Elimination and Addition Reactions. Part 32.[1] Discrimination between Concerted and Stepwise Processes in Activated Elimination Reactions

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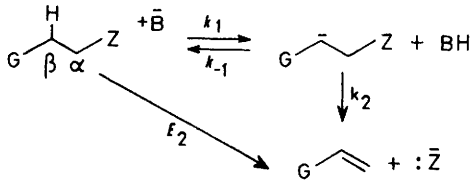
In 1,2-elimination reactions activated by phenylsulphonyl, cyano, and benzoyl groups with leaving groups SO_2Ph, SPh, and OPh, comparison of ionisation rates with elimination rates confirms that the $(E_1cB)_R$ mechanism operates in the sulphonyl and cyano activation series but in the benzoyl series the mechanism for all leaving groups is $(E_1cB)_I$. This difference in behaviour is discussed.

For all three activation series, comparison of elimination rates with predicted ionisation rates suggests assignments of $(E_1cB)_I$ mechanism when the leaving group is Cl, OAc, OTs, or OMes but E_2 mechanisms when it is I and possibly Br.

In all the cases studied, α- and β-phenyl substituents in chloro-, bromo-, and mesyloxy-sulphones affect elimination rates in a manner paralleled by the effect of these substituents on ionisation rates. The results strengthen assignments of $(E_1cB)_I$ mechanisms where these have been made.

The results are compared with those obtained in other systems in relation to current views on the relationship between stepwise and concerted processes.

In an accompanying paper [2] we examined elimination reactions in a large number of substrates activated by the phenylsulphonyl group with a view to obtaining leaving group abilities. It was pointed out that only when the mechanism of elimination is the pre-equilibrium carbanion mechanism $(E_1cB)_R$ [3] can direct information on leaving group ability be obtained. The $(E_1cB)_R$ mechanism was excluded for several of the substrates that we examined on the basis of their failing to undergo hydrogen–deuterium exchange more rapidly than elimination, or because they showed a primary kinetic



G = $PhSO_2$, CN, or PhCO

Z = Cl, Br, I, OTs, OMes, OAc, SO_2Ph, OPh, or SPh

SCHEME 1

deuterium isotope effect of greater than unity. For these substrates the mechanism of elimination must either be concerted (E_2) or have as rate-determining step ionisation of the substrate $(E_1cB)_I$.[3]

In this paper we report on the reactivity of these substrates and attempt to distinguish between $(E_1cB)_I$ and E_2 mechanisms on the basis of comparisons between elimination rates and ionisation rates predicted from Taft plots for the ionisation of simple carbon acids.[1] The effect of α- and β-phenyl substitution (Scheme 1) in these reactions has also been evaluated and the results are discussed against the background of the mechanistic assignments. Two groups of workers [4] have recently made convincing assignments of mechanism to elimination reactions producing sulphenes by these and other procedures.

The kinetic data for the substrates studied are in Tables 1 and 2. We have concentrated principally upon three series of activating groups: phenylsulphonyl, cyano, and benzoyl. We chose these three systems because the derived carbanion from each carbon acid differs in structure [1] and this allows comparison of the behaviour of different types of carbanion in the same type of reaction. Ketones differ from nitriles and sulphones in terms of ionisation equilibria in that, for a given pK_a, oxo-stabilised carbanions are reprotonated much more slowly than sulphonyl- or cyano-stabilised carbanions.[5] The implication of this behaviour is that in the steady state expression [equation (1)] for the

$$k_{obs} = k_1k_2[B^-]/(k_{-1}[BH] + k_2) \qquad (1)$$

formation of a carbanion which then undergoes elimination the term $k_{-1}[BH]$ is less likely to exceed k_2 for a ketone than, for example, a sulphone. Ketones are thus prone to give an $(E_1cB)_I$ rather than an $(E_1cB)_R$ mechanism.

Assignment of Mechanisms.—Results for the eliminations activated by phenylsulphonyl, cyano, and benzoyl groups are best seen by superimposition of the elimination results on the ionisation plots obtained in the previous paper (Figures 1—3).

It is obvious in the plots for the sulphone and nitrile series that the points for Z = SPh, OPh, and SO_2Ph all lie well below the ionisation lines as required by the $(E_1cB)_R$ mechanisms for these substrates.[2] In these cases the observed rate constant is the product of the ionisation rate, k_1, and $k_2/k_{-1}[BH]$ which is always $\ll 1$. When the activating group is PhCO, however, the points for OPh, SO_2Ph, and SPh lie within ± 1 log unit

[1] Part 31, P. J. Thomas and C. J. M. Stirling, preceding paper.
[2] D. R. Marshall, P. J. Thomas, and C. J. M. Stirling, accompanying paper (Part 30).
[3] F. G. Bordwell, M. M. Westling, and K. C. Yee, *J. Amer. Chem. Soc.*, 1970, **92**, 5950.
[4] J. F. King and R. P. Beatson, *Tetrahedron Letters*, 1975, 973; M. B. Dary, K. T. Douglas, J. S. Loran, A. Steltner, and A. Williams, *J. Amer. Chem. Soc.*, 1977, **99**, 1196.
[4] J. F. King and R. P. Beatson, *Tetrahedron Letters*, 1975, 973.
[5] D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965, p. 10.

of the ionisation line and an $(E_1cB)_I$ mechanism can reasonably be assigned.

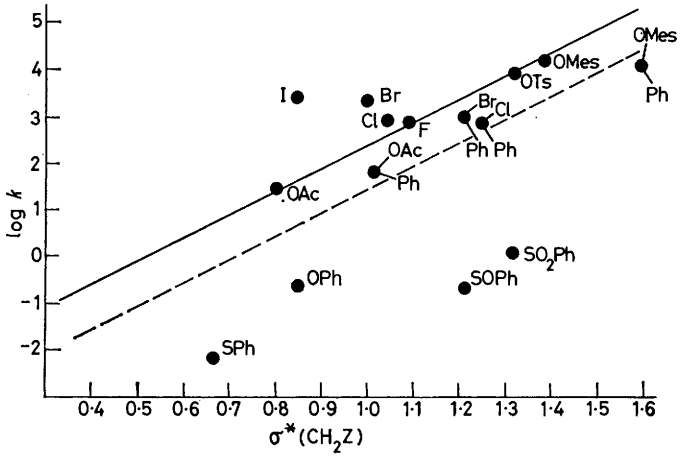


FIGURE 1 Comparison of elimination rates (●) and ionisation rates (——) in sulphones, $PhSO_2{\cdot}[CH_2]_2{\cdot}Z$, at 25 °C in EtO^-–EtOH

In all three series, the available data in the comparison between elimination rates and predicted ionisation rates strongly suggest that acetate, tosylate, mesylate, and chloride leaving groups are expelled by the $(E_1cB)_I$ mechanism irrespective of the activating group. Although the Taft relationship may be vulnerable to criticism in detail,[1] correlation of elimination rate with ionisation rate within one power of 10 seems reasonable in the assignment of the $(E_1cB)_I$ mechanism, particularly when the Taft plot for sulphone ionisation shows an exceptionally high correlation over a wide range of reactivity values (*ca.* $10^{9.5}$).[1]

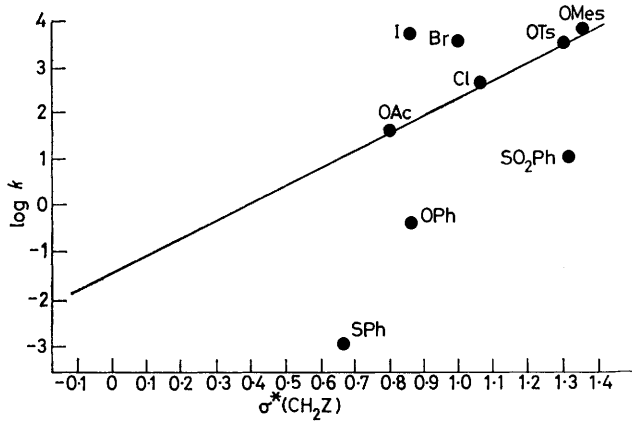


FIGURE 2 Comparison of elimination (●) and ionisation (——) rates in nitriles, $NC{\cdot}[CH_2]_2{\cdot}Z$, at 25 °C in EtO^-–EtOH

By contrast, we assign concerted (E_2) mechanisms for the reactions for the iodo- and possibly bromo-sulphones and nitriles (below). These substrates showed deviations (Br, +1.0; I, +1.9 log units) from the lines for the sulphone series, and in the nitrile series the positive deviations are 1.2 for Br and 1.9 for I. Our evidence for the assignment of concerted mechanisms is reinforced by the pattern of primary deuterium isotope effects (Table 1). In the sulphone series, values of k_H/k_D remain nearly constant for Z = OAc, F, or OTs, consistent with their regularity in matching elimination rate with predicted ionisation rate. For Cl, Br, and I, however, k_H/k_D rises sharply. A similar effect has been observed in earlier work by Naso and his collaborators,[6] who examined the fluoro-, chloro-, and bromo-sulphones in methanolic sodium methoxide and expressed the reasonable doubt that the whole series could share a common mechanism because of the trend in primary deuterium isotope effect. Their results disposed them to favour the $(E_1cB)_I$ mechanism for fluoro- and the E_2 mechanism for the bromo- and the chloro-compounds. In the nitrile series, values of primary deuterium isotope effects for substrates with Z = I or Br are much greater than with Z = Cl, OTs, or OAc, again pointing to the

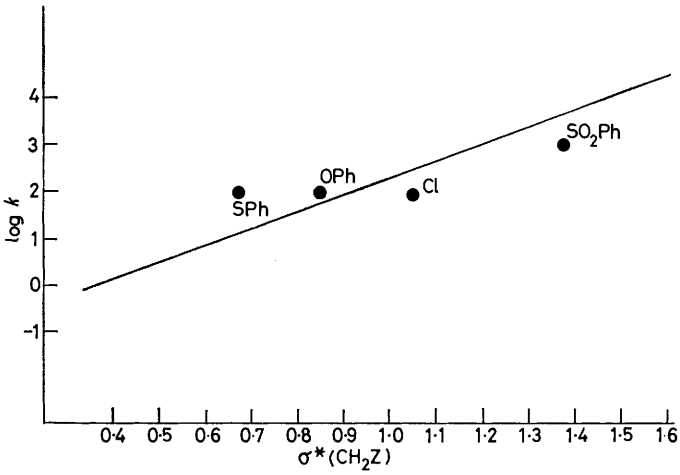


FIGURE 3 Comparison of elimination (●) and ionisation (——) rates in ketones, $PhCO{\cdot}[CH_2]_2{\cdot}Z$

operation of a different mechanism. Skell and McNamara have assigned a concerted mechanism to the elimination of iodide from 2-phenylsulphonylbutyl iodides in pyridine on the basis of the stereospecificity of the reaction.[7]

Comparison of the reactivities of the tosylate and the *p*-nitrobenzenesulphonate esters in the sulphone series (Table 1) shows very approximately that ρ for the leaving group is *ca.* +0.4. Direct comparisons with concerted processes such as in the phenethyl series, are not possible because potassium t-butoxide in t-butyl alcohol has been used as the solvent–base system. Values in the phenethyl series, however, range [8] from 0.95 to 1.3. What evidence is available suggests [9] that ρ would be higher if the base–solvent system used had been ethanolic sodium ethoxide, as in the present work.

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

[7] P. S. Skell and J. H. McNamara, *J. Amer. Chem. Soc.*, 1957, **79**, 85.

[8] J. Banger, A. F. Cockerill, and G. L. O. Davies, *J. Chem. Soc.* (*B*), 1971, 498.

[9] W. H. Saunders and A. F. Cockerill, 'Mechanisms of Elimination Reactions,' Wiley, New York, 1973, p. 64.

This very low leaving group sensitivity is, of course, consistent either with an attenuated effect on ionisation rate or a concerted process with very little C–Z bond cleavage in the transition state. The evidence from ionisation rate comparisons leads us to favour the former alternative. The $(E_1cB)_I$ mechanism has been assigned to the elimination of tosylate ion from *trans*-2-*p*-tolylsulphonylcyclohexyl toluene-*p*-sulphonate under basic conditions on the basis of a two-point Taft plot for the ionisation of *p*-tolylsulphonylcyclohexanes.[10]

The three ionisation plots [1] for sulphones, nitriles, and ketones intersect near $\sigma^*(ZCH_2) = 1.05$. This is close to the value of $\sigma^*(ClCH_2)$ and so those substrates which eliminate by the $(E_1cB)_I$ mechanism should have similar rates for this leaving group. All three chlorides (Table 1) show closely similar elimination rates consistent with a common mechanism. By the same token, the sulphone tosylate [$\sigma^*(CH_2OTs) = 1.31$] [10] and mesylate [$\sigma^*(CH_2OMes) = 1.37$] [11] should be more reactive than the cyano compounds if the $(E_1cB)_I$ mechanism operates

TABLE 1

Rates [a] of elimination in compounds, $G[CH_2]_2{\cdot}Z$ in ethanolic sodium ethoxide [a]

	G		
Z	$PhSO_2$	CN	PhCO
F	892 (2.0) [c]		
Cl	798 (3.6)	610 [d] (3.6)	768
Br	2 560 (5.0)	4 402 [d] (5.2)	
I	2 900 (5.6)	5 180 [d] (5.9)	
OAc	21.3 (1.9)	44.0 (2.1)	8.67 [h,k]
OTs	6 700 (2.0)	4 920(3.7)	
OPN*m* [e]	< 53 300		
OMes [f]	11 100	5 898 [d]	
OPh	0.36 [g] (+)	9.44 [g]	31.5 [g–i]
SPh	0.02 [j] (1.01)	0.010 [j]	108; 29.5 [h] (2.2)
SO_2Ph	1.05 (1.01)	17.1 (1.13)	1 040; 620 [h] (2.1) [d]

[a] Units 1 mol^{-1} s^{-1} at 25 °C. [b] Primary deuterium isotope effect in parentheses; + indicates hydrogen–deuterium exchange faster than elimination. [c] Derived from ref. 6 (methanolic sodium methoxide). [d] Base *p*-nitrophenoxide; value derived by use of conversion factor × 2 880. [e] *m*-Nitrophenylsulphonyloxy. [f] Methylsulphonyloxy. [g] J. Crosby and C. J. M. Stirling, *J. Chem. Soc.* (*B*), 1970, 679. [h] Value for G = MeCO. [i] For Figure 3, this value is multiplied by 3; *cf.* values for Z = SPh and SO_2Ph. [j] Value determined by R. P. Redman (ref. 28). [k] Value in H_2O–OH^- at 30 °C (L. R. Fedor, *J. Amer. Chem. Soc.*, 1967, **89**, 4479).

in all cases because $\rho^*(X = PhSO_2)$ is greater than $\rho^*(X = CN)$. Likewise, the sulphone acetate [$\sigma^*(CH_2OAc) = 0.8$] * should be *less* reactive than the cyano-acetate. Table 1 shows this to be the case.

The widespread assignment of concerted mechanisms to bimolecular eliminations has received powerful criticism from Bordwell,[12] which has been directed particularly at the making of fine distinctions from variations of isotope effects and deviations from linear free-energy plots. The applicability of our Taft ionisation plots has been discussed in the preceding paper.[1] Deviations from the Taft plots were pointed out and deviant points were ignored in determining the gradients of the Taft lines. As these deviant points all showed *negative* deviations, inclusion of these points would have the effect of making the elimination rate constants for Br, and especially I, digress even further beyond the ionisation line into the concerted region.

Our drawing of conclusions from the Taft plot may be vulnerable to criticism so far as Br is concerned, because Br, Cl, and F have closely similar $\sigma^*(CH_2Z)$ values.[13] The value of $\sigma^*(CH_2I)$, however, is substantially less than values for the other halogens [13] and yet, even with the very high value of ρ^* observed for sulphone ionisation, the iodo-sulphone is the most reactive substrate in the series. This points to the operation of a mechanism in which the C–I bond is broken in the rate-determining step. The element effect observed, I > Br > Cl, is opposite to the trend in $\sigma^*(CH_2Z)$ and is the same, albeit very much diminished, as that observed in the phenethyl series,[14,15] the concertedness of whose reactions is not seriously questioned.[12] Conformational differences have recently been shown to give rise to striking anomalies in the ionisation rates of nitro-compounds,[16] providing a further source of criticism in the use of the Taft relationship. The incursion of differential conformational factors should, however, surely not operate when the gradation in non-bonded interactions is as delicate as for the halogens, in which dipole directions and group sizes can vary only gradually. The position of tosylate on the reactivity scale provides another contrast with weakly activated systems. In the sulphone series, the order of $k_{rel.}$ values is OTs (2.6) > I (1.1) > Br (1.0) and in the phenethyl series I (68) > Br (11) > OTs (1.0).[14] A tosylate : bromide ratio greater than 1 : 1 can be expected only when the degree of extension to the leaving group is either very large or very small.[17]

Leaving group effects on addition–elimination reactions have recently received detailed study,[18] and in this work the order OMes ~ OTs > Br ~ Cl is found and regarded as characteristic of an early transition state in expulsion of a leaving group from a carbanion–ammonium

* There is no literature value for $\sigma^*(CH_2OAc)$. A plot of σ^* values against the Swain field-effect parameter (C. G. Swain and E. C. Lupton, *J. Amer. Chem. Soc.*, 1968, **90**, 4328) suggests a value *ca.* 0.90 and $\sigma_I(CH_2OAc) = 0.34$ (M. Charton, *J. Org. Chem.*, 1964, **29**, 1222) gives $\sigma^* = 0.75$. We have used $\sigma^*(CH_2OAc) = 0.80$ throughout this series.

[10] J. Hine and O. B. Ramsay, *J. Amer. Chem. Soc.*, 1962, **84**, 973.

[11] P. J. Stang and A. G. Anderson, *J. Org. Chem.*, 1976, **41**, 781 give σ_I (OMes) = +0.61 which is converted with the factor 0.45 into 1.36 for $\sigma^*(CH_2OMes)$.

[12] F. G. Bordwell, *Accounts Chem. Res.*, 1972, **5**, 374; Symposium on 1,2-Elimination Reactions, 59th Chemical Conference and Exposition of the Chemical Institute of Canada at London, Ontario, June 6—9, 1976.

[13] R. W. Taft in 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, ch. 13.

[14] C. H. De Puy and D. H. Froemsdorf, *J. Amer. Chem. Soc.*, 1957, **79**, 3710.

[15] C. H. De Puy and C. A. Bishop, *J. Amer. Chem. Soc.*, 1960, **82**, 2535.

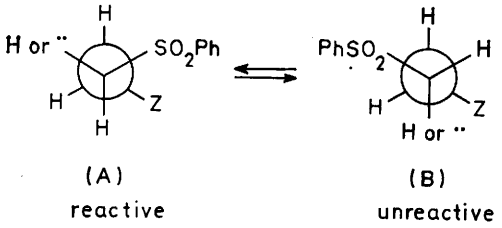
[16] F. G. Bordwell and J. E. Bartmess, unpublished work; we thank Professor Bordwell for showing us a manuscript of this work.

[17] A. F. Cockerill, *Tetrahedron Letters*, 1969, 4913.

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

zwitterion. Elimination rates in sulphones, $ArSO_2{\cdot}CH_2{\cdot}CH_2Z$, where Z = Br, Cl, or OTs, have also been measured [19] using tertiary amines in acetonitrile as the base–solvent system. The small leaving group effect (variable with the amine used) was interpreted as resulting from an $(E_1cB)_I$ process. In neither case can the evidence for discrimination between concerted and stepwise mechanisms be regarded as definitive.

It has been suggested * in relation to the behaviour of the iodo- and bromo-sulphones that the population of conformer (A) (Scheme 2) of the substrate or its derived



(A) reactive (B) unreactive

anion becomes increasingly favoured on going from Z = F to Z = I. This would explain either the greater tendency for the E_2 mechanism to be adopted or the extra facility of the $(E_1cB)_I$ mechanism because of the greater accessibility of the proton removed from (A). It is not clear, however, why conformer (A) might be preferred as Z increases in size, unless this is due to intramolecular electron donation by the halogen atom to the electronegative phenyl group.

Merging of Pathways.—The mechanistic change in this series appears to be a gradual one and our results do not favour mechanistic discontinuity at the (E_1cB)–E_2 borderline.

Such merging of transition states has been discussed by More O'Ferrall,[20] who concludes that this will happen only when the intermediate species (carbanion) is very unstable. The halogen leaving groups have previously been seen to be the most reactive [2] and so the β-halogeno-carbanion is very unstable with respect to both elimination and to reprotonation because reprotonation from sulphone-stabilised carbanions is very rapid.[5]

In a later paper, More O'Ferrall and Warren [21] compared elimination rates of fluorene derivatives with ionisation rates of model compounds. Positive deviations of elimination rates from the Taft plot led to the suggestion that E_2 mechanisms applied when the leaving group was Cl or Br. Merging of E_2 and $(E_1cB)_I$ reaction paths was, however, ruled out on the grounds of the stability of the fluorenyl carbanion.

Effects of α- and β-Phenyl Substitution on Reactivity.—Structural effects on concerted 1,2-eliminations have been studied intensively and one safe generalisation can be made. Insertion of a phenyl group at C_α or C_β is always accelerative and usually substantially so. In phenethyl bromide, for example, reactions in ethanolic sodium ethoxide are accelerated 50-fold by an α-phenyl and 350-fold by a β-phenyl group.[22] We have shown that in ionisation of sulphones [1] and nitro-compounds,[23] placement of a phenyl group at C_α depresses the ionisation rate, and Hibbert [24] has shown that β-phenyl substitution in bis-sulphones inhibits ionisation in a sterically crowded situation. Against this background, our results for the effect of α- and β-phenyl groups on elimination in halogeno-sulphones (Table 2) can be considered. α-Phenyl substitution depresses elimination rates by factors of 2—5 consistent with the rate depression of ionisation in model systems with poor leaving groups. The contrast with concerted processes is obvious and suggests that both α-phenyl halides eliminate by the $(E_1cB)_I$ mechanism. The data of Figure 1 reinforce these conclusions; the broken line is the extrapolation of ionisation rates for model substrates which contain α-phenyl substituents.[1] Elimination rates of α-phenyl sulphones with Z = OAc, Cl, Br, and OMes all lie close to this line. Similarly, β-phenyl substitution produces only slight acceleration of elimination when Z = Cl or Br. This behaviour is again not consistent with a concerted process, which is substantially accelerated by such a structural change. Neither is it consistent in detail with results for bis-sulphones,[24] but in these cases two very bulky groups, in addition to the aryl group, are attached to the ionising carbon atom. This pattern of response to phenyl substitution in these halogeno-sulphones again suggests the possibility that the unsubstituted bromo-sulphone

TABLE 2

Effects of α- and β-phenyl substitution on ionisation and elimination rates [a,b] of sulphones $PhSO_2{\cdot}C_\beta H_2{\cdot}C_\alpha H_2Z$

		Elimination [c]				Ionisation [d]	
α	β	Z = Cl	Z = Br	Z = OMes	Z = OAc	Z = NMe_2	Z = OEt
H	H	798 (3.6)	2 600 (5.0)	11 097 (2.0)	21.3 (1.93)	0.016	0.71
Ph	H	651 (1.9)	1 194 (2.1)	3 994 (2.3)	45.2 (1.86)	0.010	0.123
H	Ph	1 690 (2.9)	11 610	5 482 (2.2)	175.1 (1.9)	0.057	0.90
α-Ph/α-H		0.82	0.46	0.36	2.13		
β-Ph/β-H		2.12	4.46	0.49	8.22		

[a] Reactions in ethanolic sodium ethoxide at 25 °C. [b] Units l mol^{-1} s^{-1}. [c] Primary kinetic deuterium isotope effects in parentheses. [d] Detritiation rates.

* By a referee of the preliminary communication.

[19] Y. Yano and S. Oae, *Tetrahedron*, 1970, **26**, 27.
[20] R. A. More O'Ferrall, *J. Chem. Soc.* (*B*), 1970, 274.
[21] R. A. More O'Ferrall and P. J. Warren, *J.C.S. Chem. Comm.*, 1975, 483.
[22] E. D. Hughes, C. K. Ingold, S. Marsterman, 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.
[23] P. F. Cann and C. J. M. Stirling, *J.C.S. Perkin II*, 1974, 817.
[24] F. Hibbert, *J.C.S. Perkin II*, 1973, 1289.

eliminates by the E_2 mechanism in contradistinction to the α- and β-phenyl bromo-sulphones whose behaviour is consistent with rate-determining ionisation. Behaviour of the β-phenyl mesyloxy-sulphone does not, however, conform to this pattern.

More severe rate-depressive effects have been observed in eliminations of 9-XCH_2-fluorenyl derivatives;[21] α-phenyl substitution depresses the elimination rate by factors of 12 and 20 for Br and Cl, respectively. The response of these halides to α-phenyl substitution is similar to that for the halogeno-sulphones, but we find the rate depressive effect notably greater for Br than for Cl. The results for fluorenyl derivatives are considered to support mechanistic discontinuity at the E_2–$(E_1cB)_I$ borderline.

Acceleration of elimination in the acetoxy-sulphone by insertion of a β-phenyl group is again broadly consistent with the predicted effect on an $(E_1cB)_I$ mechanism as for the chloride and bromide. The response of the acetoxy-sulphone to α-phenyl substitution, however, is different from that of the halides and the mesylate, and in the preceding paper it was concluded that no confident explanation can, at present, be advanced for the effect of an α-phenyl group on ionisation rate. Preliminary work[25] shows that, as expected, the inhibitory or acceleratory effect of an α-phenyl group on elimination rate and its magnitude is dependent on mechanism. Further, comparison of sulphones and nitriles suggests that the effect is not related to the size of the activating group. An explanation based on steric effects is, therefore, probably not satisfactory. Current work has been directed towards evaluation of the effect of α-phenyl substitution on the ionisation rates of ketones and nitriles. These data will allow interpretation of substituent effects on activated eliminations of differing mechanisms and the results will be reported in a later paper.

EXPERIMENTAL

For general directions see Part 30.[2]

Kinetics.—These studies were carried out as described in Part 30.[2] Reactions were followed by observing the appearance of the appropriate vinylic compound.

The quantitative g.l.c. technique was used for measuring the rates of elimination of 2-cyanoethyl acetate and its [2,2-$^2H_2$]-analogue (SE30 column at 50 °C). Rates of elimination for most of the cyano-substrates were measured using *p*-nitrophenoxide as the base to enable u.v. spectroscopy to be used. Product analysis checks were carried out by this technique and a conversion factor from EtO^-–EtOH to p-$O_2N{\cdot}C_6H_4{\cdot}O^-$–EtOH was obtained by using 2-cyanoethyl tosylate.

Preparation of Substrates.—Details of yields, physical properties, and analyses are given in Table 3.

1-Chloro-2-phenylsulphonylethane was prepared by the method of Klamann and Bertoch[26] from 2-phenylsulphenylethanol. 1-Bromo-2-phenylsulphonylethane was prepared by oxidation of 1-bromo-2-phenylthioethane.[27] 2-Phenyl-2-phenylsulphonylethanol was prepared by a multistep process described by Redman;[28] details of Dr. Redman's experiments are reproduced below.

2-Chloro-2-phenylacetyl chloride. Phosphorus pentachloride (104 g, 500 mmol) was mixed with mandelic acid (38 g, 250 mmol). After 10 min the solid mass turned liquid. The mixture was then refluxed for 2 h and fractionated to give the chloride (70%), b.p. 118—120° at 16 mmHg, n_D^{21} 1.5448 (lit.,[29] b.p. 118° at 24 mmHg).

Methyl 2-chloro-2-phenylacetate. The acid chloride (3.8 g, 20 mmol) was added dropwise to methanol (15 ml) at 0 °C. After 2 h at room temperature the mixture was added to saturated sodium hydrogen carbonate solution. Extraction with ether gave the ester (92%), b.p. 130—131° at 16 mmHg, n_D^{22} 1.5250 (lit.,[30] b.p. 123—126° at 11 mmHg, n_D^{20} 1.4963).

Methyl 2-phenyl-2-(phenylthio)acetate. The ester (5.6 g, 30 mmol) and benzenethiol (3.6 g, 33 mmol) in methanol (30 ml) containing sodium (0.69 g, 30 mmol) were refluxed for 30 min. Water was added and extraction gave the *sulphide* (75%), b.p. 130—134° at 0.1 mmHg, n_D^{21} 1.5947, m.p. 40° (Found: C, 69.8; H, 5.5. $C_{15}H_{14}O_2S$ requires C, 69.9; H, 5.5%).

2-Phenyl-2-(phenylthio)ethanol. The sulphide (5.1 g, 20 mmol) in dry ether (30 ml) was added slowly to a suspension of lithium aluminium hydride (1.5 g) in ether (100 ml) and the mixture was stirred at room temperature for 15 min. Excess of hydride was destroyed with ethyl acetate and the mixture was acidified with dilute sulphuric acid. Extraction gave the *alcohol* (97%), b.p. 142—146° at 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%).

2-Phenyl-2-phenylsulphonylethanol. The sulphide alcohol was oxidised in the usual way to give the *sulphone* (98%), m.p. 156° (from ethanol) (Found: C, 64.3; H, 5.3. $C_{14}H_{14}O_3S$ requires C, 64.1; H, 5.4%).

2-Phenyl-1-phenylsulphonylethanol was prepared as described by Field.[31]

The preparation of chlorides from alcohols is typified in the preparation of *1-chloro-1-phenyl-2-phenylsulphonylethane*. The alcohol (20 mmol) in dry methylene chloride (100 ml) was added slowly to thionyl chloride (100 mmol). After 15 h at reflux, evaporation gave the chloride (96%), m.p. 89.3° (from di-isopropyl ether).

The preparation of bromides from alcohols is typified in the preparation of *1-bromo-1-phenyl-2-phenylsulphonylethane*. Phosphorus tribromide (11 mmol) in dry ether (100 ml) was added slowly to 2-phenyl-1-phenylsulphonylethanol (10 mmol) in ether (100 ml) and pyridine (0.1 ml). After refluxing for 4 h, saturated aqueous sodium hydrogen carbonate was added. Evaporation of the dried organic layer gave the bromide (99%), m.p. 99.4° (from di-isopropyl ether).

The preparation of iodides is typified by the preparation of *1-iodo-2-phenylthioethane*. 1-Bromo-2-phenylthioethane (10 mmol) in acetone (100 ml) was refluxed for 3 days with potassium iodide (4 g). Extraction gave crude iodo-

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[30] A. B. H. Funcke, R. F. Rekker, M. J. E. Ernsting, and W. T. Nauta, *Arzneimittel-Forsch.*, 1956, **6**, 60 (*Chem. Abs.*, 1956, **50**, 10,278c).
[31] L. Field, *J. Amer. Chem. Soc.*, 1952, **74**, 3919.

sulphide, which was oxidised with hydrogen peroxide and ammonium molybdate as before.[2]

The preparation of acetates is typified by the preparation of *2-phenylsulphonylethyl acetate*. 2-Phenylsulphonylethanol [32] (20 mmol) in dry toluene (100 ml) was stirred with acetyl chloride (40 mmol) for 12 h at 25 °C. Saturated aqueous sodium hydrogen carbonate was added. Evaporation of the dried organic layer gave the acetate (97%), m.p. 43.8° (from di-isopropyl ether).

Tosylates and mesylates were prepared in a similar way, typified by the preparation of *2-phenylsulphonylethyl toluene*-p-*sulphonate*. The alcohol (20 mmol) in dry methylene chloride (30 ml) and dry pyridine (30 ml) was cooled to 0 °C. Toluene-*p*-sulphonyl chloride (22 mmol) was added slowly. The mixture was maintained at 0 °C for 15 h. Water (10 ml) was added over 20 min. Addition of more water (100 ml) and extraction gave the tosylate (68%), m.p. 88.8° (from ethanol).

Deuteriated Substrates.—These were prepared using the above methods and deuteriated alcohols. The deuteriated alcohols were prepared by refluxing the alcohol (100 mmol) with NaOD in D_2O (25 ml) and sufficient dioxan to give a homogeneous solution until complete deuteriation in the β-methylene group had been achieved (^1H n.m.r.).

TABLE 3

Substrates, $G[CH_2]_2Z$, and product analyses [a]

G	Z	Yield %	B.p. (°C/mmHg) or m.p. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N	Product (%)
$PhSO_2$	Cl	98	M.p. 78.5 [b]	(Lit.,[c] m.p. 78.5)							$PhSO_2·[CH_2]_2·OEt$ [d] (98)
$PhSO_2$	Br	97 [e,f]	M.p. 95.0 [b]	(Lit.,[g] m.p. 95)							$PhSO_2·[CH_2]_2·OEt$ [d] (96)
$PhSO_2$	I	97	M.p. 100 [b]	32.4	3.1		$C_8H_9IO_2S$	32.4	3.0		$PhSO_2·[CH_2]_2·OEt$ [d] (93)
$PhSO_2$	OAc	97 [h]	M.p. 43.8 [i]	52.5	5.2		$C_{10}H_{12}O_3S$	52.6	5.3		$PhSO_2·[CH_2]_2·OEt$ [d] (87)
$PhSO_2$	OTs	68 [h]	M.p. 88.8 [b]	(Lit.,[j] m.p. 88)							$PhSO_2·[CH_2]_2·OEt$ [d] (97)
$PhSO_2$	OPN*m* [k]	95 [h]	M.p. 112.4 [b]	45.3	3.6	3.8	$C_{14}H_{13}NO_7S_2$	45.3	3.5	3.8	$PhSO_2·[CH_2]_2·OEt$ [d] (99)
$PhSO_2$	OMes [l]	89 [h]	M.p. 95.0 [m]	40.9	4.6		$C_9H_{12}O_5S_2$	40.9	4.6		$PhSO_2·[CH_2]_2·OEt$ [d] (93)
CN	Cl	88 [h]	B.p. 80/17 (n_D^{22} 1.4372)	(Lit.,[n] b.p. 85—87/20, n_D^{23} 1.436 9)							*p*-Nitrophenol [p,q,r] (97) NC·CH:CH_2 [s] (20)
CN	Br	96 [h]	B.p. 73/10 (n_D^{22} 1.479 0)	(Lit.,[u] b.p. 69°/7, n_D^{23} 1.480 0)							*p*-Nitrophenol (98)
CN	I	81 [h]	B.p. 97/15 (n_D^{20} 1.548 0)	20.0	2.2	7.8	C_3H_4IN	19.9	2.2	7.7	*p*-Nitrophenol (93) NC·CH:CH_2 [s] (40)
CN	OAc	93 [h]	B.p. 99/10 (n_D^{20} 1.418 8)	(Lit.,[u] b.p. 110/25, n_D^{20} 1.418 6)							NC·$[CH_2]_2$·OEt [d] (92) NC·CH:CH_2 [s] (73)
CN	OTs	83 [h]	M.p. 64.6 [i]	53.6	4.9	6.2	$C_{10}H_{11}NO_3S$	53.3	4.9	6.2	NC·$[CH_2]_2$·OEt [d] (90)
CN	OMes	71 [h]	B.p. 128/0.05, m.p. 27.7	32.1	4.6	9.4	$C_4H_7NO_3S$	32.2	4.7	9.4	*p*-Nitrophenol [p,q,r] (93) NC·CH:CH_2 [s] (70)
CN	SPh	93 [x]	B.p. 104/0.05 (n_D^{19} 1.576 3)	(Lit.,[cc] b.p. 102—1070/.03, n_D^{20} 1.575 8)							
CN	SO_2Ph	89 [f]	M.p. 95 [m]	55.0	4.6	7.2	$C_8H_9NO_2S$	55.4	4.6	7.2	NC·$[CH_2]_2$·OEt [d] (89) $PhSO_2H$ [q] (73)
PhCO	Cl	*v*	M.p. 49.7 [i]	(Lit.,[n] m.p. 49—50°)							PhCO·$[CH_2]_2$·OEt [d] (98)
PhCO	SPh	98 [w]	M.p. 72.4 [m]	74.3	5.8		$C_{15}H_{14}OS$	74.4	5.8		PhCO·$[CH_2]_2$·OEt [d] (89)
PhCO	SO_2Ph	97 [f]	M.p. 97.8 [m]	65.7	5.0		$C_{15}H_{14}O_3S$	65.7	5.1		PhCO·$[CH_2]_2$·OEt [d] (95)
MeCO	SPh	89 [x]	B.p. 113/0.05 (n_D^{20} 1.5625)	(Lit.,[y] b.p. 100—105/0.1)							PhSH (87)
MeCO	SO_2Ph	98 [f]	M.p. 88.1 [m]	56.7	5.7		$C_{10}H_{12}O_3S$	56.6	5.7		MeCO·$[CH_2]_2$·$NH^+[CH_2]_5$ [q] Cl^- (62) $PhSO_2H$ [q] (55)
α-Phenyl series											
$PhSO_2$	Cl	96 [h]	M.p. 89.3 [i]	(Lit.,[z] m.p. 89—90°)							(*E*) $PhSO_2$·CH:CHPh [q] (90)
$PhSO_2$	Br	99 [h]	M.p. 99.4 [i]	(Lit.,[aa] m.p. 98—101°)							(*E*) $PhSO_2$·CH:CHPh [q] (92)
$PhSO_2$	OAc	90 [h]	M.p. 90.5 [i]	60.1	4.8		$C_{16}H_{16}O_4S$	60.0	4.7		(*E*) $PhSO_2$·CH:CHPh [q] (88)
$PhSO_2$	OMes [l]	89 [h]	M.p. 81.6 [i]	52.8	4.7		$C_{15}H_{16}O_5S_2$	52.9	4.7		(*E*) $PhSO_2$·CH:CHPh [q] (94)
β-Phenyl series											
$PhSO_2$	Cl	69 [h]	M.p. 118 [i,q,bb]	60.3	4.8		$C_{14}H_{13}ClO_2S$	60.0	4.7		$PhSO_2$·CHPh·CH_2·OEt [q] (92)
$PhSO_2$	Br	79 [h]	M.p. 129 [i]	51.8	4.1		$C_{14}H_{13}BrO_2S$	51.7	4.0		
$PhSO_2$	OAc	91 [h]	M.p. 106 [m]	63.4	5.4		$C_{16}H_{16}O_4S$	63.2	5.3		
$PhSO_2$	OMes	86 [h]	M.p. 101.2 [i]	53.0	4.7		$C_{15}H_{16}O_5S_2$	52.9	4.7		

[a] From reactions in EtO^-–EtOH, unless otherwise stated. [b] From EtOH. [c] Ref. 26. [d] Distilled; i.r. and ^1H n.m.r. identical with those of authentic specimen. [e] Sulphide from dibromide. [f] By oxidation of sulphide with H_2O_2–NH_4MoO_4. [g] Ref. 27. [h] From the alcohol. [i] From $(Pr^i)_2O$. [j] M. Ishidate and T. Nambara, *Yakugaku Zasshi*, 1959, **79**, 635. [k] *m*-Nitrophenylsulphonyloxy. [l] Methylsulphonyloxy. [m] From MeOH. [n] 'Handbook of Chemistry and Physics,' 52nd edn., ed. R. C. Weast, The Chemical Rubber Co., Cleveland, Ohio, 1971. [p] From reactions in *p*-nitrophenoxide–EtOH. [q] M.p. and mixed m.p. with authentic specimen. [r] Quantitative by u.v. spectroscopy. [s] By g.l.c. [t] From the bromide. [u] K. A. Javid and T. S. Boboru, *J. Chem. Eng. Data*, 1968, **13**, 596. [v] Commercially available. [w] From chloride. [x] By addition to alkene. [y] D. Tilak, H. S. Desai, C. V. Deshpande, S. K. Jain, and N. V. Vaidya, *Tetrahedron*, 1966, **22**, 7. [z] Ref. 31. [aa] F. J. Lotspeich, *J. Org. Chem.*, 1965, **30**, 2068. [bb] Ref. 28. [cc] Z. Ejmocki and Z. Eckstein, *Roczniki Chem.*, 1971, **45**, 345.

Product Analyses.—For reactions in ethanolic ethoxide these were carried out as described in Part 30.[2] For reactions carried out with *p*-nitrophenoxide as base, the yield of *p*-nitrophenol was obtained by quantitative u.v. spectroscopy and the formation of acrylonitrile was proved by g.l.c. (SE30 at 45 °C).

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