# Elimination and Addition Reactions. Part 31.[1] Polar Effects on the Ionisation of Sulphones, Nitriles, and Ketones

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Rates of ionisation in ethanolic sodium ethoxide of a series of sulphones, $PhSO_2{\cdot}CH_2{\cdot}CH_2{\cdot}Z$, have been measured by radioisotopic and n.m.r. techniques. The derived Taft plot is rectilinear over a range of reactivity values of $10^{9.5}$ and shows that the ionisation of sulphones is very senstive to polar effects ($\rho^* = 4.89$). Taft plots for the ionisation of nitriles and of ketones have also been constructed, and comparison with earlier work on nitro compounds, fluorenes, and esters shows that the sensitivity of the ionisation rates of carbon acids ($G{-}CH{<}$) is in the order G = $PhSO_2 > CN > PhCO >$ fluorenyl $> NO_2 \sim CO_2Et$. This order is discussed in terms of the degree of delocalisation of negative charge in the derived carbanion.

Deviations from the Taft plots for sulphones, nitriles, and ketones are seen when the polar group Z is $PhSO_2$ or CN. In the sulphone series, deviations from the Taft plot are seen when phenyl groups are inserted adjacent to the group Z. The nature of these deviations is discussed briefly and comparisons are drawn with other results.

IONISATION of carbon acids has been widely investigated recently.[2] This is because of the inherent mechanistic interest of these reactions, which generally involve a rather slow proton transfer,[3] and because of the involvement of the rupture of a C–H bond either concertedly or by a stepwise process in 1,2- and higher order elimination reactions.[4] Much previous work has been carried out on nitroalkanes,[5,6] carbonyl compounds,[2] and fluorenes,[7] but few attempts [7] have been made to match systematic studies of polar effects on ionisation of carbon acids with studies on polar effects in elimination reactions activated by carbanion-stabilising groups. In the three accompanying papers we report on activated eliminations in which reactivity is determined by the leaving group and by structural effects. In this paper we report on a study of the ionisation of three series of carbon acids in which the derived carbanion is stabilised by a phenylsulphonyl, cyano, or benzoyl group. We had three main objectives: (i) to evaluate the sensitivity of sulphonyl-stabilised carbanions, in particular, to polar effects so as to allow leaving group ability in elimination reactions to be accurately calibrated;[1] (ii) to allow distinction between concerted and stepwise mechanisms for those elimination reactions which did not show the reversible $(E_1cB)_R$ mechanism by comparison of elimination rates with ionisation rates;[8] and

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[1] Part 30, D. R. Marshall, P. J. Thomas, and C. J. M. Stirling, preceding paper.

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

[3] J. Hine, J. C. Phillips, and J. I. Maxwell, *J. Org. Chem.*, 1970, **35**, 3943.

[4] A. F. Cockerill in 'Comprehensive Chemical Kinetics,' ed. C. H. Bamford and C. F. H. Tipper, Elsevier, London, vol. 9, ch. 3.

[5] F. G. Bordwell, W. J. Boyle, jun., and K. C. Yee, *J. Amer. Chem. Soc.*, 1970, **92**, 5926 and following papers.

[6] P. F. Cann and C. J. M. Stirling, *J.C.S. Perkin II*, 1974, 817, and references cited therein.

[7] R. A. More O'Ferrall and P. J. Warren, *J.C.S. Chem. Comm.*, 1975, 483.

[8] D. R. Marshall, P. J. Thomas, and C. J. M. Stirling, following paper (Part 32).

(iii) to evaluate the influence of phenyl groups on the ionisation rate of simple carbon acids so as to understand the effects of these substituents in elimination reactions.[8,9]

We chose to examine the ionisation rates of sulphones, nitriles, and ketones because of the frequent involvement of sulphonyl, cyano, and acyl groups in activated elimination reactions. There is controversy [10,11] as to the geometry of sulphonyl-stabilised carbanions and recent evidence [12] suggests that for a variety of carbanions, $G\bar{C}HG'$, where G′ is $PhSO_2$, CN, or PhCO, delocalisation of the negative charge increases in the order $PhSO_2 < CN < PhCO$.

The quantification of leaving group ability by removal of the differential ionisation component from the relative rate constants of sulphone-activated eliminations has been described in the preceding paper.[1] In the following paper, the use of ionisation rates in mechanistic assignment is described [8] together with the application of ionisation rate measurements to the diagnosis of structural effects.

## METHODS AND RESULTS

For each of the three series, ionisation rates have been determined by measuring the rates of detritiation of tritiated substrates under the conditions used for elimination reactions (ethanolic sodium ethoxide at 25 °C). The assumption is made that no internal return is involved. In the sulphone series the primary tritium isotope effects for phenyl and methoxy derivatives are 7.15 and 7.05, respectively. These values are intermediate between that found [13] for triphenylmethane (1.75), in which internal return is probably involved, and that for 9-methylfluorene [14] (11.9), in which it is probably not.

TABLE 1

Rate constants [a,b] for detritiation of carbon acids, $GC_{\beta}H_2{\cdot}C_{\alpha}H_2Z$

| Z | $\sigma^*(CH_2Z)$ | G<br>$PhSO_2$ | <br>CN | <br>PhCO |
|---|---|---|---|---|
| $^+NMe_3$ | 1.90 | $1.5 \times 10^{-1}$ [c] | | |
| $^+NMe_3$,β-Ph | | $3.6 \times 10^{-2}$ [c] | | |
| $^+NMe_3$,α-Ph | 2.12 | 1.2 [c] | | |
| $PhSO_2$ | 1.32 | 31 | | |
| CN | 1.30 | | $2.2 \times 10^{-2}$ | 6.9 |
| OPh | 0.85 | 6.3 | 6.4 | |
| SPh | 0.66 | $7.0 \times 10^{-1}$ | 1.8 | |
| EtO | 0.66 | $7.1 \times 10^{-1}$ | | 2.5 |
| EtO,β-Ph | | $9.0 \times 10^{-1}$ | | |
| EtO,α-Ph | 0.88 | $1.2 \times 10^{-1}$ | | |
| MeO | 0.64 | $4.4 \times 10^{-1}$ | 1.3 | 2.2 |
| HO | 0.56 | $2.0 \times 10^{-1}$ | $6.3 \times 10^{-1}$ | |
| $PhSO_2CH_2$ | 0.47 | $6.6 \times 10^{-2}$ | | |
| $NMe_2$ | 0.40 | $1.6 \times 10^{-2}$ | | $3.7 \times 10^{-1}$ |
| $NMe_2$,β-Ph | | $5.7 \times 10^{-2}$ | | |
| $NMe_2$,α-Ph | 0.62. | $1.0 \times 10^{-2}$ | | |
| Ph | 0.22 | $7.1 \times 10^{-3}$ | $4.5 \times 10^{-2}$ | |
| H | 0.00 | $3.7 \times 10^{-4}$ | $3.1 \times 10^{-3}$ | $1.95 \times 10^{-2}$ |
| Me | −0.10 | $1.2 \times 10^{-4}$ | $2.1 \times 10^{-3}$ | $8.9 \times 10^{-3}$ |

[a] $EtO^-$–EtOH at 25 °C. [b] Units l $mol^{-1}$ $s^{-1}$. [c] Reactions in $Et_3N$–EtOH.

Detritiation rate constants were then corrected for the primary tritium isotope effect for the substituents Z = Ph and OMe in the sulphone series and Z = OMe in the nitrile series. Rates of incorporation of deuterium from EtOD under similar conditions were measured and these rates were then corrected for the solvent deuterium isotope effect by measurement of detritiation rates for the same model substrates in EtOD. The assumption was made that detritiation and deprotonation rates would be subject to identical solvent isotope effects. This seemingly tortuous overall procedure was preferred to direct deuterium incorporation studies on the grounds of precision and convenience. The primary and solvent isotope effects were found not to depend upon $\sigma^*(CH_2Z)$ in the sulphone series.

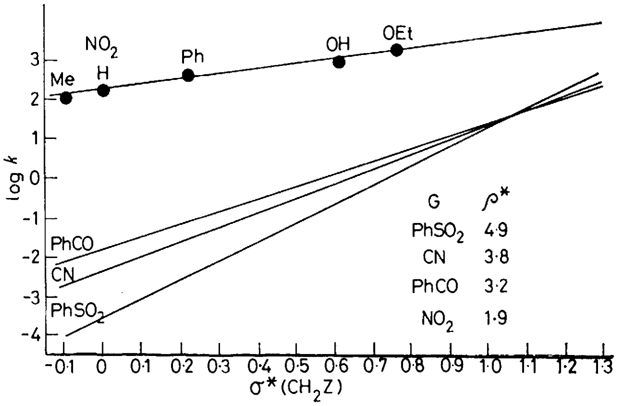

FIGURE 1 Ionisation of carbon acids. Values for $NO_2$ series are for deprotonation; the others are for detritiation (reactions in $EtO^-$–EtOH at 25 °C)

Detritiation rate constants for the three carbon acids series are in Table 1, and in Figure 1 the three carbon acid series are compared with a corresponding series of nitro-compounds.[6] In Figure 2 the Taft plot for the sulphone series is shown together with the effect of α-phenyl substituents on ionisation rates.

## DISCUSSION

Because of the significance of the Taft plot for the ionisation of sulphones in the conclusions reached in the accompanying papers, it was important to establish firmly its range of applicability. The following points are relevant.

(i) The plot is rectilinear over a range of reactivity values of $10^{9.5}$ if the point for $^+NMe_3$ is included. This

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[9] K. N. Barlow, D. R. Marshall, and C. J. M. Stirling, accompanying paper (Part 33).

[10] D. C. Ayres, ' Organic Reaction Mechanisms,' 1971, eds. B. Capon and C. W. Rees, Wiley, London, 1972.

[11] F. G. Bordwell, N. R. Vanier, W. S. Matthews, J. B. Hendrickson, and P. L. Skipper, *J. Amer. Chem. Soc.*, 1975, **97**, 7160.

[12] F. G. Bordwell, M. van der Puy, and N. R. Vanier, *J. Org. Chem.*, 1976, **41**, 1883.

[13] A. Streitwieser, W. B. Hollyhead, G. Sonnichsen, A. H. Pudjaatmaka, C. J. Chang, and T. L. Kruger, *J. Amer. Chem. Soc.*, 1971, **93**, 5096.

[14] A. Streitwieser, W. B. Hollyhead, A. H. Pudjaatmaka, P. H. Owens, T. L. Kruger, P. A. Rubenstein, R. A. MacQuarrie, M. L. Brokaw, W. K. C. Chu, and H. M. Niemeyer, *J. Amer. Chem. Soc.*, 1971, **93**, 5088.

point deviates by $-1$ log unit from the Taft plot, but the ionisation rate is approximate to the extent that it had to be determined by using triethylamine as base and correcting the observed rate constant with a conversion factor ($3.3 \times 10^5$) derived from comparison of rates of $(E_1cB)_R$ reactions of phenylsulphonyl 'onium salts.[9] Even if the ammonium point is disregarded, the range of reactivity values is *ca.* $10^5$.

(ii) The slope of the Taft plot is neither dependent upon nor determined by the points for alkyl groups which are the main targets of criticism of the use of Taft plots.[15]

(iii) $\sigma^*$ Values used for $MeCH_2$,[16] $CH_3$,[16] $PhCH_2$,[16] $CH_2OMe$,[16] $CH_2OPh$,[16] and $CH_2SPh$[17] are all absolute values in the Taft sense being derived from ester hydrolysis measurements and not, for example by interpolation on Taft plots for dissociation constants of acetic acids.

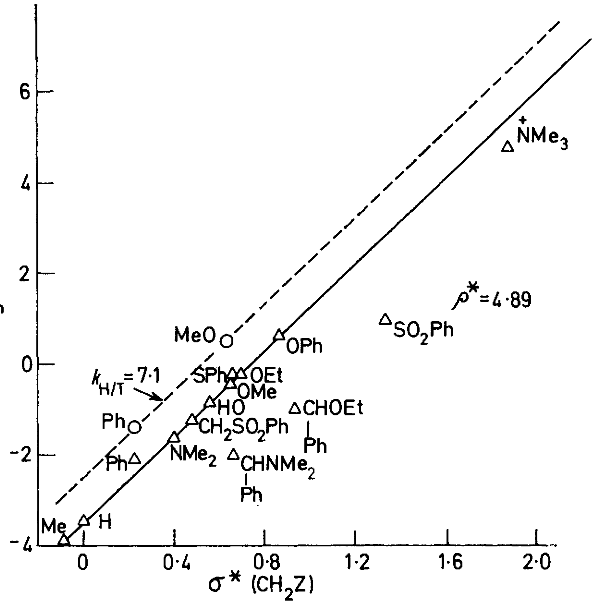

FIGURE 2 Detritiation of sulphones. Broken line values corrected for primary tritium isotope effect; △, detritiation; ○, calc. values of deprotonation

(iv) A wide variety of substituents has been employed to define the Taft line for sulphones and these include substituents connected through atoms in groups 4, 5, and 6. A second row substituent, $PhSCH_2$, shows consistent behaviour as does the homologous sulphonyl substituent, $PhSO_2{\cdot}CH_2{\cdot}CH_2$.

We believe, therefore, that the Taft plot for sulphones provides a secure basis for interpolations that we have made in the previous paper to establish leaving group orders and in the following paper to assign mechanisms.

*Magnitudes of* $\rho^*$ *Values.*—The very large value (4.9) of $\rho^*$ for the sulphone series is to be compared with the lower values for the nitriles (3.8) and ketones (3.2), together with values for nitro-compounds[6] (1.8), fluorenes (2.25 in methanolic sodium methoxide),[7] and esters (1.9 in methanolic sodium methoxide).[18] In the three series studied in the present work, the Taft lines intersect at $\sigma^*(CH_2Z) \simeq 1.05$, so that absolute values of ionisation rates in these three series change in relative magnitude with the magnitude of the polar effect of the substituent.

The trend in $\rho^*$ in the series $SO_2 > CN > CO > NO_2$ (Figure 2) is striking and consistent with the increasing degree of delocalisation of negative charge in the derived carbanion. The result is understandable in that when the negative charge of the carbanion is located primarily on the single atom nearest to the polar substituent, the effect of the polar substituent will be at a maximum. This phenomenon is also seen[19] in the comparison of the effects of the same groups on the thermodynamic acidities of water and of methane. In the former series, the anion has the structure $G{-}O^-$, and the order is $NO_2 \sim SO_2 > CN > Ac$, but for the series $G{-}CH_2^-$ the order is $NO_2 \gg Ac > CN \sim SO_2Me$.[20] The fact that the p*K* value of nitromethane is higher than that of nitroethane is consistent with the considerable degree of delocalisation in the nitronate anion, and, by contrast, bisethylsulphonylmethane is substantially more acidic than 1,1-bisethylsulphonylethane.[21]

*Deviations from the Taft Plots.*—(a) ***Effects of cyano and sulphonyl groups.*** Deviant behaviour in all three carbon acid series is seen when the polar group, Z, is CN or $SO_2Ph$. The deviations (units of log *k*) are as follows: $G = SO_2Ph$, $SO_2Ph = -1.5$; $G = CN$, $CN = -3.3$; $G = PhCO$, $CN = -1.7$. The cyano substituent shows the greater deviations but correlates well on a Taft plot for the dissociation of acetic acids, $Z{-}CH_2{\cdot}CO_2H$, using the absolute $\sigma^*(CH_2CN)$ value.[16] The value[17] for $\sigma^*(CH_2SO_2Ph)$ is itself derived from acetic acid dissociation.

This anomalous behaviour is clearly not due simply to the large polar effect of these substituents. The $Me_3\overset{+}{N}CH_2$ group ($\sigma^* = 1.9$) shows much smaller deviation. A similar anomaly in the behaviour of these substituents on interaction with benzylic carbanions has recently been observed.[22] When methylsulphonyl, methylsulphinyl, and cyano substituents were directly attached at $C_\alpha$ in a benzylic carbanion, the electron-withdrawing effect, as monitored by nuclear $^{13}C$ chemical shifts, was much less than expected by comparison with aryl, oxo-, or nitro-substituents.

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[15] C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1964, **2**, 323.

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

[17] A. Chambers and C. J. M. Stirling, *J. Chem. Soc.*, 1965, 4558.

[18] J. Hine, L. G. Mahone, and C. L. Liotta, *J. Amer. Chem. Soc.*, 1967, **89**, 5911.

[19] J. Hine, 'Structural Effects on Equilibria in Organic Chemistry,' Wiley-Interscience, New York, 1975, Section 6-5.

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

[21] R. P. Bell and B. G. Cox, *J. Chem. Soc. (B)*, 1971, 652.

[22] S. Bradamante, F. Gianni, and G. A. Pagani, *J.C.S. Chem. Comm.*, 1976, 478.

We can reach no firm conclusions as to the reason for this anomalous behaviour by these substituents and are further investigating the scope of this behaviour.

(b) *α-Phenyl substitution in sulphones.* Insertion of a phenyl group adjacent to the polar group, Z, causes similar slight depression in the ionisation rate of sulphones in which Z = OEt or $NMe_2$. The phenyl group should exert an accelerative effect commensurate with its polar effect [$\sigma^*(CH_2Ph) = 0.22$] and the negative deviations from the Taft plot using $\sigma^*(CH_2Ph) + \sigma^*(CH_2Z)$ are $-1.9$ in each case. Similar rate depression by α-phenyl substitution has been observed previously for ionisation of nitro-compounds.[6]

The existence of these rate-depressive effects explains some unexpected behaviour in α-phenyl-substituted substrates undergoing elimination [8] and, as will be seen, allows the strengthening of some conclusions drawn about mechanistic assignments. In striking contrast, however, the ionisation of the sulphone ammonium salt ($Z = {}^+NMe_3$) is *accelerated* by α-phenyl substitution (Table) and the detritiation results are confirmed by ionisation rates derived from kinetics of elimination of these salts in buffer systems.[9] Different behaviour is seen, however, in nitrile 'onium salts [9] in which α-phenyl substitution, as for neutral polar groups in the sulphone series, is slightly rate depressive.

The nature of the rate-depressive effects is not at present clear. We are hesitant to suggest the operation, in broad terms, of a steric effect exerted by the α-phenyl group because this would not be expected in the nitrile 'onium salts and there is no apparent correlation of the magnitude of the effect with the bulk of the polar group Z.[8]

We shall report later on the results of an examination of the effect as a function of the groups G and Z in the carbon acid.

(c) *β-Phenyl substitution in sulphones.* Placement of a phenyl group on the carbon atom at which deprotonation occurs causes small increases in ionisation rate when Z = OEt or $NMe_2$. These increases are much less than those to be expected on the basis of the effect on the $pK_a$ values of sulphones in dimethyl sulphoxide [23] and we are much more confident in ascribing the effect to steric interference with proton removal or planarity in the incipient carbanion. The comparison between cyano- and sulphonyl-activated elimination reactions of ammonium salts is very telling in this respect and the effect of β-phenyl substitution is more fully discussed in accompanying papers.[8,9]

## EXPERIMENTAL

Ethanol was dried by the magnesium–iodine method.[24] Solids were recrystallised to constant m.p. (quoted in °C). Extraction was performed with dichloromethane and extracts were dried over $MgSO_4$.

The scintillation fluid used was prepared from Butyl P.B.D. (5 g) in AnalaR toluene (1 000 ml). Counting was carried out on a Philips liquid scintillation analyser.

*Labelled Substrates.*—These were usually prepared by treating the substrate (5 mmol) in 1,4-dioxan (5—10 ml) with sodium hydroxide (0.05 g) in water (3 ml) and tritiated water (0.25 ml, 1.25 mCi) either at 25 °C or at elevated temperatures, depending on the substrate (see Table 2).

TABLE 2

Conditions for preparation of labelled substrates $G[CH_2]_2Z$ by the standard method

| G | Z | Time | Temp. (°C) |
|---|---|---|---|
| $PhSO_2$ | $PhSO_2$ [a] | 30 min | 25 |
| | OPh [a] | 30 min | 25 |
| | SPh [a] | 30 min | 25 |
| | OEt [a] | 2 h | 25 |
| | OEt,β-Ph [b] | 2 h | 25 |
| | OEt,α-Ph [b] | 2 h | 25 |
| | OMe [a] | 3 h | 25 |
| | OH [a] | 6 h | 40 |
| | $PhSO_2{\cdot}CH_2$ | 6 h | 25 |
| | $NMe_2$ [c] | 6 h | 50 |
| | $NMe_2$,β-Ph [c] | 12 h | 25 |
| | $NMe_2$,α-Ph [c] | 12 h | 25 |
| | Ph [d] | 12 h | 80 |
| | H [e] | 15 h | 100 |
| | Me [f] | 24 h | 100 |
| NC | CN | 1 h | 25 |
| | OPh [g] | 30 min | 25 |
| | SPh [h] | 1 h | 25 |
| | OMe | 3 h | 25 |
| | OH | 6 h | 40 |
| | Ph | 12 h | 60 |
| | H | 12 h | 80 |
| | Me | 12 h | 80 |
| PhCO | OEt [i] | 3 h | 25 |
| | OMe [i] | 3 h | 25 |
| | $NMe_2$ | 12 h | 25 |
| | H | 12 h | 60 |
| | Me | 24 h | 60 |

[a] For preparation or reference to preparation see ref. 1. [b] R. P. Redman, Ph.D. Thesis, London, 1970. [c] See ref. 9. [d] L. Field, J. R. Holsten, and R. D. Clark, *J. Amer. Chem. Soc.*, 1959, **81**, 2572. [e] W. Otto, *Ber.*, 1880, **13**, 1274. [f] W. A. Baldwin and R. Robinson, *J. Chem. Soc.*, 1932, 1448. [g] J. Crosby and C. J. M. Stirling, *J. Chem. Soc.* (*B*), 1970, 671. [h] Z. Ejmocki and Z. Eckstein, *Roczniki Chem.*, 1971, **45**, 345. [i] F. Straus and A. Berkow, *Annalen*, 1913, **401**, 121.

The mixture was then poured into saturated brine (20 ml) and extraction gave the labelled substrate, which was purified by distillation or by recrystallisation to constant m.p., mixed m.p., and scintillation count. To ensure that the isotopic label was present in the methylene group adjacent to the activating group and nowhere else, the above experiment was repeated for each substrate with deuterium oxide (3.25 ml), and the products were examined by $^1H$ n.m.r. spectroscopy. For some substrates randomisation of the label would have occurred if the above technique had been used, *e.g.* β-benzoylpropiononitrile; also some of the substrates were labelled during their preparation. These exceptions to the above general method are described below.

The labelled ammonium salts were prepared as above using triethylamine (0.2 ml) as base. Samples of the three salts $PhSO_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3I$, $PhSO_2{\cdot}CHPh{\cdot}CH_2NMe_3I$, and

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[23] F. G. Bordwell and W. S. Matthews, *J. Amer. Chem. Soc.*, 1974, **96**, 1214.

[24] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 1956.

$PhSO_2{\cdot}CH_2{\cdot}CHPhNMe_3I$ were prepared as described elsewhere.[9] Owing to solubility difficulties the counter ion was changed to tetraphenylborate by refluxing the iodide (5 mmol) with sodium tetraphenylborate (5 mmol) in methanol (150 ml) for 4 days, resulting in the three new *salts* $PhSO_2{\cdot}CH_2{\cdot}CH_2NMe_3BPh_4$, m.p. 198.3° (from toluene) (Found: C, 76.8; H, 7.0; N, 2.6. $C_{35}H_{38}BNO_2S$ requires C, 76.8; H, 6.9; N, 2.5%); $PhSO_2{\cdot}CHPh{\cdot}CH_2NMe_3BPh_4$, m.p. 183° (from toluene) (Found: C, 79.0; H, 6.7; N, 2.2. $C_{41}H_{42}BNO_2S$ requires C, 79.0; H, 6.7; N, 2.3%), and $PhSO_2{\cdot}CH_2{\cdot}CHPh{\cdot}NMe_3BPh_4$, m.p. 201° (from toluene) (Found: C, 78.9; H, 6.8; N, 2.4. $C_{41}H_{42}BNO_2S$ requires C, 79.0; H, 6.7; N, 2.3%).

*Labelled* 2-*dimethylamino*-2-*phenylethyl phenyl sulphone*. Phenyl styryl sulphone[25] (1.05 g, 5 mmol) in 1,4-dioxan (6 ml) was treated with aqueous 30% dimethylamine (10 ml) and tritiated water (0.3 ml; 1.5 mCi). After 3 h extraction gave the sulphone amine (93%), m.p. and mixed m.p. 134° (from di-isopropyl ether) (lit.,[9] 134°).

*Labelled* 2-*dimethylamino*-1-*phenylethyl phenyl sulphone*. 1-Phenyl-2-phenylsulphonylethyl acetate[9] (0.7 g, 2 mmol) in methanol (7 ml) was treated with an excess of aqueous 30% dimethylamine (4 ml) and tritiated water (0.3 ml; 1.5 mCi) at 20 °C for 24 h. Extraction gave the sulphone amine (90%), m.p. and mixed m.p. 137° (from ethanol) (lit.,[26] 138°).

*Labelled* β-*benzoylpropiononitrile*. 3-Chloropropiophenone (0.84 g, 5 mmol) in methanol (10 ml) was treated with sodium cyanide (0.3 g, 5.2 mmol) in water (3 ml) and tritiated water (0.4 ml; 2 mCi) for 3 h at 25 °C. Extraction gave the nitrile (94%), m.p. and mixed m.p. 75.7° (from di-isopropyl ether) (lit.,[9] 76.0°).

This experiment was repeated using $D_2O$ and MeOD. The product was shown by $^1H$ n.m.r. to be $PhCO{\cdot}CD_2{\cdot}CH_2{\cdot}CN$.

Most of the substrates used in this study were either commercially available or well described in the literature. Some are described in the accompanying papers.[1,8,9] References for their preparations (where applicable) are given in Table 2.

1,3-*Bisphenylsulphonylpropane*.—Benzenethiol (10 mmol) in methanol (100 ml) was treated with sodium methoxide [from sodium (10 mmol)] in methanol (50 ml) and 1,3-dibromopropane (2.02 g) at reflux for 2 h. Extraction gave the disulphide, which was oxidised with hydrogen peroxide (25 ml; 100 vol.) in methanol (75 ml) in the presence of ammonium molybdate (0.5 g). After 12 h at 20 °C extraction gave the *disulphone* (99%), m.p. 125.2° (from ethanol) (Found: C, 55.6; H, 5.0. $C_{15}H_{16}O_4S_2$ requires C, 55.6; H, 4.9%).

*Kinetics*.—Sodium ethoxide solutions were prepared by dissolution of clean sodium in dry ethanol and were standardised against hydrochloric acid. Detritiation rate measurements were carried out as follows using a base : substrate ratio of at least 10 : 1.

A solution of the labelled substrate in dry ethanol was allowed to equilibrate in a thermostat at 25 °C. A solution of sodium ethoxide (or triethylamine) in ethanol, similarly equilibrated, was added. Samples (10 ml) were removed at intervals, quenched by pouring into acidified saturated brine (30 ml), and extracted with methylene chloride (3 × 50 ml). The extracts were dried and evaporated and the residues dissolved in the scintillation fluid (9 ml). Nine to twelve samples and an infinity sample were taken per run. At least three rate determinations were carried out on each substrate.

*Determination of the Isotope Effect* $k_H/k_T$.—The rate of abstraction of a proton from $GCH_2{\cdot}CH_2Z$ was measured by $^1H$ n.m.r. using the procedure described above with EtOD as solvent, and dissolving the residues from the evaporated samples in $CDCl_3$. The results were compared with the rates of removal of tritium from $GCHT{\cdot}CH_2Z$ in EtOH. The solvent isotope effect which must be accounted for is obtained by comparing the rate of tritium removal in EtOD with that in EtOH.

These three experiments were carried out for the following four substrates: 2-methoxyethyl phenyl sulphone $k_H/k_T = 7.05$; 2-phenylethyl phenyl sulphone $k_H/k_T = 7.15$; 3-methoxypropiononitrile $k_H/k_T = 6.90$; 2-methoxyethyl phenyl ketone $k_H/k_T = 6.22$.

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[25] L. Field, *J. Amer. Chem. Soc.*, 1952, **74**, 3919.

[26] E. B. Knott, *J. Chem. Soc.*, 1947, 1190.