# Elimination and Addition Reactions. Part XXV.[1] † Addition–Elimination Reactions of Phenoxyvinyl Sulphones

By **Marijke J. van der Sluijs** and **Charles J. M. Stirling,*** School of Physical and Molecular Sciences, University College of North Wales, Bangor, Caerns.

Reactions of *cis*- and *trans*-2-phenoxyvinyl *p*-tolyl sulphones with alcoholic alkoxides have been studied. Product analyses and kinetic studies show that in each case a two-stage addition–elimination pathway is followed. The elimination step is assigned the $(E1cB)_R$ mechanism on the basis of measurements carried out in deuteriated solvents. The rate constants and activation parameters for both addition and elimination stages match closely the rate constants and activation parameters obtained for models which simulate the two stages individually. The results are discussed against the background of earlier work on elimination of poor leaving groups from activated saturated substrates, and of good leaving groups, particularly halide, from activated, unsaturated substrates. It is now shown that in an activated, unsaturated system with a poor leaving group, elimination with formation of acetylene does not compete effectively with an initial addition step.

SEVERAL earlier papers [2-4] in this series have reported on reactivity in 1,2-elimination reactions of substrates which bear very poor leaving groups such as phenoxy and phenylthio. These groups are expelled under basic conditions when the substrates are activated by β-cyano, acyl, sulphonyl, and other groups.

† Part of this work was presented at a meeting of the Organic Reaction Mechanisms Discussion Group of The Chemical Society, Liverpool, January 9th and 10th, 1974.

Recent work on reactions of nucleophiles with activated unsaturated substrates bearing good leaving groups has been summarised by Modena.[5] In these systems, two types of process occur: addition followed

[1] Part XXIV, P. F. Cann and C. J. M. Stirling, *J.C.S. Perkin II*, 1974, 820.
[2] J. Crosby and C. J. M. Stirling, *J. Chem. Soc.* (*B*), 1970, 671.
[3] J. Crosby and C. J. M. Stirling, *J. Chem. Soc.* (*B*), 1970, 679.
[4] R. P. Redman and C. J. M. Stirling, *Chem. Comm.*, 1970, 633.
[5] G. Modena, *Accounts Chem. Res.*, 1971, **4**, 73.

by elimination (termed substitution by Modena) and direct elimination with formation of an acetylene.

Our work had the objective of providing a comparison with earlier work on saturated systems which contain poor leaving groups and with other work on unsaturated systems bearing good leaving groups. The substrates that we have examined are shown in the Scheme; our chief interest was in the reactivity of the phenoxyvinyl sulphones (1) with alkoxides in alcohols. These reactions have been studied with reference to variation in reactivity with stereochemistry and with the nature of the leaving group. Comparisons with model systems (Scheme) and with systems studied earlier have been drawn.

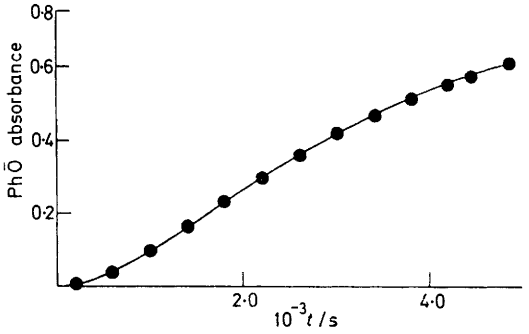
## METHODS AND RESULTS

*Substrates and Products.* The *cis*-ether (1a) was obtained by base-catalysed stereospecific addition of phenol to *p*-tolylsulphonylacetylene (7) under carefully controlled conditions (Experimental section). The *trans*-isomer (1b) was obtained from the corresponding chloride by treatment with sodium phenoxide in benzene. When phenol was used as solvent, the bisphenoxy-compound (8) was obtained. Configurations were readily assigned on the basis of the n.m.r. coupling constants of the vinylic protons.

Treatment of the *cis*- or *trans*-phenoxyvinyl sulphones (1) and of the bisphenoxy-derivative (8) with an excess of ethanolic sodium ethoxide gave the bisethoxy-derivative (5; R = Et). The bisphenoxy-compound with one molar proportion of ethoxide gave a mixture of the *trans*-phenoxy-sulphone (1b) and the *trans*-ethoxysulphone (4b; R = Et). No *cis*-isomers, which would have been clearly identifiable from the difference in vinylic coupling constants, were obtained. Similarly, neither *cis*- nor *trans*-phenoxy-derivatives (1a and b) on treatment with ethanolic sodium ethoxide gave any detectable amount of *cis*-ethoxy-compound (4a), whereas this was easily obtained pure from the acetylene (7) under the same conditions. Careful examination of the products of partial reactions of the phenoxyvinyl sulphones with ethanolic sodium ethoxide failed to reveal any trace of the acetylene (7) and showed only (4b) as the intermediate product. The products, therefore, exclude the elimination–addition route: (1a or b) ⟶ (7) ⟶ (4).

Formation of the stoicheiometric amounts of the complementary product, phenol, was confirmed spectroscopically in rate measurements on each substrate. It was consistently observed that for reactions lasting up to several hours, the stoicheiometric phenoxide concentration was about 94% of the theoretical values. This short-fall was traced to the effect of irradiation in the spectrometer. Solutions of comparable concentrations of sodium phenoxide in ethanol showed similar slow decreases of absorbance on irradiation. This photochemical process was a slowly attained equilibrium; when irradiated ' infinity ' solutions showing lower than theoretical absorbance values were kept in the dark, subsequent rapid measurement of phenoxide concentration gave theoretical absorbance values. Sodium perchlorate, used to maintain a constant ionic strength, was shown to have no effect on the phenomenon, and neither did oxygen. The nature of this process is not understood but it is known that for nitrophenols under long periods of irradiation, reversibility is lost.[6] Appropriate corrections have been made to the kinetic results.

*Kinetics.*—Reactions of the phenoxy-derivatives were followed by measurement of the formation of phenoxide ion by its absorbance at 300 nm. For substrates (1a and b), plots of absorbance against time gave sigmoid curves, similar to those reported [7] for consecutive first-order reactions. A typical plot is shown in the Figure.




Formation of phenoxide ion from reaction of *cis*-2-phenoxyvinyl *p*-tolyl sulphone with methanolic sodium methoxide (up to 80% completion); curve calculated from $k_1$ and $k'$; points are experimental values

Plots of absorbance against wavelength showed shifting isosbestic points indicating that reactions did not involve a single-stage conversion of reagent into product. It was assumed that a single kinetically important intermediate (3) was formed (Discussion section) and that $k_{-2} \gg k_1$ and $k_{-2} \gg k_2$ (Scheme). This led to the rate equations (i)—(iii), where $k'$ is the experimentally found

$$d[(1)]/dt = -k_1[(1)][\bar{O}R] \quad \text{(i)}$$

$$d[(3)]/dt = k_1[(1)][\bar{O}R] - k'[(3)][\bar{O}R] \quad \text{(ii)}$$

$$d[\bar{O}Ph]/dt = k'[(3)][\bar{O}R] \quad \text{(iii)}$$

rate constant for the overall reaction (3) ⟶ (4). As large excesses of base were used, [ŌR] can be considered constant and the reactions, therefore, showed first-order kinetics. The rate constants $k_1$ and $k'$ were experimentally found to be second-order. Integration [7] of the three equations gave equation (iv), and computer calculations yielded $k_1$ and $k'$ (Experimental section).

$$[\bar{O}Ph] = [(1)]_0\left[1 + \frac{1}{k' - k_1}(k_1 e^{-k'[\bar{O}R]t} - k' e^{-k_1[\bar{O}R]t})\right] \quad \text{(iv)}$$

Values of $k_1$ and $k'$ are shown in the Table. The calculation does not assign $k_1$ and $k'$ to the processes so labelled

[6] P. G. N. Moseley, personal communication.
[7] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' 2nd edn., Wiley, London, 1961, p. 166.

in the Scheme, as equation (iv) is symmetrical in $k_1$ and $k'$. The assignment is made on the basis of $k_1$ values measured directly by following the rate of disappearance of the phenoxyvinyl sulphones (Experimental section).

The accuracy of the larger rate constant decreases as the ratio large $k$ : small $k$ increases. In the extreme case, the smaller constant becomes rate-determining and the larger constant cannot be measured. For the *trans*-sulphone (1b) the ratio $k'$ : $k_1$ is typically 15 : 1 and for the *cis*-isomer (1a), 5 : 1. This must be borne in mind when considering the results.

The complexities mentioned above applied only to the phenoxyvinyl sulphones; simple first-order rate constants were obtained for the other substrates studied. The addition reaction (4b) ⟶ (5) was followed at 265 nm after completion of the formation of phenoxide from both (1a) and (1b). The addition rate constant was found to be independent of the stereochemistry of the starting compound. The addition reaction (4a) ⟶ (5) was followed at 245 nm after completion of the rapid addition [8] of one mole of ethanol to the acetylene (7). The rate constant for (4a) was found to decrease slowly as the reaction proceeded. The Table gives the values calculated up to 25% completion. Between 40 and 65% completion the rate constant obtained was 30% lower. This is probably owing to slow isomerisation of the *cis*-ethoxyvinyl sulphone (4a) to the *trans*-isomer (4b), which has a much lower rate of addition. When the addition reaction of (4a) was stopped half-way, the reaction mixture was found to consist of (4a), (4b), and the end-product (5).

The elimination reaction (8) ⟶ (1b) was easily followed in the first quarter of the total reaction (8) ⟶ (1b) ⟶ (4b), as the first elimination of phenol from (8) is about 10 times faster than the following two-step reaction of (1b). The elimination rate constants were statistically corrected as either of the phenoxy-groups may be eliminated.

## DISCUSSION

*Two-step Process.*—The two-step pathway (Scheme) involving addition followed by elimination is proposed for reactions with the phenoxyvinyl sulphones. Several lines of evidence support this proposal.

Rate constants for addition and elimination reactions

| Substrate | Base–Solvent [a] | $T$/K | $10^3 k_1$ [b] (addition) | $\Delta H^{\ddagger}$ [c] | $\Delta S^{\ddagger}$ [d] | $10^3 k'$ [b,h] (elimination) | $\Delta H^{\ddagger}$ [c] | $\Delta S^{\ddagger}$ [d] |
|---|---|---|---|---|---|---|---|---|
| (1a) | EtŌ–EtOH | 298 | 44 [e] ± 4 | 62 ± 10 | −61 ± 35 | 215 ± 15 | 80 ± 11 | +9 ± 35 |
| | | 303 | 63 ± 4 | | | 380 ± 30 | | |
| | | 308 | 105 ± 5 | | | 630 ± 60 | | |
| | EtŌ–EtOD | 298 | 77 ± 5 | | | 540 ± 50 | | |
| | MeŌ–MeOH | 298 | 4·9 ± 0·2 | | | 10·5 ± 1 | | |
| (1b) | EtŌ–EtOH | 298 | 22 [e] ± 2 | 40 ± 7 | −142 ± 23 | 285 ± 30 | 54 ± 17 | −73 ± 57 |
| | | 303 | 25 ± 1 | | | 400 ± 40 | | |
| | | 308 | 38·5 ± 2 | | | 600 ± 70 | | |
| | EtŌ–EtOD | 298 | 38 ± 2 | | | 540 ± 50 | | |
| | MeŌ–MeOH | 298 | 4·1 ± 0·2 | | | 25 ± 2 | | |
| (8) | EtŌ–EtOH | 298 | | | | 194 [f,g] ± 3 | 84 [f] ± 4 | +24 [f] ± 15 |
| | | 303 | | | | 337 [f,g] ± 5 | | |
| | | 308 | | | | 608 [f,g] ± 10 | | |
| | MeŌ–MeOH | 298 | | | | 5 [f,g] ± 0·1 | | |
| (4a) | EtŌ–EtOH | 298 | 19·5 [g] ± 0·5 | 68·5 ± 3 | −47 ± 11 | | | |
| | | 303 | 31·2 [g] ± 0·5 | | | | | |
| | | 308 | 50 [g] ± 1 | | | | | |
| | EtŌ–EtOD | 298 | 38 ± 1 | | | | | |
| (4b) | EtŌ–EtOH | 298 | 3·2 ± 0·5 | | | | | |
| (6) | EtŌ–EtOH | 298 | | | | 181 [i] ± 3 | | |

[a] All solutions made to 0·1M with $NaClO_4$. Units: [b] l mol$^{-1}$ s$^{-1}$. [c] kJ mol$^{-1}$. [d] J K$^{-1}$ mol$^{-1}$. [e] Rate constant directly determined from disappearance of substrate (see Experimental section). [f] Rate constants and activation parameters statistically corrected for this substrate. [g] Rate constants derived from first 25% of reaction. [h] $k'$ is the experimentally found rate constant for the overall reaction (3) + RŌ ⟶ (4) + ŌPh + ROH. [i] Part XX, ref. 3.

Examination of the products failed to disclose any formation of *p*-tolylsulphonylacetylene under conditions in which, had it been present even in small amounts, it would have been detected. Elimination of phenoxide is undoubtedly much slower than elimination of chloride in the corresponding halogenovinyl sulphones. The concentration of intermediate acetylene, therefore, would be much lower than that previously detected for the chlorides.[8] Notwithstanding this situation, however, the *stereochemistry* of product (4b) subsequently formed is decisive in showing that no acetylene is formed. Isomerisation of the *cis*-ethoxy-adduct (4a), the *kinetic* product of addition [8] to the acetylene (7), was found to be slow in comparison with the rate of formation of phenoxide from the phenoxy-sulphones and with the rate of formation of (4a) from the acetylene.[8] This implies that although any acetylene formed might be at a very low stationary concentration, the past history of its formation would show plainly in the products. None was formed.

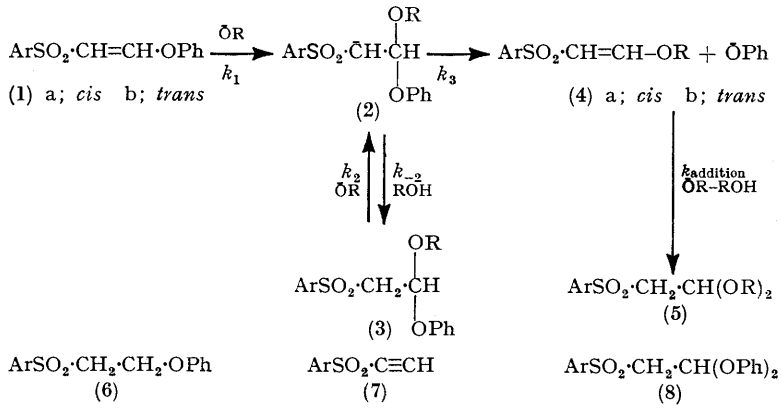
With the elimination–addition pathway excluded, addition–elimination and direct one-step vinylic substitution remain as alternatives. However, direct substitution in one step from vinylic carbon can reasonably be excluded. Displacement of phenoxide ion from

[8] L. Di Nunno, G. Modena, and G. Scorrano, *J. Chem. Soc.* (*B*), 1966, 1186.

anisole is very slow [9] ($k_{subst.} \gg 10^{-10}$ l mol$^{-1}$ s$^{-1}$) under these conditions. Direct displacement of phenoxide from $sp^2$-hybridised carbon is, therefore, inconceivable.[10]

The addition–elimination pathway is supported in detail by results from systems which are models for the separate addition and elimination steps. For the *cis*- and *trans*-phenoxyvinyl sulphones (1a and b) activation parameters for the putative addition and elimination stages have been obtained. These are compared (Table) with corresponding values for addition to the *cis*-ethoxy-compound (4a) and with the addition rate constant of the *trans*-ethoxy-compound (4b). The similarity in activation parameters is close, especially between the two *cis*-compounds (1a and 4a). Likewise, the source is probably sensitive to any out-of-plane deformation around the central carbon–carbon double bond. Such distortion is likely in the *cis*-isomer and has the effect of reducing the decelerative effect of the ethoxy-substituent.

The agreement between the elimination stage for (1a) and for the model bisphenoxy-compound (8) is close enough not to warrant much discussion of differences. For the *trans*-isomer (1b) there is greater disparity in the rate constants for the two stages, and the parameters for the second (elimination) stage are, therefore, much less precise than for the *cis*-isomer (1a). They do not agree at all well with the *cis*-isomer, nor with the model (8). Little significance should be attached to these activation




SCHEME

bisphenoxy-compound (8) serves as a model for the elimination stage of the overall reaction pathway. Here again the correspondence in activation parameters with the *cis*-isomer (1a) is remarkably close.

The differences between the rate constants and activation parameters for the individual stages of the two-stage process and the two single-stage models deserve comment. Both *cis*- and *trans*-phenoxyvinyl sulphones (1a and b) are more reactive in the addition stage than the corresponding model *cis*- and *trans*-ethoxyvinyl sulphones (4a and b). We ascribe this greater reactivity of the phenoxy-compounds to the fact that the carbon–carbon double bond is less depolarised by a phenoxy-group than by an ethoxy-group. This effect appears to be important notwithstanding the fact that the phenoxy-group is considerably more bulky than the ethoxy-group and that nucleophilic addition to carbon–carbon double bonds is known to be extremely sensitive to steric obstruction.[11]

Comparison of the phenyl ethers with ethyl ethers shows that the ratio of rate constants for addition to the *trans*-isomers (1b) and (4b) is 7 : 1 whereas this ratio is about 2 : 1 for the *cis*-isomers (1a) and (4a). The degree of interaction between the sulphonyl group and the ether oxygen atom acting as a conjugative electron parameters because of their poor accuracy. The rate constants for the elimination steps of the *cis*- and *trans*-compounds (1a and b) are in reasonable agreement with each other, as expected for a common process.

trans : cis *Addition Ratio.*—The *trans*-isomer is less reactive than the *cis*-isomer towards addition of ethoxide and methoxide ions. The *cis*-isomer undoubtedly has a higher initial state energy than the *trans*- but this is not directly reflected in the activation parameters. The enthalpy of activation for the *trans*-isomer is markedly less than for the *cis*-. Modena [5,12] has reported similar differences for the reaction of the geometric β-halogenostyrene isomers with benzenethiolate ion in methanol. A *trans* : *cis* ratio of 3 : 1 was found for β-bromo-*p*-nitrostyrene, whereas for β-bromo-2,4-dinitrostyrene [13] this ratio was 35 : 1. Enthalpies of activation for the *trans*-compounds were always smaller than those for the *cis*-compounds. This effect was attributed to lack of coplanarity in the *cis*-isomers, which hinders the efficient transmission of the accelerating effect of the nitro-group.

In the present case, the *trans* : *cis* ratio for the ethoxy-compounds is 0·17 : 1, but for the phenoxy-compounds this ratio is greater (0·5 : 1), in agreement with Modena's

[9] D. R. Marshall, P. J. Thomas, and C. J. M. Stirling, unpublished results.

[10] J. Hine, ' Physical Organic Chemistry,' 2nd edn., McGraw-Hill, London, 1962, p. 399.

[11] S. T. McDowell and C. J. M. Stirling, *J. Chem. Soc.* (*B*), 1967, 351.

[12] G. Marchese, F. Naso, and G. Modena, *J. Chem. Soc.* (*B*), 1968, 958.

[13] G. Marchese, G. Modena, and F. Naso, *Tetrahedron*, 1968, **24**, 663.

conclusions. For the corresponding 2-chlorovinyl *p*-tolyl sulphones Modena [5] reports a *trans* : *cis* ratio of 0·5 : 1 for the reaction with benzenethiolate ion in methanol.

*Reaction Mechanisms.*—We are able to suggest detailed mechanisms for each step in the reaction pathway.

For base-catalysed additions of alcohols to αβ-unsaturated sulphones, rate-determining formation of an intermediate carbanion [*cf.* (2)] has been suggested.[14,15] Rapid proton transfer from the solvent to the carbanion follows. This mechanism corresponds on our scheme to $k_1$ followed by $k_{-2}$ and seems most likely ($k_1 \ll k_{-2}$).

The rate constants $k_1$ and $k'$ are both second-order and this excludes an elimination mechanism which involves the direct pathway (1) ⟶ (2) ⟶ (4). The rate constant $k'$ should, therefore, be designated as the overall rate constant for the conversion (3) ⟶ (4). This conversion may occur stepwise as shown in the Scheme, involving, as rate-limiting step, either that designated by $k_2$ or that designated by $k_3$. The third possible alternative is direct conversion of (3) into (4) in a single-stage concerted process.

Both steps for the phenoxyvinyl isomers have their rate constants approximately doubled by transfer from ethanol to ethan[$^2$H]ol. As the direct pathway (1) ⟶ (2) ⟶ (4) is excluded, intermediate (3) must pick up deuterium from the solvent. If the conversion of (3) into (4) involves a concerted process or formation of (2) *via* rate-determining ionisation of (3), a primary deuterium isotope effect would operate so as to reduce the rate constant of the second stage of the overall sequence. This is not observed. This leaves the pre-equilibrium $(E1cB)_R$ [16] mechanism for conversion of (3) into (4) as the only likely one. Conversion of (3) into (4) *via* (2) by this mechanism is entirely analogous to earlier [3] results of elimination in saturated phenoxy-compounds. Surprisingly, the $k'$ values for the *cis*- and *trans*-phenoxyvinyl isomers (1) and for the bisphenoxy-derivative (8) are all the same as for the monophenoxy-derivative (6) within a factor of 1·5. Inductive increase of $k_2$ and decrease of $k_3$ might be expected for the bis-ethers. The effects appear to cancel.

Stereochemistry of the elimination steps requires comment. Only *trans*-alkoxyvinyl sulphone is formed from all three phenoxy-derivatives under conditions in which, had *cis*-alkoxyvinyl sulphones been formed, they would have been detected. This specificity indicates that the energy differences between the conformers which allow antiperiplanar elimination of phenoxide from (2) are sufficiently large to make that which leads to the *trans*-product the only observable one. Modena [17] finds in the reaction of *p*-nitro-β-halogenostyrenes with methoxide in methanol that when a very good leaving group (chloride or bromide) is displaced, configuration is retained for both *trans*- and *cis*-isomers in the addition–elimination pathway but with the poorer leaving group, fluoride, the thermodynamically more stable *trans*-isomer is always formed. Change of stereospecificity with leaving group simply reflects the fact that conformational equilibration partially competes with shedding of the leaving group, and is complete if the leaving group is a poor one, *i.e.* if $k_3$ is small.

Results of reactions in methanol provide further confirmation for the mechanisms suggested. For the addition stage, broadly similar EtŌ : MeŌ ratios are observed for the *cis*- (9 : 1) and *trans* (5 : 1) phenoxyvinyl sulphones. These ratios compare very well with those reported previously. For phenylvinyl sulphone [14] the ethoxide : methoxide ratio is 6 : 1 and for *trans*-2-chlorovinyl *p*-tolyl sulphone [18] it is 3 : 1.

For the phenoxyvinyl isomers (1), the elimination rate constants are reduced by a factor of about 20 in methanol. This is consistent with the lower basicity of the medium. For the bisphenoxy-model (8), this ratio (40 : 1) is maintained and is broadly similar to those obtained [19] for related activated systems: $PhSO_2{\cdot}CH_2{\cdot}CH_2{\cdot}Cl$ [$(E1cB)_I$ or concerted mechanism] (ratio 36 : 1) and $PhSO_2{\cdot}CH_2{\cdot}CH_2{\cdot}SO_2Ph$ [$(E1cB)_R$ mechanism] (ratio 105 : 1).

*Comparison with Other Work.*—Our results allow comparison of the reactivity in addition reactions of phenoxy- or alkoxy-vinyl sulphones with the chlorovinyl sulphones studied by Modena.[5,8,18] The greater reactivity of the chlorides (by a factor of about 20) is reasonably accounted for by smaller depolarisation of the double bond occasioned by the smaller mesomeric interaction between the sulphonyl group and the chlorine atom. The unsubstituted phenylvinyl sulphone is reported [14] to have about the same rate constants for addition of MeOH and EtOH as the 2-chloro-substituted compounds.[18] These results however are not precisely comparable with each other as a solution of sodium hydroxide in the alcohol was used for the unsubstituted compounds whereas Maioli and Modena [18] used the sodium alkoxide, as in our work.

## EXPERIMENTAL

*Substrates.*—trans-2-*Chlorovinyl* p-*tolyl sulphone*. This was prepared as described by Montanari.[20] His product was later [18] established to be the *trans*-isomer.

trans-2-*Phenoxyvinyl* p-*tolyl sulphone* (1b). *trans*-2-Chlorovinyl *p*-tolyl sulphone (1 g) was refluxed with a suspension of dry sodium phenoxide (1 mol) in dry benzene (10 ml) for 5 h. The mixture was washed with water and evaporated. Crystallisation of the residue (1·13 g) gave the pure *sulphone* (0·581 g, 46%), m.p. 114·7° (from methanol) (Found: C, 65·8; H, 5·25. $C_{15}H_{14}O_3S$ requires C, 65·7; H, 5·1%), τ ($CDCl_3$) 1·7—2·7 (10H, m), 3·7 (1H, d, *J* 12 Hz), and 7·4 (3H, s).

[14] W. G. Davies, E. W. Hardisty, T. P. Nevell, and R. H. Peters, *J. Chem. Soc.* (*B*), 1970, 998.
[15] R. N. Ring, G. C. Tesoro, and D. R. Moore, *J. Org. Chem.*, 1967, **32**, 1091.
[16] F. G. Bordwell, M. M. Vestling, and K. C. Yee, *J. Amer. Chem. Soc.*, 1970, **92**, 5950.
[17] G. Marchese, F. Naso, and G. Modena, *J. Chem. Soc.* (*B*), 1969, 290.
[18] L. Maioli and G. Modena, *Gazzetta*, 1959, **89**, 854.
[19] R. W. Howsam, D. R. Marshall, P. J. Thomas, and C. J. M. Stirling, unpublished work.
[20] F. Montanari, *Gazzetta*, 1956, **86**, 406.

2,2-*Bisphenoxyethyl* p-*tolyl sulphone* (8). *trans*-2-Chlorovinyl *p*-tolyl sulphone (0·0053 mol) was kept with sodium hydroxide (0·0070 mol) and phenol (0·1 mol) at 100° for 1 h. The dark oil was poured into water and extracted with dichloromethane. The extract was washed with saturated aqueous sodium hydrogen carbonate, dried, and evaporated. Excess of phenol was removed by sublimation at 100° and 0·1 mmHg, and the residue, on crystallisation from methanol, afforded the *bis-sulphone* (50%), m.p. 104·6° (Found: C, 68·4; H, 5·6. $C_{21}H_{20}O_4S$ requires C, 68·5; H, 5·4%), τ ($CDCl_3$) 1·8—2·9 (14H, m), 3·4 (1H, t, *J* 6 Hz), 6·05 (2H, d, *J* 6 Hz), and 7·4 (3H, s).

p-*Tolylsulphonylacetylene* (7). This was obtained by oxidation [21] of ethynyl *p*-tolyl sulphide.[22]

cis-2-*Phenoxyvinyl* p-*tolyl sulphone* (1a). *p*-Tolylsulphonylacetylene (7) (0·015 mol) and phenol (0·23 mol) were kept at 60° for 8 h together with sodium carbonate (0·5 g). The mixture was taken up in dichloromethane and the solution washed with brine, and evaporated. Excess of phenol was distilled off at 50° and 0·1 mmHg. The residue was extracted with light petroleum (b.p. 90—100°). The extract was evaporated and the residue, in the minimum amount of *hot* methanol, was filtered. The filtrate, at 0°, afforded the cis-*sulphone* (25%), m.p. 90·2° (from methanol) (Found: C, 65·5; H, 5·3%), τ ($CDCl_3$) 1·6—2·9 (10H, m), 3·85 (1H, d, *J* 7 Hz), and 7·5 (3H, s).

*Product Analyses.*—(a) *Reaction with* p-*tolylsulphonylacetylene* (7). The acetylene (0·5 mmol) was treated with ethanolic sodium ethoxide (0·05 mmol) so as to give a 0·005M-solution. After 4 min (first addition complete), acetic acid (0·05 mmol) was added. Work-up as above afforded a product whose n.m.r. spectrum showed it to be *cis*-2-ethoxyvinyl *p*-tolyl sulphone (4a), as found previously.[8] If, however, the reaction mixture was kept for 1 h, then a mixture of *cis*- and *trans*-2-ethoxyvinyl sulphone (4a and b) and 2,2-bisethoxyethyl *p*-tolyl sulphone (5) was found (n.m.r.).

The *cis*-ethoxy-compound (4a) showed τ ($CDCl_3$) 1·7—2·4 (4H, m), 3·1 (1H, d, *J* 7 Hz), 4·2 (1H, d, *J* 7 Hz), 5·7—6·1 (2H, q, $CH_2$), 7·5 (3H, s), 8·6—9·1 (3H, m, Me). The *trans*-ethoxy-compound (4b) showed τ ($CDCl_3$) 1·7—2·5 (5H, m), 4·1 (1H, d, *J* 12 Hz), 5·7—6·1 (2H, q), 7·5 (3H, s), and 8·6—9·1 (3H, m). [For $^1$H n.m.r. data of the bisethoxy-compound, see below (complete reaction).]

(b) *Reactions with* 2-*phenoxyvinyl* p-*tolyl sulphones* (1). *Partial reactions.* cis-2-*Phenoxyvinyl* p-*tolyl sulphone* (1a). This (0·5 mmol) was treated with ethanolic sodium ethoxide (0·57 mmol) so as to give a 0·02M-solution. After about 1 h (*i.e.* about 60% completion) acetic acid (0·56 mmol) was added and the solution was evaporated. The residue in tetrachloromethane was filtered and evaporated. The n.m.r. spectrum of the residue showed a mixture of the starting compound (1a) and *trans*-2-ethoxyvinyl *p*-tolyl sulphone (4b). Signals with the characteristic coupling constants of the *cis*-isomer (4a) were absent.

trans-2-*Phenoxyvinyl* p-*tolyl sulphone* (1b). This was treated as above. The n.m.r. spectrum of the product showed a mixture of (1b) and (4b), again without any *cis*-ethoxy compound (4a) present.

*Complete reaction. trans*-2-Phenoxyvinyl *p*-tolyl sulphone (1b) (0·004 mol) in ethanol was treated with ethanolic sodium ethoxide (0·018 mol) so as to give a 0·2M-solution. After 2 days, the solution was poured into saturated brine, acidified with acetic acid, and extracted with dichloromethane. The residue from evaporation (1·18 g) was distilled to give a fore-run of phenol and then 2,2-*bisethoxyethyl* p-*tolyl sulphone* (5; R = Et) (84%), b.p. 98° at 1·5 × $10^{-4}$ Torr (Found: C, 57·0; H, 7·4. $C_{13}H_{20}O_4S$ requires C, 57·3; H, 7·4%), τ ($CDCl_3$) 1·7—2·4 (4H, m), 4·8 (1H, t, *J* 6 Hz), 6·2—6·6 (6H, m, 2 × $CH_2O$ and $CH_2S$), 7·5 (3H, s), and 8·9 (6H, t, *J* 7 Hz).

(c) *Reactions with* 2,2-*bisphenoxyethyl* p-*tolyl sulphone* (8). Reactions with an excess of ethanolic sodium ethoxide as for the preceding compound, gave the bisethoxy-sulphone (92%). When the reaction was repeated with an equimolar proportion of ethanolic sodium ethoxide and the reaction mixture was set aside for 1 h, work-up as above gave a product mixture (1·6 g) recrystallisation of which from methanol gave *trans*-2-phenoxyvinyl *p*-tolyl sulphone (1b) (55%), m.p. and mixed m.p. 114·3°. The mother liquors from recrystallisation were combined and evaporated. The n.m.r. spectrum of the residue showed the presence of a mixture of the *trans*-phenoxyvinyl and the *trans*-ethoxyvinyl sulphone. Signals with the characteristic coupling constants of *cis*-vinylic protons were absent.

*Kinetics.*—Ethanol and methanol were dried by the magnesium–iodine method.[23] All reaction mixtures were maintained at an ionic strength of 0·1M by addition of sodium perchlorate previously dried at 150° for 24 h.

Reactions yielding phenoxide ion were followed by observing the change of absorbance at 300 nm. Typical substrate concentrations were in the range 4—7 × $10^{-4}$M and base concentrations in the range 0·01—0·08M.

For reactions with *cis*-2-ethoxyvinyl *p*-tolyl sulphone (4a), *p*-tolylsulphonylacetylene (7) was added to the basic solution and the rapid (1—2 min) formation of the *cis*-isomer was allowed to occur. Subsequently, the absorption at 245 nm was followed, the decrease corresponding to formation of the bisethoxy-compound. The substrate concentration used was 4 × $10^{-5}$M and base concentrations were in the range 0·02—0·05M.

Rates of addition to *trans*-2-ethoxyvinyl *p*-tolyl sulphone (4b) were obtained by following the absorbance change at 265 nm after the initial relatively rapid change in absorbance due to elimination of phenoxide ion from the 2-phenoxyvinyl compound (1a or b) was complete.

For the independent determination of the addition rate constant, $k_1$, for the phenoxyvinyl sulphone (1)–ethoxide reaction, absorbance changes at 285 and 299 nm were measured. Absorbance at 285 nm is the sum of the decreasing absorbance of the phenoxyvinyl sulphone and the increasing absorbance of phenoxide ion. At 299 nm, however, the absorbance of the phenoxyvinyl sulphone is negligible, and the phenoxide absorbance is equal to that at 285 nm so that subtraction of the absorbance at 299 nm from that at 285 nm gives an accurate value for the changing absorbance of the *trans*-phenoxy-compound at 285 nm. Small corrections were applied to take account of the time lapse between measurements at 285 and 299 nm.

*Determination of* $k_1$ *and* k′. To evaluate $k_1$ and $k'$ from equation (iv) one assumes $k' > k_1$ [the numerical results will be the same if one assumes $k' < k_1$, as (iv) is symmetrical in $k_1$ and $k'$]. Equation (iv) can then be simplified for high values of $t$ into equation (v). Starting from 25%

$$[\bar{O}Ph]/[(1)]_0 = 1 - [a/(a-1)]e^{-k_1[\bar{O}R]t} \quad (a = k'/k_1) \quad (v)$$

[21] L. Maioli and G. Modena, *Ricerca Sci.*, 1959, **29**, 1931.
[22] E. Angeletti, F. Montanari, and A. Negrini, *Gazzetta*, 1957, **87**, 1115.
[23] A. I. Vogel, ' Practical Organic Chemistry,' 3rd edn., Longmans, London, 1956, p. 167.

reaction, the computer program took $n$ (where $n$ is about 40) pairs of points from the absorbance *versus* time curve, $t_1$ and $t_2$ in each pair differing roughly by 10% of reaction.

With each pair of points a calculation of $k_1$ and $k'$ was done as follows: $t_1$ and $[\bar{O}Ph]_1$ and $t_2$ and $[\bar{O}Ph]_2$, respectively, were substituted into equation (v). Elimination of $k_1$ between the two resulting equations gives equation (vi).

$$[a/(a - 1)]^{(t_1/t_2)^{-1}} = \{1 - [\bar{O}Ph]_2/[(1)]_0\}^{t_1/t_2}/\{1 - [\bar{O}Ph]_1/[(1)]_0\} \quad \text{(vi)}$$

The parameter $a$ was evaluated from equation (vi) and then $k_1$ from equation (v). A complete theoretical absorbance *versus* time curve was then calculated using equation (iv) and the values of $k_1$ and $k'$ just obtained. The deviation of the calculated curve from the experimental one was evaluated by taking the root mean square (r.m.s.) error over all the points of the curve. As experimental errors of about 1% in the measured absorptions give rise to errors of up to 50% in the rate constants calculated with such a point, it is necessary to compare the $n$ sets of calculations and to select the best pair of rate constant values. However, when the ratio $k_{large} : k_{small}$ falls below 10 : 1 the approximation of equation (v) becomes less accurate and the $n$ pairs of calculated rate constants all give large r.m.s. errors (*e.g.* 5% of the mean absorbance). A second program allowed calculation of a curve using equation (iv) for a large number (about 400) pairs of $k_1$ and $k'$ values and compared each calculated curve with the experimental one using the r.m.s. error. This process resulted in a number of reasonable pairs of $k_1$ and $k'$ values from which the best pair were selected. Usually the r.m.s. error of the corresponding calculated curve was 0·5% of the mean absorbance. The first computer program is required to give an indication of the boundaries to be set up for $k_1$ and $k'$ values in the second program. When necessary, the second calculation was repeated with different boundaries. The Figure shows a typical fit between the experimental points and the calculated curve.

*Errors.*[24] The estimated error in the one-step rate constants of (8) and (4a) is around 2%, as is the experimental reproducibility given in the Table. This results in errors in the activation parameters as indicated, the error in $\Delta S^{\ddagger}$ being about 3·5 times larger than the one in $\Delta H^{\ddagger}$ in the units used.

An error of 10—15% can be expected for (4b), where only the last part of the reaction curve could be measured.

For the two-step processes of (1a) and (1b) the error in the smaller rate constant, $k_1$ is estimated at 5—10%. The larger rate constant, $k'$, is less accurate, with an error of at least 10%, increasing to around 20% as $k'/k_1$ increases. These errors give rise to quite large uncertainties in the activation parameters, especially in those for the elimination step for (1b).

We thank Dr. D. R. Marshall and Dr. J. C. A. van der Sluijs for discussions, the S.R.C. for an equipment grant, and U.C.N.W. for a fellowship (to M. J. v. d. S.).

[4/325 *Received*, 19*th February*, 1974]

[24] L. L. Schaleger and F. A. Long, *Adv. Phys. Org. Chem.*, 1963, **1**, 1.