Elimination and Addition Reactions. Part 35.[1]† Substituent Effects on Alkene-forming Eliminations from Carbanions

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Effect of substituents on reactivity in eliminations from carbanions in the systems $G\cdot\overset{\beta}{C}HR\cdot\overset{\alpha}{C}HR\cdot Z$, where G = $PhSO_2$, Bz, or CN and Z = OPh, OMe, SPh, or SO_2Ph have been determined.

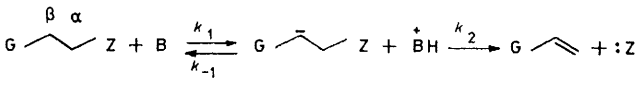
β-Phenyl substitution greatly accelerates carbanion formation in nitriles but depresses that of ketones. Sulphones, except when both α- and β-phenyl groups are present, are insensitive. These markedly different effects of β-phenyl substitution in the three different systems are discussed in terms of steric interference with the formation of a planar carbanion.

α-Phenyl substitution slightly accelerates deprotonation of nitriles but depresses that of ketones and sulphones. Methyl substitution in sulphones at α or β positions slightly retards deprotonation.

Substrates with G = $PhSO_2$ or CN react by the $(E_1cB)_R$ mechanism and phenyl and methyl substituents at α- or β-carbon atoms all accelerate expulsion of the leaving group to a small extent. The effects are generally smaller than those of the same substituents in concerted processes and it is concluded, in conformity with earlier work, that extension of the bond to the leaving group in the transition state is small.

Phenoxy-sulphones with both α- and β-phenyl substituents behave exceptionally. Interconversion of the *erythro*- and *threo*-isomers does not occur under the reaction conditions and deprotonation of the *threo*-isomer occurs much more slowly than in the *erythro*-isomer or the unsubstituted substrate. Expulsion of the leaving group from the derived carbanion, however, occurs more rapidly in the *threo* than in the *erythro*-isomer.

PRECEDING papers in this series [1,2] have defined the conditions under which measurement of leaving-group ability can be assessed for reactions in which a leaving group, Z, is expelled from a carbanion stabilised by a group G (see Scheme). It was seen to be necessary to



SCHEME

make measurements on systems in which loss of the leaving group from the carbanion (k_2) is rate determining and in which the polar effect of the leaving group on the magnitude of the equilibrium constant (k_1/k_{-1}) could be estimated.

We now report upon the effect of phenyl and methyl substituents at α and β positions in such systems and, using the same principles, we have obtained information about the effects of such substitution both on depronation rate (k_1) and upon leaving group expulsion (k_2).

Methods and Results.—Reactions in ethanolic sodium ethoxide with the substrates listed in Tables 1, 3, and 4 were carried out as before.[2] Detritiation rates [3] were measured (Table 2) to allow calibration of substituent effects on deprotonation rates.

Distinction between $(E_1cB)_R$, $(E_1cB)_I$, and E_2 processes is crucial to the discussion which follows. The $(E_1cB)_R$ mechanism has been assigned to those reactions which satisfy one or more of the following criteria:[2]

(i) Primary deuterium isotope effect at C_β of unity within experimental error; (ii) deuterium–hydrogen exchange at C_β occurring more rapidly than elimination; (iii) rate of elimination very much slower than rate of deprotonation predicted from Taft ionisation plots.[3] The method of mechanistic assignment is shown for each substrate in Tables 1, 3, or 4. The $(E_1cB)_R$ mechanism operates for all substrates in which the activating group, G, is $PhSO_2$ or CN. Those substrates in which G = Bz fail to satisfy any of these criteria and reactions with these substrates have been assigned the $(E_1cB)_I$ mechanism. For the ketones, most such assignments are strengthened by the close correlation of elimination rate with ionisation rate predicted from model substrates as found earlier.[4]

The substituted and unsubstituted substrates are compared in Tables 1, 3, and 4. The overall substituent effect has then been adjusted for the known effect of the substituent on the deprotonation rate of the appropriate model compound (Part 31 [3] and Table 2). The resulting ratio shows the effect of the substituent on the $k_2 : k_{-1}$ ratio.

DISCUSSION

We have shown that for all the nitriles and sulphones studied, elimination is by the $(E_1cB)_R$ mechanism. Observed rate constants are therefore composite. For the ketones, the irreversible $(E_1cB)_I$ mechanism is followed and the effect of substitution is upon the rate-determining deprotonation only. We discuss the effects of substituents on the ketones first.

Ketones: β-Phenyl Substitution.—For compounds (14)—(17) the $(E_1cB)_I$ mechanism (deprotonation rate-determining) is assigned and the $k_{obs.}$ values, adjusted for the effect of the β-phenyl group on deprotonation rate in models, gives βPh : βH ratios [of $k_{obs.}/k_1$(calc.)] close to unity as expected. The substantial depression of

† Preliminary discussions of part of this work have appeared: C. J. M. Stirling, *Internat. J. Sulfur Chem.* (*C*), 1971, **6**, 41; R. P. Redman and C. J. M. Stirling, *Chem. Comm.*, 1971, 633.

[1] Part 34, P. J. Thomas and C. J. M. Stirling, preceding paper.

[2] D. R. Marshall, P. J. Thomas, and C. J. M. Stirling, *J.C.S. Perkin II*, 1977, 1898.

[3] P. J. Thomas and C. J. M. Stirling, *J.C.S. Perkin II*, 1977, 1909.

[4] D. R. Marshall, P. J. Thomas, and C. J. M. Stirling, *J.C.S. Perkin II*, 1977, 1914.

TABLE 1

Effects of β-phenyl substitution on elimination rates

	Substrate							
No.	G	β CHR	α CHR	Z	Mechanism * (criterion) †	$k_{cbs.}$ [a]	Ratio subs : unsubs	$k_2 : k_1$ § subs : unsubs [b]
(1)	$PhSO_2$	H	H	OPh	R (D)	0.35 [c]	65	27
(2)	$PhSO_2$	Ph	H	OPh	R (D′)	22.8		
(3)	$PhSO_2$	H	Ph	OPh	R (D′)	0.50	2.18 ‡	0.5 ‡
(4)	$PhSO_2$	Ph	Ph	OPh-*erythro*	R (E)	1.09	0.034 ‡	3.5 ‡
(5)	$PhSO_2$	Ph	Ph	OPh-*threo*	R (E)	0.017		
(6)	$PhSO_2$	H	H	SPh	R (D)	0.021 [d,c]	52	22
(7)	$PhSO_2$	Ph	H	SPh	R (D′)	1.03		
(8)	$PhSO_2$	H	H	SO_2Ph	R (k_H/k_D = 2.2)	1.05 [e]	1.3	25 [g]
(9)	$PhSO_2$	Ph	H	SO_2Ph [f]	R (D)	1.35		
(10)	CN	H	H	SPh	R (D)	0.0104 [h]	9.2×10^4	11
(11)	CN	Ph	H	SPh	R (D′)	926		
(12)	CN	H	H	SO_2Ph	R (D)	17.1 [h]	2.94×10^5	35
(13)	CN	Ph	H	SO_2Ph	R (D′)	5.01×10^6		
(14)	Bz	H	H	SPh	I (D)	108 [h]	0.014	(1.1)
(15)	Bz	Ph	H	SPh	I (D′)	1.18		
(16)	Bz	H	H	SO_2Ph	I (k_H/k_D = 2.1)	1 040 [h]	0.016	(1.2) [i]
(17)	Bz	Ph	H	SO_2Ph	I (D′)	17.1		

* R = $(E_1cB)_R$; I = $(E_1cB)_I$. † Criteria: D = measrued deprotonation rate ≫ $k_{elimination}$; D′ = deprotonation rate derived from Taft $\rho^*\sigma'$ plot ≫ $k_{elimination}$; E = hydrogen-deuterium exchange ≫ $k_{elimination}$; k_H/k_D = primary deuterium isotope effect. ‡ Ratios relative to α-phenyl. § = $k_{obs.}/k_1$ (obs. or calc.).

[a] Units: l mol^{-1} s^{-1} in EtO^-–EtOH at 25.0 °C. [b] Factors used: G = $PhSO_2$: 0.42; G = CN: 1.17×10^{-4}; G = PhCO : 77. [c] J. Crosby and C. J. M. Stirling, *J. Chem. Soc.* (*B*), 1970, 671. [d] R. P. Redman and C. J. M. Stirling, *Chem. Comm.*, 1970, 633. [e] Part 30, ref. no. 2. [f] Identical with substrate 20 in Table 3. [g] Calc. using measured detritiation ratio. [h] Preparation, product analysis, and kinetics in Part 32, ref. no. 4. [i] Ratio of observed : calc. deprotonation rates.

TABLE 2

Substituent effects [a,b] on detritiation of sulphones, nitriles, and ketones, G·βCH_2·αCH_2·Z

G Substituent	Z	OEt	NMe_2	$\overset{+}{N}Me_3$	SO_2Ph
	H [c]	1.13×10^{-4} [g]			
		0.71, [d]			
		6.30 [d,c]	0.016	0.15 [f]	27 [d]
	β-Ph	1.27 [d]	3.56	0.24 [d]	0.052
	α-Ph	0.17 [d]	0.88 [d]	8.2 [d]	0.96
$PhSO_2$	β-Me	0.035,			
		0.019 [c]			
	α-Me	0.45,			
		0.28 [c]			
	α-, β-Ph *erythro*	2.2 [c,g]			
	α-, β-Ph *threo*	0.0051 [c,g]			
	H [c]	1.3 [h]	0.18	0.08 [j]	
		6.35 [c]			
CN	β-Ph	8.5×10^3 [h]		420 [i,j]	
	α-Ph		1.82	3.95 [g,j]	
PhCO	H [c]	2.54, [d]	0.37 [d]		
		2.24 [h]			
	β-Ph	0.013 [h]		0.024 [k]	
	α-Ph		0.23		

[a] Rate ratios relative to H; not statistically corrected. [b] Ethanolic sodium ethoxide at 25 °C. [c] Absolute value. Units: l mol^{-1} s^{-1}. [d] Values from Part 31, ref. no 3. [e] Value for Z = OPh. [f] Reaction in Et_3N–EtOH at 25 °C. Conversion factor Et_3N–EtO^- = 1.7×10^5. [g] Relative rates for Et_3N–EtOH reactions. [h] Value for Z = OMe. [i] For $Et_3N/Et_3\overset{+}{N}H\overset{-}{Cl}$–EtOH buffers. Value from Part 33, ref. no. 14. [j] Comparison between Z = $\overset{+}{N}Me_2Ph$ adjusted for differential when G = $PhSO_2$, *cf.* ref. no. 14. [k] $Et_3N/Et_3NHCl/H_2O$ buffers, ref. no. 11.

deprotonation rate is striking. The β-phenyl group may have two effects: (i) the equilibrium acidity of the carbon acid should increase [5] and with it the rate of deprotonation as generally observed [6] within a series sharing the same activating group. Phenyl substitution adjacent to the carbonyl group in acetophenone for example, lowers the pK by 7 units.[7] (ii) The phenyl group is bulky (A value = 2.5 [8]) and ketones are well known to be susceptible to steric suppression of deprotonation rate.[9] In this system, maximum stabilisation of the carbanion can be achieved only when the

[5] F. G. Bordwell, W. S. Matthews, and N. R. Vanier, *J. Amer. Chem. Soc.*, 1975, **97**, 442.

[6] J. R. Jones, 'The Acidity of Carbon Acids,' Academic Press, London, 1973.

[7] W. S. Matthews, J. E. Banes, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Druker, Z. Margolin, R. J. McCallum, G. J. McCollum, and N. R. Vanier, *J. Amer. Chem. Soc.*, 1975, **97**, 7006.

[8] E. L. Eliel, N. L. Allinger, S. J. Angyal, G. A. Morrison, 'Conformational Analysis,' New York, Wiley, 1965.

[9] J. A. Feather and V. Gold, *J. Chem. Soc.*, 1965, 1752; J. Hine, J. G. Houston, J. H. Jensen, and J. Mulders, *J. Amer. Chem. Soc.*, 1965, **87**, 5050.

phenyl group, C_β, and the carbonyl group are coplanar. Models suggest considerable steric restraints in this system emphasised by the observation that when two phenyl groups are attached to the ionising atom, pK leaving groups in buffer systems.[11] In these latter systems, the observed rate constants can be dissected to give values of k_1 and the $k_2 : k_{-1}$ ratio. To our knowledge these effects are the largest ever observed and they again

TABLE 3

Effects of α-phenyl substitution on elimination rates

	Substrate							
No.	G	β CHR	α CHR	Z	Mechanism * (criterion) †	$k_{obs.}$ [a]	Ratio subs : unsubs	$k_2 : k_{-1}$ § subs : unsubs
(1)	$PhSO_2$	H	H	OPh	R (D)	0.35 [c]	1.43	2.9
(18) [d]	$PhSO_2$	H	Ph	OPh	R (D′)	0.50		
(2)	$PhSO_2$	Ph	H	OPh	R (D′)	22.8	4.8×10^{-2} ‡	0.05 ‡
(4)	$PhSO_2$	Ph	Ph	OPh-erythro	R (E)	1.09		
(5)	$PhSO_2$	Ph	Ph	OPh-threo	R (E)	0.017	7.5×10^{-4} ‡	0.4‡
(6)	$PhSO_2$	H	H	SPh	R (D)	0.021 [e,f]	11	22
(19)	$PhSO_2$	H	Ph	SPh	R (D′)	0.222		
(8)	$PhSO_2$	H	H	SO_2Ph	R (k_H/k_D)	1.05 [f]	37	39 [h]
(20) [g]	$PhSO_2$	H	Ph	SO_2Ph	R (D)	38.8		
(35)	$PhSO_2$	H	Ph	OMe	R (D)	4.3×10^{-5} [e]	22	44
(36)	$PHSO_2$	H	PH	OMe	R(D′)	9.5×10^{-4}		
(10)	CN	H	H	SPh	R (D) [i]	0.0104 [i]	12.8	7.2
(21)	CN	H	Ph	SPh	R (D′)	0.133		
(12)	CN	H	H	SO_2Ph	R (k_H/k_D)	17.1 [i]	12.1	6.8
(22)	CN	H	Ph	SO_2Ph	R (k_H/k_D)	208		
(14)	Bz	H	H	SPh	I (D′)	108 [i]	6.4×10^{-2}	0.28
(23)	Bz	H	Ph	SPh	I (D′)	6.91		
(16)	Bz	H	H	SO_2Ph	I (D′)	1 040 [i]	2.5×10^{-1}	1.1
(24)	Bz	H	Ph	SO_2Ph	I (D′)	260		
(25)	Ac	H	H	SPh	I (D′)	29.5 [i]	4.3×10^{-1}	1.9 [j]
(26)	Ac	H	Ph	SPh	I (D′)	12.7		
(27)	Ac	H	H	SO_2Ph	I (k_H/k_D)	620 [i]	4.3×10^{-1}	1.9 [j]
(28)	Ac	H	Ph	SO_2Ph	I (D′)	265.5		

*,†,§ See Table 1.

[a] Units: 1 mol^{-1} mol^{-1} at 25 °C for EtO^-/EtOH. [b] Obtained by correction for the α-effect on model substrates (Table 2) for G = SO_2Ph factor 2.0; G = CN = 0.55. [c] J. Crosby and C. J. M. Stirling, *J. Chem. Soc.* (*B*), 1970, 671. [d] Identical with substrate (3) in Table 1. [e] R. P. Redman and C. J. M. Stirling, *Chem. Comm.*, 1970, 633. [f] Part 30. [g] Identical with substrate 9 in Table 1. [h] Calc. using measured ratio of detritiation rates. [i] Part 32 prep. and product analysis. [j] Calc. using G = Bz model. ‡ Relative to β-phenyl.

actually *rises*.[10] For ketones then, the second factor is clearly dominant and severe rate depression results. These findings are directly matched by detritiation rates demonstrate the severe steric restraints which operate on carbanions of this type. The β-phenyl group may affect not only coplanarity in the carbanion but also

TABLE 4

Effects of α- and β-methyl substitution on eliminations from phenoxy- and thiophenoxy-sulphones

	Substrate							
No.	G	β CHR	α CHR	Z	Mechanism * (Criterion) †	$k_{obs.}$ [a]	Ratio of $k_{obs.}$ subs : unsubs	$k_2 : k_{-1}$ [b] subs : unsubs
(1)	$PhSO_2$	H	H	OPh	R (D,E)	0.35		
(29)	$PhSO_2$	H	Me	OPh	R (D,E)	0.133	0.38	1.3
(30)	$PhSO_2$	H	Me_2	OPh	R (D′)	0.145	0.41	4.5
(31)	$PhSO_2$	Me	H	OPh	R (D,E)	8.0×10^{-3}	0.02	1.2
(6)	$PhSO_2$	H	H	SPh	R (D)	0.022		
(32)	$PhSO_2$	H	Me	SPh	R (D′,E)	0.028	1.27	4.5
(33)	$PhSO_2$	H	Me_2	SPh	R (D′)	0.034	1.54	17
(34)	$PhSO_2$	Me	H	SPh	R (D′,E)	1.38×10^{-3}	0.063	3.3

*,† See Table 1.

[a] Units: 1 mol^{-1} s^{-1} for reactions in EtONa–EtOH at 25.0 °C. [b] Values obtained by division of $k_{obs.}$ ratios by detritiation ratios (Table 2). Factors used: β-Me 0.019, α-Me 0.28, α,α-Me 0.28 × $k_{detrit.}$ ratio of $PhSO_2CH_2CH_3$: $PhSO_2CH_2CH_2CH_3$ (Part 31, ref. no. 3) = 0.32 ≡ 0.091. [c] J. Crosby and C. J. M. Stirling, *J. Chem. Soc.* (*B*), 1970, 671.

(Table 2). For the methoxy-ketone, β-phenyl substitution depresses detritiation rate by a factor of 77. Even larger depressions (300-fold) are found in eliminations of β-phenyl substituted ketones with 'onium interfere with solvation of the developing carbanion so as to inhibit deprotonation. We do not consider that approach of the base to the site of deprotonation is directly restricted.[9] Studies in aqueous amine buffer systems [11] show no sensitivity to the steric demands of

[10] F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. J. McCollum, M. Van Der Puy, N. R. Vanier, and W. S. Matthews, *J. Org. Chem.*, 1977, **42**, 321.

[11] D. R. Marshall, K. N. Morris, C. J. M. Stirling, *J.C.S. Perkin II*, in preparation.

the base. Ketones show little sensitivity of deprotonation rate to the size of substituents at C_α. Change of the thiophenoxy leaving group ($A = 0.8$ [8]) to the much bulkier phenylsulphonyl group ($A = 2.5$) has no effect on the βPh : βH ratio [substrates (14)—(17) in Table 1].

Ketones: α-Phenyl Substitution.—This is rate depressive throughout the series in spite of the fact that the polar effect of an α-phenyl group and the ρ* value for ketone deprotonation [3] predicts an increase in deprotonation rate of *ca.* 5. The effect on elimination rate is again parallelled by the effect on the deprotonation rate of the model dimethylamino-compound (Table 2). An α-phenyl [12] like an α-methyl [13] group, however, also depresses deprotonation of nitro-compounds and sulphones.[3] This does not appear to be a steric effect operating from the α-position as there is no change in the α-Ph : H ratio for the methyl ketone series when the leaving group is changed from SPh to the much bulkier SO_2Ph. The benzoyl-activated α-phenyl sulphide (23) is somewhat anomalous and the depressive effect of α-phenyl substitution in this case is even greater than for the sulphone (24). Attention has already been called to the insensitivity of deprotonation rates to the size of the group, Z, even in the ultra-sensitive β-phenyl ketones (Table 1). In extreme cases, however (below) there is evidence that the size of the leaving group can affect deprotonation rates.

Sulphones and Nitriles: the Effect of β-Phenyl Substitution on Deprotonation.—The cyano- and sulphonyl-activated substrates eliminate *via* the $(E_1cB)_R$ mechanism [$k_{-1}[BH] \gg k_2$ in equation (1)]. The effect of

$$k_{obs.} = k_1 \cdot k_2/k_{-1}\,[BH] + k_2 \qquad (1)$$

substitution on $k_{obs.}$ is thus both on deprotonation rate k_1 and on the $k_2 : k_{-1}$ ratio. The effect on k_1, as for ketones, is predicted from models. These have shown (Part 31 [3] and Table 2) that in sulphones with uncharged Z groups, β-phenyl substitution is mildly accelerative. [With 'onium leaving groups, β-substitution is actually slightly depressive.[11,14]] The small effect on k_1, in contrast to the substantial effects expected and discussed above again suggests that formation of the carbanion is sterically inhibited. Such inhibition has been discussed earlier for 'onium salt eliminations [14] and it was concluded that the major restraint is to coplanarity in the carbanion.[15] The restrictions on the conformation required for maximum stabilisation of carbanions derived from sulphones are less strict than those from ketones. The outstanding difference, however, between the sulphones and nitriles, which share the reversible mechanism, is the very large acceleration of $k_{obs.}$ produced by β-substitution in the nitrile (Table 1). Models (Table 2) show that β-phenyl substitution accelerates the deprotonation of nitriles by nearly four orders of magnitude when the group Z is uncharged. [Substantially smaller acceleration is again found when $Z = \overset{+}{N}R_3$.[11,14]]

The β-phenyl group imposes sp^2 hybridisation on the carbanion and the very much smaller cyano-group ($A = 0.17$ [8]) interferes much less with the developing coplanarity of the three bonds to the ionising carbon in the transition state for deprotonation. These arguments apply most particularly to deprotonations with a late transition state and this seems likely in view of the very large pK differences between the carbon acids and the base.[16-18]

A striking consequence of steric interference with carbanion formation in sulphones is seen in the orientation of elimination in the phenyl-substituted bis-sulphone (9). There is overwhelming preference for ejection of the phenylsulphonyl group adjacent to the phenyl group (α- *vs.* β- to the phenyl group = 96.5 : 3.5). In the following sections, it is seen that the effect of phenyl substitution on the $k_2 : k_{-1}$ ratio for sulphones is similar whether the phenyl group is α or β. Detritiation measurements show that removal of the proton from carbon bearing the phenyl group occurs 18 times more slowly than from the adjacent methylene group and the orientation of elimination is thus dictated by the steric effect on deprotonation. In this case the leaving group does have an adverse effect on deprotonation at C_β.

Even more dramatic effects upon reactivity of phenoxy-sulphones are seen when phenyl groups are present at *both* β and α positions. Their behaviour is discussed separately below.

Sulphones and Nitriles: the Effect of β-Phenyl Substitution on the $k_2 : k_{-1}$ *Ratio.*—Because k_{-1} is very large for sulphones [19] and nitriles,[18] the β-phenyl substituent must have a small effect on k_{-1} and, if anything, this will be depressive raising $k_{obs.}$ [equation (1)]. The depressive effect on k_{-1} is not, however, sufficient to change the balance between k_{-1} and k_2 to such an extent as to pass from the reversible to the irreversible mechanism of elimination; $k_{-1}[BH]$ remains the larger term in the denominator of equation (1). Because k_{-1} values are close to the diffusion-controlled limit, we shall assume,[20] in the discussion that follows, that k_{-1} values are independent of structural variation.

Division of the $k_{obs.}$ values by factors derived by direct measurement or by extrapolation from results on model substrates for the effect of β-phenyl substitution on k_1, shows (Table 1) that generally modest increases of $k_2 : k_{-1}$ ratios result. Two opposing effects on k_2 may be expected. First, in the transition state for k_2, β-phenyl substitution should be accelerative due to the

[12] P. F. Cann and C. J. M. Stirling, *J.C.S. Perkin II*, 1974, 817.
[13] F. G. Bordwell, W. J. Boyle, and K. C. Yee, *J. Amer. Chem. Soc.*, 1970, **92**, 5926.
[14] K. N. Barlow, D. R. Marshall, and C. J. M. Stirling, *J.C.S. Perkin II*, 1977, 1920.
[15] L. A. Paquette, J. P. Freeman, and M. J. Wyvratt, *J. Amer. Chem. Soc.*, 1971, **93**, 346.
[16] Ref. 6, p. 145.
[17] R. P. Bell, ' The Proton in Chemistry,' 2nd edn., Chapman and Hall, London, 1973.
[18] F. Hibbert, F. A. Long, and E. A. Walters, *J. Amer. Chem. Soc.*, 1971, **93**, 2829.
[19] J. Hine, J. C. Phillips, and J. I. Maxwell, *J. Org. Chem.*, 1970, **35**, 3943.
[20] M. B. Davy, K. T. Douglas, J. S. Loran, A. Steltner, and A. Williams, *J. Amer. Chem. Soc.*, 1977, **99**, 1196.

extra stabilisation of the transition state afforded by interaction between the phenyl group and the developing carbon–carbon double bond. The magnitude of this effect will depend on the degree of double-bond character in the transition state and it is clearly seen in concerted processes (Table 5).[21] All observations that we have so far made on $(E_1cB)_R$ reactions, however, suggest that the degree of bond extension to the leaving group in the transition state for k_2 is small. Particularly relevant in this respect are the small leaving group β_{LG} values for phenoxy-sulphones (0.40) and nitriles (0.55),[1] together with the insensitivity of $k_2 : k_{-1}$ ratios to structural changes in 'onium leaving groups for cyano- and sulphonyl-activated eliminations.[11,14] An increase of k_2 due to interaction between the developing double bond and the phenyl group is, therefore, likely to be small. the second factor which may alter k_2 is the reduced reactivity of the carbanion which results from attachment of the phenyl group. Little direct evidence exists on this point; the rather small overall changes which result from β-substitution suggest partial cancellation of these opposing effects.

The increase in k_2 due to β-phenyl substitution in sulphonyl-activated substrates is essentially invariant with the rank of the leaving group. It might be expected that the lower the rank of the leaving group, the greater should be the assistance to its expulsion by the β-phenyl group. Just the reverse of this expectation is seen for the nitriles (10)—(13). In this series, the rank order [1] is $PhSO_2 > PhS$ but the β-phenyl effect on k_2 is substantially greater for the better leaving group.

Nitriles and Sulphones: the Effect of α-Phenyl Substitution (*Table* 3).—All compounds follow the E_1cB_R mechanism and, as for the β-phenyl analogues, the effect of α-substitution upon three processes must be considered. For deprotonation, k_1, the effect of the α-phenyl group is assessed from model substrates (Table 2 and Part 31).[3] The effect is somewhat variable with the group Z, but for sulphones, depression of k_1 by a factor of 2 is typical and the overall α-effect on $k_{obs.}$ has been adjusted, as before, by this factor. For nitriles, model studies show that α-phenyl substitution slightly accelerates deprotonation and again the overall α-effect has been adjusted appropriately. We shall not comment further on the rather small changes produced by α-phenyl substitution on deprotonation rates whose origin is not clear.

It can be seen (Table 3) that for sulphones, the α-Ph : α-H ratio for $k_{obs.}$ when adjusted for deprotonation, increases in the series $OPh < SPh < SO_2Ph < OMe$. This is the reverse of the rank order of groups ejected from sulphonyl-stabilised carbanions.[2] If, as for the β series, it is assumed that the effect of the α-phenyl substituent is on k_2 and not on k_{-1} then ejection of the leaving group is accelerated by factors of *ca.* 3 to 50-fold. These factors are rather typical of the effect of α-phenyl substitution on concerted processes (Table 5) in which, for example, reaction of ethyl bromide with ethanolic sodium ethoxide is accelerated 50-fold by α-phenyl substitution. A similar picture emerges for the α-substituted nitriles. In these cases, the deprotonation correction factor is also small but in the opposite sense. α-Phenyl substitution (Table 3) produces changes in the value of k_2 smaller in magnitude than those for the sulphones and with inversion of the magnitude of the effects on sulphides and sulphones. The rank order, however, for leaving groups in nitrile activated eliminations is $SO_2Ph > SPh$. It is tempting to conclude that assistance by an α-phenyl group is the less the higher is the rank of the leaving group. The effects of methyl substituents at both β and α positions (below) substantiate this conclusion. Data on addition [22] of ethoxide ion to cinnamonitrile in ethanol allows calculation of the rate of elimination of ethoxide ion from the α-phenyl ethoxynitrile. Comparison of this value (*ca.* 9×10^{-3} l mol^{-1} s^{-1} at 25 °C) with that for elimination of the methoxide ion from 2-methoxypropionitrile [1] and correction for the

TABLE 5

Relative effects of substituents upon concerted elimination and upon eliminations from sulphonyl-stabilised carbanions

	Concerted		Carbanionic [a] k_{rels}		
Substituent	CH_3CH_2Br	$CH_3CH_2\overset{+}{S}Me_2$	$PhSO_2CH_2CH_2OPh$	$PhSO_2CH_2CH_2SPh$	$PhSO_2CH_2CH_2SO_2Ph$
H	1	1	1	1	1
α-Me	2.5 [b,c]	11.4 [c,d]	1.3	4.5	
α,α-Me_2	27 [b,c]	65 [c,d]	4.5	17	
β-Me	3.3 [b]	0.5 [d,e]	1.2	3.3	
β-Ph	350 [b]	430 [e]	27	22	25
α-Ph	50 [b]	100 [d,e]	2.9	22	39
α,β-Ph	3 [f]		*erythro* 1.4 (0.08) [g]		
			threo 9.6 (7.5 × 10^{-4}) [g]		

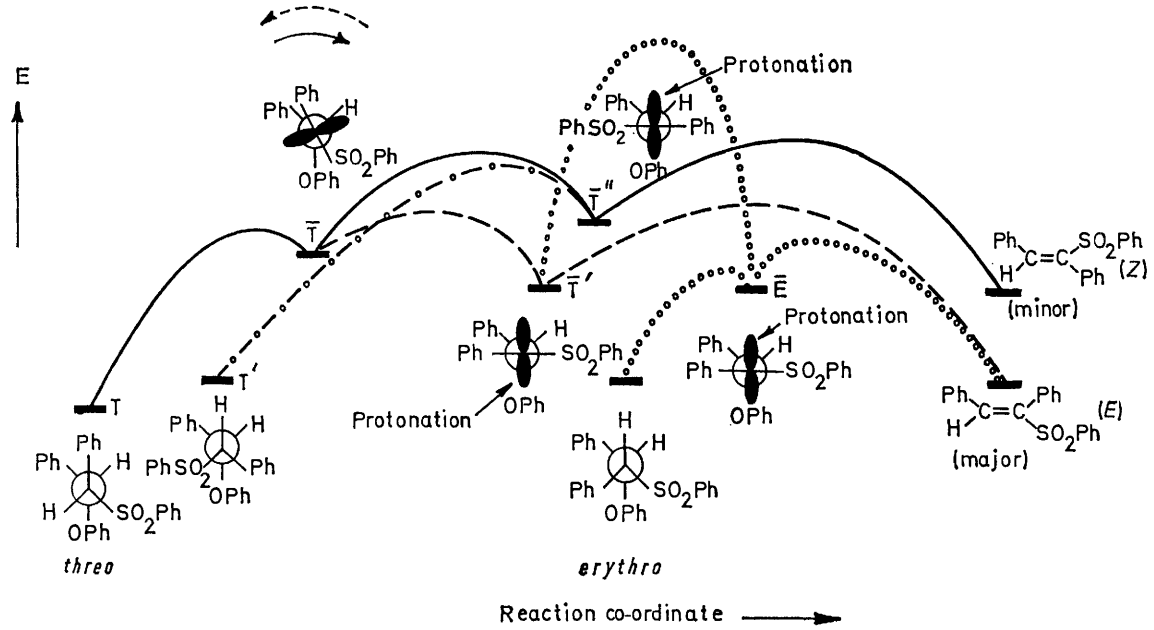
[a] $k_2 : k_{-1}$ ratios for subs : unsubs. Data from Tables 1, 3, and 4. [b] For reactions in NaOEt–EtOH at 25° C, E. D. Hughes, C. K. Ingold, S. Masterman, and B. J. McNulty, *J. Chem. Soc.*, 1940, 899; M. L. Dhar, E. D. Hughes, C. K. Ingold, and S. Masterman, *ibid.*, 1948, 2055; M. L. Dhar, E. D. Hughes, and C. K. Ingold, *ibid.*, pp. 2058—2065. [c] Statistically corrected. [d] For reactions in NaOEt–EtOH at 45 °C, E. D. Hughes, C. K. Ingold, and L. I. Woolf, *J. Chem. Soc.*, 1948, 2084. [e] For reactions in NaOEt–EtOH at 64 °C, E. D. Hughes, C. K. Ingold, and G. A. Maw, *J. Chem. Soc.*, 1948, 2072. [f] For chlorides at 50 °C calculated from the data of C. H. De Puy and C. A. Bishop, *J. Amer. Chem. Soc.*, 1960, **82**, 2535 and ref. 27. [g] Data from ref. 26 for Ph = *p*-tolyl and OPh = Cl in MeONa–MeOH at 25 °C in parentheses.

[21] Data summarised by C. K. Ingold in 'Structure and Mechanism in Organic Chemistry,' Bell, London, 1953, pp. 436—437.

[22] B. A. Feit, R. Pazhenchevsky, and B. Pazhenchevsky, *J. Org. Chem.*, 1976, **41**, 3246.

effect of the α-phenyl group on deprotonation, also suggests that α-phenyl substitution even with a poor leaving group has only a modest accelerative effect. It was seen (above) that the results for β-phenyl substitution on leaving-group expulsion do not conform to this generalisation.

α,β-*Bisphenyl Substitution in Sulphones*.—Comparison of the results for the phenoxy-sulphones (4) and (5) with sulphone (2) (Table 3) shows that insertion of a β-phenyl group in addition to an α-phenyl group, produces dramatic effects on reactivity. For the more reactive *erythro*-isomer, $k_{obs.}$ is reduced by a factor of 20 and for the *threo*-isomer by a factor of 1 300. Measurement of the detritiation rate of each sulphone shows that the additional α-phenyl substituent does not affect detritiation in the case of the *erythro*-isomer [ratio (2) : (4) = 1.1] but for the *threo*-isomer the detritiation rate is reduced by a factor of 475.



In the *erythro*-isomer deprotonation produces ion $\bar{E}$ from the conformation *E*, shown by ^{1}H n.m.r. measurements to be the most populated (Figure). C_β Becomes planar and non-bonded interactions between the phenoxy-group and the gauche phenyl and phenylsulphonyl groups are reduced. A gauche phenyl–phenyl interaction, however, develops. Expulsion of the phenoxy-group from this rotamer leads directly to the more stable [23] *E*-phenylsulphonylstilbene. For the *threo*-isomer, *T* and *T*′ are the most populated ground-state conformations (^{1}H n.m.r.). Deprotonation of *T* leads to $\bar{T}$ of higher energy than $\bar{E}$. Coplanarity of the *p*-orbital of the carbanion and of the C–OPh bond is the optimum conformation for expulsion of the phenoxy-group. This is achieved by rotation in $\bar{T}$ to give $\bar{T}'$ or $\bar{T}''$. $\bar{T}'$ is a C-S rotamer of $\bar{E}$, but interconversion of *threo*- and *erythro*-isomers *via* $\bar{T}$, $\bar{T}'$, and $\bar{E}$ does not occur. That interconversion of the rapidly reacting *erythro*-isomer does not occur is simply shown by the absence of *threo*-isomer in the products from a partial reaction. Proof of the converse is more difficult because the *erythro*-isomer is 60 times more reactive than the *threo*-isomer. Cumulative scanning (2 050 scans) of the ^{1}H n.m.r. spectrum of the products of a partial reaction of the *threo*-isomer confirmed that after approximately 50% reaction no *erythro*-isomer was present under conditions in which 0.5% of this isomer could easily have been detected. We conclude therefore, that $\bar{T}'$ and $\bar{E}$ reprotonate stereospecificially more rapidly than the carbanions form product or epimer. Such stereospecific reprotonation of sulphonyl-stabilised carbanions is familiar.[24]

Use of the measured detritiation rates of the *erythro*- and *threo*-isomers to calculate the $k_2 : k_{-1}$ ratios for each isomer, shows that the carbanion derived from the *threo*-isomer expels the leaving group seven times as rapidly as that derived from the *erythro*-isomer. This is consistently the case whether the comparison is made with α- (Table 3) or β- (Table 1) mono-phenyl substitution. The pattern that emerges, therefore, is that the *erythro*-isomer, of higher ground-state energy, deprotonates 430 times more rapidly than the *threo*-isomer but this differential is slightly offset by the seven-fold greater tendency of the carbanions derived from the *threo*-isomer to shed phenoxide ion.

These results may be compared with two sets of earlier data. Naso and his collaborators [25] studied elimination

[23] S. J. Cristol and P. Pappas, *J. Org. Chem.*, 1963, **28**, 2066.
[24] F. G. Bordwell, D. D. Phillips, and J. M. Williams, *J. Amer. Chem. Soc.*, 1968, **90**, 426.
[25] V. Fiandanese, C. V. Maffeo, F. Naso, and L. Ronzini, *J.C.S. Perkin II*, 1976, 1303.

in the *erythro*- and *threo*-chlorosulphones, *p*-tolylSO_2CH(Ph)·CH(Ph)Cl (Table 5) under conditions similar to those used in the present work. For the *threo*-isomer, the mechanism of elimination is probably $(E_1cB)_I$ (*cf.* Part 32 [4]) and thus it is solely deprotonation which is affected by the insertion of aryl groups. Deprotonation is even more severely affected when Z = Cl rather than, as in the present work, when Z = OPh. Thus, the *erythro*-isomer reacts 12.5 times but the *threo*-isomer 1 330 times more slowly than the unsubstituted chloro-sulphone.[26] The results, however, broadly match those obtained from detritiation measurements.

Dehydrohalogenation of 2-phenethyl chloride [27] is accelerated by a factor of only 3 when a phenyl group is inserted at the α-position. Our results (Table 2) suggest that an α-phenyl group inhibits proton removal (contrary to the authors' [27] views) and this effect is undoubtedly partly responsible for the very small rate change which is observed by comparison with insertion of an α-phenyl group into ethyl bromide (Table 5). The implication that the degree of double-bond character is very small even in this poorly activated system is striking.

The results in Tables 1 and 3 show that for the $(E_1cB)_R$ process, insertion of a phenyl group at either α or β carbon atoms, when the other carbon atom already bears a phenyl group, inhibits expulsion of the leaving group from the carbanion in the *erythro*-isomer. This is also true of the *threo*-isomer when a β-phenyl group is already present (Table 3) but when an α-phenyl group is already present (Table 1) then insertion of a β-phenyl group slightly accelerates expulsion of the leaving group. These effects are probably due to the eclipsing of groups which develops in the transition state for leaving-group expulsion. Again, effects are small, consistent with a small degree of double-bond formation in the transition state.

Methyl Substitution.—Results are given in Table 4. α-Methyl substitution produces a small depression of $k_{obs.}$ for the phenoxy and a small increase in $k_{obs.}$ for the thiophenoxy-leaving group. Detritiation studies (Table 2) show that the effect of the methyl group on deprotonation is small and adjustment of $k_{obs.}$ as before shows very small effects on k_2 for the phenoxy-derivative. This observation is consistent, as before, with very little double-bond formation in the expulsion of the leaving group and the effect of the α-methyl group matches that of the α-phenyl group in the phenoxy-sulphone series. Even two α-methyl groups have rather little effect. The contrast with the effects of methyl substitution on concerted processes is seen in Table 5 where the concerted systems are substantially more sensitive. For the thiophenoxy-leaving group, α-methyl substitution is slightly accelerative [substrates (32) and (33)]. It is assumed that the effect of methyl substitution on the deprotonation rate is the same for thiophenoxy- and phenoxy-derivatives. The corrected α-Me : α-H ratios show that the depressive effect of the α-methyl group on k_1 is slightly overbalanced by the accelerative effect on k_2. Thiophenoxy is a lower rank leaving group than phenoxy- in the sulphone-activated series. The greater accelerative effect of methyl substitution is then consistent with the greater degree of double-bond character in the transition state expected for the expulsion of this poorer leaving group. All effects are, however, small.

β-*Methyl Substitution.*—Results for the sulphonyl-activated phenoxy- and thiophenoxy-derivatives are given in Table 4. Detritiation measurements (Table 2) confirm the depression of deprotonation rates observed in systems with 'onium leaving groups.[11,14] Adjustment of $k_{obs.}$ values for the substituent effect on deprotonation rate shows that the effects of β-methyl substitution on k_2 are small and positive and, as for the α-substituents, greater for thiophenoxy than for the phenoxy leaving group.

Conclusions.—In oxo-activated eliminations, deprotonation is rate determining when the leaving group, Z, is $PhSO_2$ or PhS. It is extremely sensitive to steric interference by substituents at C_β but not C_α.

Deprotonation of sulphones is susceptible to steric interference but this is not true of nitriles in which β-phenyl substitution causes very large acceleration of deprotonation. For both nitriles and sulphones, extraction of $k_2 : k_{-1}$ ratios from $k_{obs.}$ values and making the assumption that k_{-1} is insensitive to structural effects, reveals that substituents mildly accelerate expulsion of the leaving group by comparison with the larger effects of the same groups on concerted processes. α-Substituents accelerate the expulsion of leaving groups from sulphones and nitriles to an extent which increases the lower is the rank of the leaving group, thus pointing to the greater assistance rendered by the substituent the more difficult the leaving group is to expel. This is not true of β-substitution in either the sulphone or nitrile series, however, and in the sulphone series, phenyl groups at both β- and α-positions suppress expulsion of the leaving group from the *erythro*-isomer and severely depress protonation in the *threo*-isomer.

Expulsion of leaving groups from carbanions is remarkably insensitive to substituent effects. The present results confirm the impressions formed in the preceding paper and are directly in accord with conclusions reached for different systems in different media.[27,28]

EXPERIMENTAL

For general directions on kinetics of elimination reactions and product analysis see Part 30.[2] For kinetics of detritiation see Part 31.[3]

Preparation of Substrates.—Phenoxy-sulphones. For substrates (2), (3), (29), and (31), the general route: phenoxy-alcohol ⟶ tosylate or chloride ⟶ sulphide ⟶ sulphone

[26] V. Fiandanese, G. Marchese, and F. Naso, *J.C.S. Perkin II*, 1973, 1538.

[27] E. Baciocchi, P. Perucci, and C. Roi, *J.C.S. Perkin II*, 1975, 329.

[28] Z. Rappoport and A. Topol, *J.C.S. Perkin II*, 1975, 863.

was used. Formation of tosylates was with toluene-*p*-sulphonyl chloride in pyridine and of chlorides with thionyl chloride according to standard procedures. Sulphides were obtained from chlorides or tosylates by treatment with a 10% excess of sodium thiophenoxide in ethanol at 80 °C for 1 h. Isolation was by dilution with water and extraction

TABLE 6

Substrates and product analyses

Substrate [a] no.	Yield	M.p. (°C)	Found (%) C	H	N	Formula	Reqd. (%) C	H	N	Products (%)	
(2)	64 [b]	125 [c]	70.7	5.1		$C_{20}H_{18}O_3S$	71.0	5.4		$PhSO_2$·CHPh·CH_2OEt [d] 91	PhOH 91
(3) *	91 [b]	110 [c]	71.0	5.7		$C_{20}H_{18}O_3S$	71.0	5.4		$PhSO_2$·CHCHPh·OEt [e] 97	PhOH 93
(4) †	74 [b]	173 [c]	75.4	5.2		$C_{26}H_{22}O_3S$	75.4	5.3		$PhSO_2$·CPh:CHPh (*E*) [f] 97	PhOH 87
(5)	76 [b]	185 [c]	75.2	5.2		$C_{26}H_{22}O_3S$	75.4	5.3		$PhSO_2$CPh:CHPh (*E*) [f] 77 $PhSO_2$CPh:CHPh (*Z*) [g] 21	PhOH 83
(7)	69 [b]	113 [c]	67.9	5.1		$C_{20}H_{18}O_2S_2$	67.8	5.1		$PhSO_2$CHPh·CH_2OEt [d] 92 $PhSO_2$CH:CHPh [i]	PhSH 85
(9) [20]	97 [b]	179	62.7	4.7		$C_{20}H_{18}O_4S_2$	62.2	4.7		$PhSO_2$CHPh·CH_2OEt [i]	
(11)	39 [h]	153/0.007 [j]	75.4	5.4	5.8	$C_{15}H_{13}NS$	75.3	5.4	5.9	CN·CHPh·CH_2OEt [k] 92	PhSH 87
(13)	78 [b]	109 [l]	66.3	4.9	5.3	$C_{15}H_{13}NO_2S$	66.4	4.8	5.2	CN·CHPh·CH_2OEt [k] 90	$PhSO_2H$ [m] 77
(15)	93 [h]	140/0.1 [j] n_D^{17} 1.5870	79.1	5.6		$C_{21}H_{18}OS$	79.3	5.7		PhCOCHPh·CH_2OEt [n] 96	PhSH 83
(17)	98 [b]	107 [o]	72.1	5.3		$C_{21}H_{18}O_3S$	72.0	5.1		PhCOCHPh·CH_2OEt [n] 89	$PhSO_2H$ [m] 81
(18)	91 [b]	110 [c]	71.0	5.7		$C_{20}H_{18}O_3S$	71.0	5.4		$PhSO_2CH_2$CHPh·OEt [e]	PhOH 93
(19)	40 [d]	140 [c]	68.0	5.1		$C_{15}H_{16}O_2S_2$	68.0	5.1		$PhSO_2$·CH_2·CHPh·OEt [e]	PhSH 77
(21)	90 [h]	129/0.05 [j]	75.2	5.3	6.0	$C_{15}H_{13}NS$	75.3	5.4	5.9	CNCH:CHPh 92	PhSH 78
(22)	99 [b]	124.7 [o]	66.2	4.7	5.0	$C_{15}H_{13}NO_2S$	66.4	4.8	5.2	CNCH:CHPh 91	$PhSO_2H$ [m] 79
(23)	99 [h]	113 [l]	79.4	5.8		$C_{21}H_{18}OS$	79.3	5.7		PhCOCH:CHPh 87	PhSH 71
(24)	97 [b]	155.1 [o]	72.1	5.1		$C_{21}H_{18}O_3S$	72.0	5.1		PhCOCH:CHPh 93	
(26)	98 [h]	58 [p]	74.8	6.4		$C_{16}H_{16}OS$	75.0	6.3		CH_3COCH:CHPh 96	PhSH 78
(28)	96 [b]	118.6 [o]	66.5	5.4		$C_{16}H_{16}O_3S$	66.7	5.6		CH_3COCH:CHPh 93	$PhSO_2H$ [m] 87
(29)	97 [b]	169/0.05 [j] 42—43 [c] n_D^{22} 1.5704	65.1	6.1		$C_{15}H_{16}O_3S$	65.1	5.8		$PhSO_2CH_2$·CHMe·OEt [q] 98	PhOH 89
(30)		63 [c]	65.7	6.1		$C_{16}H_{18}O_3S$	66.1	6.3		$PhSO_2CH_2$·C(Me):CH_2 [r] 91	PhOH 88
(31)	90 [b]	169/0.05 [j] 41—42 n_D^{24} 1.5720	64.8	5.8		$C_{15}H_{16}O_3S$	65.1	5.8		$PhSO_2$CMe·HCH_2·OEt [s] 97	PhOH 87
(32)	83 [h]	173/0.1 [j] n_D^{21} 1.5976	61.8	5.6		$C_{15}H_{16}O_2S_2$	61.5	5.5		$PhSO_2CH_2$·CHMe·OEt [q] 95	PhSH 84
(33)		65 [c]	62.6	6.0		$C_{16}H_{18}O_2S_2$	62.7	5.9		$PhSO_2CH_2C$(Me):CH_2 [r] 92	PhSH 80
(34)	85 [h]	177/0.05 [j] n_D^{22} 1.6017	61.8	5.5		$C_{15}H_{16}O_2S$	61.5	5.5		$PhSO_2$·CHMe·CH_2OEt [s] 93	PhSH 81
(36)	93 [t]	76 [o]	65.1	5.7		$C_{15}H_{16}O_3S$	65.2	5.8		$PhSO_2CH_2$CHPhOEt [u] 91	

* ^{1}H n.m.r. ($CDCl_3$) Aromatics + τ 3.5 (1 H, d, J = 3 Hz), 5.6 (1 H, d, J = 3 Hz). † ^{1}H n.m.r. ($CDCl_3$) Aromatics + τ 4.0 (1 H, d, J = 9 Hz), 5.3 (1 H, d, J = 9 Hz). Both spectra unchanged at −60 °C.

[a] Tables 1—4. [b] By oxidation of the sulphide with $H_2O_2/(NH_4)_6Mo_7O_{24}$. [c] From EtOH. [d] M.p. 75 °C (from ethanol) (Found: C, 66.2; H, 6.2. $C_{19}H_{18}O_3S$ requires C, 66.2; H, 6.3%). [e] M.p. 100 °C (from ethanol) (Found: C, 66.0; H, 6.3%). [f] M.p. 184 °C (from ethanol) (Found: C, 75.1; H, 5.1. Calc. for $C_{20}H_{16}O_2S$: C, 75.0; H, 5.1%). Lit. (Y. Sharota, T. Nagai, N. Tokura, *Bull. Chem. Soc. Japan*, 1966, **39**, 405), m.p. 182.5—183 °C. [g] M.p. 128 °C (from ethanol) (Found: C, 75.3; H, 4.7%), lit. (H. Hellmann and D. Eberle, *Annalen*, 1963, **662**, 188), m.p. 122 °C. [h] By addition of PhSH to alkene. [i] See text. [j] B.p. °C/mmHg. [k] B.p. 146 °C/12 mmHg, n_D^{20} 1.5210 (Found: C, 75.3; H, 7.3; N. 7.8. $C_{11}H_{13}NO$ requires C, 75.4; H, 7.4; N, 8.0%). [l] From Pr^i_2O. [m] As 4-nitrobenzyl sulphone. [n] M.p. 73 °C (Found: C, 80.4; H, 7.0; $C_{17}H_{18}O_2$ requires C, 80.3; H, 7.1%). [o] From MeOH. [p] From pentane. [q] B.p. 122 °C/0.05 mmHg, n_D^{24} 1.5150, m.p. 40 °C (Found: C, 57.7; H, 7.1. $C_{11}H_{16}O_3S$ requires C, 57.9; H, 7.1%). [r] M.p. and mixed m.p. [s] B.p. 126 °C/0.05 mmHg, n_D^{17} 1.5200 (Found: C, 58.4; H, 7.4%). [t] By addition of methanol to alkene. [u] Ref. no. 3.

TABLE 7

Phenoxy-sulphides, $PhSCHR^1$·CHR^2·OPh

R^1	R^2	Yield (%)	B.p. (m.p)	Found (%) C	H	Formula	Reqd. (%) C	H
H	Ph	88 [a]	168/0.1 [b] n^{22} 1 623 [c]	78.3	6.0	$C_{20}H_{18}OS$	78.4	5.9
H	Me	87 [a]	130/0.05 [b]	74.2	6.8	$C_{15}H_{16}OS$	73.7	6.6
H	Me_2	*d,e,f*	120/0.2 [b] n^{19} 1.5790 [c]	74.1	7.0	$C_{16}H_{18}OS$	74.3	7.0
Ph	H	58 [a]	(84) [g]	78.5	5.9	$C_{20}H_{18}OS$	78.4	5.9
Me	H	90 [a]	128/0.05 [b] n^{25} 1.5875 [c]	73.5	6.9	$C_{15}H_{16}OS$	73.7	6.6
Ph	Ph [h]	24 [e,f]	138 [g]	81.9	6.1	$C_{26}H_{22}OS$	81.7	5.8
Ph	Ph [i]	24 [e,f]	156 [g]	81.3	5.8	$C_{26}H_{22}OS$	81.7	5.8

[a] From the tosylate. [b] °C/mmHg. [c] At D line. [d] Record destroyed. [e] From the chloride. [f] See text. [g] M.p. from ethanol. [h] *Erythro*. [i] *Threo*.

with chloroform. Sulphones were obtained by oxidation of sulphides with hydrogen peroxide and ammonium molybdate using Rydon's [29] procedure.

Substrate (2). 2-Phenoxy-1-phenylethanol was obtained by sodium borohydride reduction of ω-phenoxyacetophenone (75%), m.p. 60 °C (lit.,[30] m.p. 63—64 °C).

Substrate (3). Methyl 2-chloro-2-phenylacetate [31] (0.01 mol) was heated under reflux with phenol (0.01 mol) and sodium phenoxide (0.01 mol) in dioxan (20 ml) for 1 h. Dilution with water and extraction with ether gave the phenoxy-ester (80%), b.p. 136/0.1 mmHg, n_D^{23} 1.5614 (Found: C, 73.9; H, 5.9. Calc. for $C_{15}H_{14}O_3$: C, 74.3; H, 5.8%) (lit.,[32] b.p. 120 °C/10 mmHg). Reduction of the ester with lithium aluminium hydride in the usual way gave 2-phenoxy-2-phenylethanol (85%), m.p. 80 °C (lit.,[30] m.p. 80—81 °C).

Substrate (29). Treatment of 2-phenoxypropionic acid with boron trifluoride in methanol [33] gave the methyl ester, b.p. 75 °C/0.05 mmHg, n_D^{22} 1.5028 (Found: C, 73.9; H, 6.0. Calc. for $C_{15}H_{14}O_3$: C, 74.3; H, 5.8%) (lit.,[34] b.p. 76 °C/0.03 mmHg, n_D^{20} 1.5031). Reduction of the ester with lithium aluminium hydride gave 2-phenoxypropan-1-ol (88%), b.p. 129 °C/15 mmHg, n_D^{22} 1.5234 (lit.,[35] b.p. 120 °C/10 mmHg, n_D^{25} 1.4760).

Substrate (31). Treatment of methyloxiran with sodium phenoxide and phenol in benzene [36] gave 1-phenoxypropan-2-ol (30%), b.p. 123 °C/15 mmHg, n_D^{23} 1.5221 (lit.,[37] b.p. 125—130 °C/21 mmHg, n_D^{20} 1.5232).

Substrate (30). Addition of 2-methylpropene to benzenesulphenyl chloride [38] in carbon tetrachloride gave *2-chloro-2-methyl-1-phenylthiopropane*, b.p. 88 °C/0.2 mmHg, n_D^{19} 1.5988 (Found: C, 60.3; H, 6.8. $C_{19}H_{13}ClS$ requires C, 59.9; H, 6.6%). Treatment of the chloro-sulphide with phenol, as before, gave *2-methyl-2-phenoxy-1-phenylthiopropane*, b.p. 120 °C/0.2 mmHg, n_D^{19} 1.5790 (Found: C, 74.1; H, 7.0. $C_{16}H_{18}OS$ requires C, 74.3; H, 7.0%).

Substrate (4). Treatment of *E*-stilbene with benzenesulphenyl chloride [38] in carbon tetrachloride gave erythro-*2-chloro-1,2-diphenyl-1-phenylthioethane*. The chloride (0.01 mol) was kept at 90 °C with a solution of phenol (0.01 mol), and sodium phenoxide (0.01 mol) in dioxan (20 ml) for 45 min. Dilution with water and extraction with ether gave the *phenyl ether*.

Substrate (5). The threo-*sulphide* was obtained in the same way *via* the *chloro-sulphide*, obtained from *Z*-stilbene.

Phenylthio and Phenylsulphonyl Derivatives.—All substrates with the thiophenoxy-leaving group were prepared by triethylamine catalysed addition of thiophenol to the appropriate α,β-unsaturated sulphone, nitrile, or ketone which had been synthesised separately or generated *in situ* from the chloride or quaternary Mannich base. Oxidation of sulphides yielded sulphones.

Sulphone-sulphides. Substrates were derived as follows: (7) from phenyl 1-phenylethenyl sulphone. *Methyl 2-phenyl-2-phenylthioacetate* was obtained (75%) from methyl 2-chloro-2-phenyl acetate on treatment with sodium thiophenoxide in ethanol. It had b.p. 132 °C/0.1 mmHg, n_D^{21} 1.5947, m.p. 40 °C (Found: C, 69.8; H, 5.5. $C_{15}H_{14}O_2S$ requires C, 69.9; H, 5.5%). Reduction of the ester with lithium aluminium hydride gave the *sulphide-alcohol* (97%), b.p. 145 °C/0.1 mmHg, n_D^{23} 1.6180 (Found: C, 73.6; H. 6.0. $C_{14}H_{14}OS$ requires C, 73.2; H, 6.1%). Oxidation of the sulphide-alcohol gave the *sulphone-alcohol* (98%), m.p. 156 °C (from ethanol) (Found: C, 64.3; H, 5.3. $C_{14}H_{14}O_3S$ requires C, 64.1; H, 5.4%). Treatment of the sulphone-alcohol with thionyl chloride gave the *chloro-sulphone* (69%), m.p. 118 °C (from benzene–light petroleum) (Found: C, 60.3; H, 4.8. $C_{14}H_{13}ClO_2S$ requires C, 60.0; H, 4.7%). The chloro-sulphone was kept with an excess of triethylamine in benzene. When precipitation was complete, filtration and evaporation yielded the *alkenylsulphone* (35%), m.p. 73.5 °C (from ethanol–water) (Found: C, 68.3; H, 5.0. $C_{14}H_{12}O_2S$ requires C, 68.7; H, 5.4%). Treatment of the alkene (0.016 mol) with thiophenol (0.016 mol) and triethylamine (1 ml) in benzene (100 ml) gave, on evaporation after 18 h, the sulphone-sulphide (Table 6).

Substrate (19) from 2-phenylethenyl phenyl sulphone.[39]

Substrate (32) from phenyl propenyl sulphone.[40]

TABLE 8

Phenoxy-chlorides and tosylates, $ZCHR^1{\cdot}CHR^2OPh$

					Found (%)			Reqd. (%)	
R^1	R^2	Z	Yield (%)	M.p.[a]	C	H	Formula	C	H
H	Ph	OTs	81 [b]	88 [c]	69.0	5.2	$C_{21}H_{20}O_4S$	68.6	5.5
H	Me	OTs	89 [b]	44 [c]	62.7	6.0	$C_{16}H_{18}O_4S$	62.7	5.9
H	Me_2	Cl [d]	*e, f*	88/0.2 [g,h] n^{19} 1.5988	60.3	6.8	$C_{10}H_{13}ClS$	59.9	6.6
Ph	H	Cl	70 [j]	54 [k]	71.7	5.6	$C_{14}H_{13}ClO$	72.2	5.6
Me	H	OTs	93 [b]	93 [c]	63.0	5.8	$C_{16}H_{18}O_4S$	62.7	5.9
Ph	Ph [l]	Cl [d,f]	64	124 [m]	73.7	5.0	$C_{20}H_{17}ClS$	73.9	5.3
Ph	Ph [n]	Cl [d,f]	100	40 [p]	73.8	5.4	$C_{20}H_{17}ClS$	73.9	5.3

[a] °C. [b] From the alcohol. [c] From ethanol. [d] Thiophenoxy chloride. [e] Record destroyed. [f] From alkene and PhSCl. [g] B.p. [h] °C/mmHg. [i] At D line. [j] From alcohol and thionyl chloride. [k] M.p. from light petroleum, b.p. 40—60 °C. [l] *Erythro*. [m] From ether. [n] *Threo*. [p] Decomp. on attempted recrystallisation.

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Substrate (33) from 2-chloro-2-methyl-1-phenylsulphonylpropane by dehydrochlorination and subsequent addition of thiophenol to the alkene.[41]

Substrate (34) from 2-phenylsulphonylpropene. Ethyl benzene sulphinate[42] was prepared by ethanolysis of benzenesulphinyl chloride[43] and treatment with prop-2-enylmagnesium bromide[44] gave *2-phenylsulphinyl propene* (61%), b.p. 90 °C/0.1 mmHg, n_D^{22} 1.5728 (Found: C, 65.1; H, 5.9. $C_9H_{10}OS$ requires C, 65.1; H, 6.1%). Oxidation of the alkenyl sulphoxide gave the sulphone (80%), b.p. 110 °C/0.1 mmHg, n_D^{26} 1.5437 (Found: C, 58.9; H, 5.5. Calc. for $C_9H_{10}O_2S$: C, 59.2; H, 5.5%) (lit.,[45] b.p. 142 °C/4.5 mmHg, n_D^{20} 1.5470).

2-Methoxy-2-phenylethyl phenylsulphone by addition of methanol to 2-phenylethenyl phenyl sulphone.

Cyano-sulphides. Substrate (11) by addition of thiophenol to 2-phenylacrylonitrile.[46]

Substrate (21) by addition of thiophenol to cinnamonitrile.

Oxo-compounds. Substrate (23) by addition of thiophenol to chalcone.

Substrate (26) by addition of thiophenol to 4-phenylbut-3-en-2-one.

Substrates (9), (20). *Product analysis.* The bis-sulphone (3 g), in 0.2M-ethanolic sodium ethoxide, was kept at 25 °C for 30 min. The mixture was diluted with brine and extraction with dichloromethane gave a residue (1.90 g) which, on trituration with ethanol gave phenyl 2-phenylethenyl sulphone (1.56 g), m.p. and mixed m.p. 74 °C (lit.,[47] m.p. 75 °C). The ethanolic filtrates were evaporated and ^{1}H n.m.r. and g.l.c. (SE 30 column at 200 °C) analysis of the residue (0.32 g) showed phenyl 2-phenylethenyl sulphone and 1-phenyl-2-ethoxyethyl phenyl sulphone present in the ratio 3 : 1 giving the overall yields: 1-phenyl-2 ethoxyethyl phenyl sulphone, 3.3%; 2-phenylethenyl sulphone, 96.1%.

Product analysis for substrate (5) was carried out similarly.

Substrate (15). Treatment of 1′-phenyl-2′-dimethylaminopropiophenone[48] with methyl iodide in ether gave the *methiodide* (73%), m.p. 178 °C (Found: C, 54.4; H, 5.6; N, 3.7. $C_{18}H_{22}INO$ requires C, 54.7; H, 5.6; N, 3.5%). The salt with sodium thiophenoxide in methanol gave the sulphide (15) (93%).

2-Diethylamino-2-phenylpropiophenone was obtained by addition of dimethylamine to benzylideneacetophenone.

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