phenylsulphonylethanol (12).—One molar equivalent of methyl iodide in hexamethylphosphotriamide (10 ml) was added to the THF solution of the lithium alkoxide resulting from the condensation of the sulphone (1a) with 2,3-dimethoxybenzaldehyde. The reaction mixture was stirred for 10 h at −10 to −20 °C then extracted to give a solid (yield 90%). This was crystallised twice from ether to give (12) (yield 42%) as white needles, m.p. 139.5 °C; n.m.r.: 6.75—8.2 (8 H, m), 5.1 (1 H, dd), 3.75 (6 H, 2s), 3.5 (2 H, bd), and 3.18 (3 H, s); m/e 336 (M^+). $C_{17}H_{20}O_5S$ = 336 (Found: S, 9.38. $C_{17}H_{20}O_5S$ requires S, 9.51%).

Preparation of αβ-Unsaturated Sulphides (6).—*Z*-Sulphides were prepared according to literature procedure [5a] by heating phenylacetylene with the sodium salt of the desired arenethiol in ethanol. *Z*-2-Phenylvinyl phenyl sulphide *Z*-(6a), m.p. 42—44 °C (from pentane) (lit.,[5a] 45 °C); *Z*-2-phenylvinyl *p*-tolyl sulphide *Z*-(6b), m.p. 65 °C (from pentane) (lit.,[5a] 64.5 °C).

The corresponding *E*-sulphides were obtained by treating *E*-β-bromostyrene with the sodium salt of the arenethiol in DMF for 6 h at 130 °C. After hydrolysis, extraction (ether), and evaporation of the solvent, the residue was distilled to remove unchanged bromostyrene.

E-2-phenylvinyl phenyl sulphide *E*-(6a) had b.p. 135 °C at 0.3 Torr (lit.,[5a] 142—143 °C at 0.5 Torr), m.p. 28—29 °C; *E*-2-phenylvinyl *p*-tolyl sulphide *E*-(6b) had m.p. 45 °C (from pentane) (lit.,[5a] 44—45 °C).

Preparation of an Authentic Sample of Z-Enol Ethers.—Treatment of phenylacetylene with the desired alkoxide in alcohol [24a] gives the title compounds. Attempts to prepare the *Z*-benzyl ether (5c) by this technique were unsuccessful; no identifiable product was formed. *Z*-2-Phenylvinyl methyl ether *Z*-(5a), b.p. 44 °C at 0.2 Torr (lit.,[24a] 44 °C at

[20] K. Ogura, M. Yamashita, and G. Tsuchihashi, *Synthesis*, 1975, 385.
[21] G. E. Vennstra and B. Zwanenburg, *Synthesis*, 1975, 519.
[22] C. M. Suter, 'The Organic Chemistry of Sulphur', John Wiley, New York, 1944.
[23] (*a*) W. E. Truce, T. C. Klingler, *J. Org. Chem.*, 1970, **35**, 1834; (*b*) J. M. Paris, Thesis, Paris, 1973.
[24] (*a*) J. E. Baldwin and L. E. Walker, *J. Org. Chem.*, 1966, **31**, 3895; (*b*) R. Tanaka, M. Rodgers, R. Simonaitis, and S. I. Miller, *Tetrahedron*, 1971, 2651.

0.3 Torr); n.m.r. C*H*=C*H* J = 7 Hz (lit.,[24b] 7 Hz); DNP; m.p. and mixed m.p. 121 °C (from ethanol); *Z*-2-phenylvinyl hexyl ether *Z*-(5b), b.p. 76 °C at 0.2 Torr, n.m.r.: C*H*=C*H*, J = 7 Hz; DNP, m.p. and mixed m.p. 121 °C (from ethanol).

TABLE 4

N.m.r. and mass spectra of enol ethers, acetals, and acetylenic compounds

Cmpds	δ Values (J in Hz)	*m/e* *
E-(5a)	7.42br (5 H, s), 7.24 (1 H, d, J 14), 5.98 (1 H, d, J 14), 3.76 (3 H, s)	135 (M^+ + 1), 134 (M^+)
E-(5b)	7.43br (5 H, s), 7.23 (1 H, d, J 14), 6.03 (1 H, d, J 14), 3.97br (2 H, t, J 7), 0.8—2 (11 H, m)	204 (M^+)
E-(5c) †	Identical to literature values.	
E-(9a)	6.6—7.4 (5 H, m), 5.83 (1 H, d, J 12.5), 3.78 (3 H, s), 3.66 (3 H, s)	
E-(9b)	6.8—7.3 (5 H, m), 5.88 (1 H, d, J 12), 3.78 (3 H, s), 3.67 (3 H, s)	164 (M^+)
E-(9c)	6.62—7.33 (4 H, m in which d at 7.18 J 13.5), 6.06 (1 H, d, J 13.5), 3.82 (6 H, s), 3.7 (3 H, s)	194 (M^+), 136, 151, 91
E-(9d)	7.76 (5 H, m in which d at 7.1 J 14), 6.16 (1 H, d, J 14), 3.38 (3 H, s)	168/170 (M^+)
E-(9f)	6.5—7.2 (6 H, m), 3.58 (3 H, s), 2.9 (1 H, m), 1.18 (6 H, d, J 7)	161, 176 (M^+), 128, 91, 118
(9g)	7.3 (6 H, m), 3.66 (3 H, s), 2.04 (3 H, s)	148 (M^+), 105, 43, 91, 133
(10e)	7.2—7.5 (3 H, m), 4.62 (1 H, t, J 5.5), 3.35 (6 H, s), 3.04 (2 H, d, J 5.5)	75, 159
(11g)	7.38br (5 H, s), 2.08 (3 H, s)	115, 116 (M^+)
(11h) ‡	6.84—7.38 (4 H, AA'BB' 9), 3.76 (3 H, s), 2 (3 H, s)	146 (M^+)
(14)	7.2—8.6br (4 H, 2 d), 4.6 (1 H, t, J 6.5), 3.33 (6 H, s), 2.9 (2 H, d, J 6.5)	

* Mass spectra peaks in order of decreasing intensity. † $\lambda_{max.}$(EtOH) 207 nm (ε 22 000) (lit.,[2] 207 nm). ‡ N.m.r. spectrum agrees well with literature data.[25]

Reactions of α,β-Unsaturated Sulphones with Sodium Alkoxides.—General procedure. The desired alcohol (10^{-2} mol) was added to a suspension of one molar equivalent of sodium hydride (0.48 g of a 50% dispersion of sodium hydride in oil washed twice with pentane) in DMSO (10 ml).* The resulting grey slurry was stirred for 16 h at 24 °C. An M-solution of the unsaturated sulphone in dimethyl sulphoxide (10 ml) was added dropwise over 15 min. The coloured mixture was stirred for 48 h at room temperature, and then poured into ice–water and extracted with methylene chloride (3 × 50 ml). The organic layers were thoroughly washed with water and then dried (K_2CO_3). Evaporation of solvent followed by short-path distillation (bulb tube) gave the ethers which are relatively unstable and were, after structural determination (Table 4), transformed into the DNP derivatives (Table 5).

Reaction of E*-Styryl Phenyl Sulphone* (3) *with Thiols (Sodium Salts).*—Sodium salts of aromatic thiols were prepared by addition of 10^{-2} mole of either benzene- or toluene-*p*-thiol to one molar equivalent of sodium hydride in DMSO (10 ml). After release of hydrogen (1 h), the sulphone (10^{-2} mol), with or without added cuprous iodide–tributylphosphine (10^{-3} mol), in DMSO (10 ml) was rapidly added. The mixture was stirred for 8 h at 100 °C, hydrolysed, and extracted (cyclohexane). Filtration on a short column of silica gel and evaporation of the solvent, gave an oily residue, the n.m.r. spectrum of which was recorded; the oil was then distilled (bath temp. 180 °C, 0.3 Torr); crystallisation was then induced by trituration under pentane.

Reaction with benzenethiol (without cuprous ions) gave in 34% yield (b.p. 138 °C at 0.1 Torr) *E*-styryl phenyl sulphide (6a) [retention time on g.l.c. (SE 30); n.m.r. and mass spectra as authentic (see above)].

Reaction with toluene-*p*-thiol (without cuprous ions) gave in 30% yield *E*-(6b), m.p. and mixed m.p. 45 °C.

Reaction with toluene-*p*-thiol (with added cuprous ions) gave in 70% yield *E*-(6b), m.p. and mixed m.p. 45 °C; n.m.r. on the crude product [C*H*=C*H*, δ 6.63br (d)] indicated the absence of the *Z*-isomer (δ 6.32, s); g.l.c. (SE 30) showed the presence of a small impurity which was found to be *p*-tolyl disulphide [*m/e* 246 (M^+)].

Reaction of E*-Styryl Sulphone* (3) *with Thiols under Free-radical Conditions.*—The sulphone (3) (1.22 g, 5 × 10^{-3} mol) thiophenol (1 ml, 10^{-2} mol, distilled under argon just before use), and azobisisobutyronitrile (200 mg) were stirred for 10 h at 60 °C, then for 16 h at 25 °C in benzene (10 ml). The resulting homogeneous solution was washed

TABLE 5

DNP derivatives of the corresponding arylacetaldehydes obtained from either enol ethers or acetals

Substrate	DNP yield (%)	M.p. (°C)	Lit. m.p. (°C)	Ref.	Formula	Found	Required	*m/e* *
E-(5a)	100	120 †						
E-(5b)	100	120—121 †						
E-(5c)	100	121 †						
(9a)	100	137	134	26*c*				
(9b)	79	132	137	26*b*				
(9c)	76	151	136—137	27	$C_{16}H_{16}N_4O_6$	N15.35	N15.55	91, 136, 162, 360 (M^+)
(9d)	82	135	134—136	26*a*				
(9f)	91	119.5			$C_{17}H_{18}N_4O_4$	N16.2	N16.35	117, 155, 133, 342 (M^+), 307
(9g)	82	149.5—100 †						
(10e)	100	217—218			$C_{14}H_{10}Cl_2N_4O_4$	N15.35	N15.15	159, 152, 161, 368 (M^+)
(14)	89 ‡	226—230 (dec.)			$C_{12}H_{12}ClN_5O_8$	N17.6	N17.45	104, 92, 301 M^+-($HClO_4$)

* Mass peaks in order of decreasing intensity. † M.p. and mixed m.p. ‡ Perchlorate salt.

* In one case [the reaction of sodium benzyl oxide with the styryl sulphone (3)] dimethylformamide was substituted for the dimethyl sulphoxide but since it gave a poorer yield, it was not further used.

[25] P. Gramatica, D. Monti, and P. Manitto, *Gazzetta*, 1974, **104**, 629.

[26] (*a*) G. Signarella, L. Mariani, and E. Testa, *Gazzetta*, 1965, **95**, 831; (*b*) R. B. Lotfield, *J. Amer. Chem. Soc.*, 1950, **72**, 2499; (*c*) A. K. D. Gupta and J. K. Chakrabarti, *J. Sci. Ind. Res. India*, 1961, **20B**, 394.

[27] A. I. Meyers and J. C. Sricar, *J. Org. Chem.*, 1967, **32**, 4134.

with 5% sodium hydroxide (3 × 50 ml), dried over potassium carbonate, and evaporated. The residue (1.98 g) was a rather complex mixture (t.l.c., pentane) and was chromatographed on silica gel (methylene chloride). This gave first 1.25 g of an oil, then 0.7 g of unchanged sulphone (3). The oily fraction was again chromatographed (p.l.c., eluting three times with pentane) and gave four fractions. Two of these (0.26 g), which had the lowest retention times, were unidentified products and not further studied. The two others, with longer retention times, were well crystallised and identified (n.m.r., *m/e*, mixed m.p. with authentic samples) as being diphenyl disulphide (0.5 g) and *E*-2-phenylvinyl phenyl sulphide (6a) (0.11 g, 25%, based on reacted sulphone).

Unsuccessful Substitution Reactions.—(a) *With potassium phthalimidate.* Heating of the sulphone (3) with one equimolecular amount of the potassium salt of phthalimide in DMSO at 80 °C for several hours gave unchanged (3).

(b) *With the sodium salt of* N-*methylaniline.* Absence of any substitution product was confirmed by comparison (n.m.r.) of the reaction mixture with an authentic sample [28] of enamine.

(*c*) *With potassium acetate.* Potassium acetate was melted before use. Compound (3) was recovered unchanged after several hours of heating.

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[28] P. Ramart-Lucas and J. Hoch, *Bull. Soc. chim. France*, 1936, 918; J. Hoch, *Compt. rend.*, 1934, **199**, 1438.