# Elimination and Addition Reactions. Part 33.[1,2] Formation and Behaviour of Carbanions derived from Sulphones and Nitriles bearing β-'Onium Substituents

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Kinetics of elimination reactions of β-arylsulphonylethyl- and β-cyanoethyl-ammonium and -sulphonium salts have been measured in ethanolic triethylamine buffers. The reactions show buffer saturation kinetics; at low buffer base concentrations ionisation to form the intermediate carbanion is rate-determining, but at higher buffer base concentrations the intermediate carbanion is formed in a rapidly established pre-equilibrium step and the observed rate constant does not change with increasing base concentration at constant buffer ratio.

The rate data separately yield the ionisation rates of the substrates studied, together with the ratio ($k_2 : k_{-1}$) of the rate constants for loss of the 'onium leaving group from the carbanion and its reprotonation.

Formation of a carbanion from a sulphone is very sensitive to steric and polar effects; ionisation of nitriles is less sensitive in both respects, particularly the former.

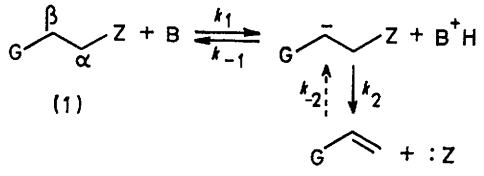
The elimination-reprotonation ratio ($k_2 : k_{-1}$) depends upon the activating group, but for a given activating group and type of leaving group it is insensitive to the structure of the leaving group. It is also insensitive to substitution at either $C_\alpha$ or $C_\beta$.

Comparisons are drawn with unactivated elimination reactions of 'onium salts, and the Hammett ρ value has been obtained for expulsion of the leaving group in the 2-phenylethylammonium series.

STUDIES of carbanionic, alkene-forming 1,2-eliminations have embraced considerations of activation [3-5] and leaving group ability.[6-9] In the great majority of previous investigations of eliminations in which carbanions are formed, the observed rate constants are composite, being derived from the steady-state expression [equation (1)] for the pre-equilibrium formation

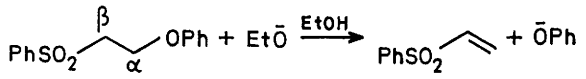
$$k_{obs} = k_1k_2[B]/(k_{-1}[\overset{+}{B}H] + k_2) \qquad (1)$$

of the carbanion (Scheme 1), which may be further complicated by an equilibrium involving addition to the electrophilic alkene produced.



SCHEME 1

As overall rate constants of reactions involve ionisation of the substrate, reprotonation of the derived carbanion, and loss of the leaving group from the carbanion, the drawing of conclusions about structural effects on any one process is difficult. Generalizations about structural effects on one particular process have, therefore, had to be accompanied by assumptions relating to the effects of the same structural changes on other accompanying reactions. Thus, for example, in the reaction of 2-phenoxyethyl phenyl sulphone with ethanolic sodium ethoxide (Scheme 2), substitution of phenyl for hydrogen at $C_\beta$ produces a 64-fold increase in the overall rate constant.[10] This acceleration could be produced by an



SCHEME 2

increase in $k_1$, the ionisation rate, an increase in $k_2$, the rate constant for loss of the leaving group from the carbanion intermediate, or a decrease in $k_{-1}$, the reprotonation rate constant. This structural change may, of course, affect all of these processes simultaneously but to varying degrees.

Earlier attempts [5] to remove some ambiguities by using very reactive nitro-activated substrates, in which decomposition of the carbanion can be directly observed, were partly frustrated by mechanistic changes which accompany the structural changes being investigated. This was particularly seen in the change from the $(E_1cB)_R$ to the $(E_1cB)_I$ or $E_2$ mechanisms [11] when the leaving group is changed from OPh to SPh. A wide range of highly activated substrates has been studied by Rappoport and his collaborators.[7,9,12] These have yielded much significant information on the behaviour of carbanions in elimination reactions, but aprotic solvents have usually been employed and the substrates studied have generally had two groups on each of the α- and β-carbon atoms. Comparison with our results, obtained with simpler substrates in protic solvents, cannot, therefore, always be direct.

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[2] Preliminary report, K. N. Barlow, D. R. Marshall, and C. J. M. Stirling, *J.C.S. Chem. Comm.*, 1973, 175.
[3] J. Crosby and C. J. M. Stirling, *J. Chem. Soc.* (*B*), 1970, 671, and references cited therein.
[4] Z. Rappoport, *J. Chem. Soc.* (*B*), 1971, 171.
[5] P. F. Cann and C. J. M. Stirling, *J.C.S. Perkin II*, 1974, 821.
[6] D. R. Marshall, P. J. Thomas, and C. J. M. Stirling, accompanying paper (Part 30).
[7] S. Hoz, M. Albeck, and Z. Rappoport, *Tetrahedron Letters*, 1972, 3511.
[8] R. A. Bartsch and J. F. Bunnett, *J. Amer. Chem. Soc.*, 1969, **91**, 1376.
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[10] R. P. Redman and C. J. M. Stirling, *Chem. Comm.*, 1970, 633.
[11] F. G. Bordwell, M. M. Vestling, and K. C. Yee, *J. Amer. Chem. Soc.*, 1970, **92**, 5950.
[12] Z. Rappoport and A. Topol, *J.C.S. Perkin II*, 1975, 863, and references cited therein.

In the present work, our objective was to separate the component rate constants of the rate equation (1), and we decided to concentrate on systems which possess a single activating group and a single leaving group. We selected for study 'onium salts activated towards elimination by either β-arylsulphonyl or β-cyano groups. These salts have the particular advantage that they are reactive enough to undergo elimination *via* carbanion intermediates (below) in triethylamine buffers. This permits separate evaluation of the ionisation rate constant, $k_1$, and the ratio of the elimination and reprotonation rate constants, $k_2 : k_{-1}$. Additionally, these substrates allow for variation in the size and electronic properties of the leaving group, and substituents may be readily incorporated into the chain connecting leaving and activating groups. We chose to use protic solvents, as equilibria are better quantified and ion-pairing in the very dilute solutions used for spectroscopic studies may be neglected.

## METHODS AND RESULTS

*Substrates.*—β-Sulphonylethyl- and β-cyanoethyl-ammonium salts (1; G = $PhSO_2$ or CN, Z = $^+NR_3$) were

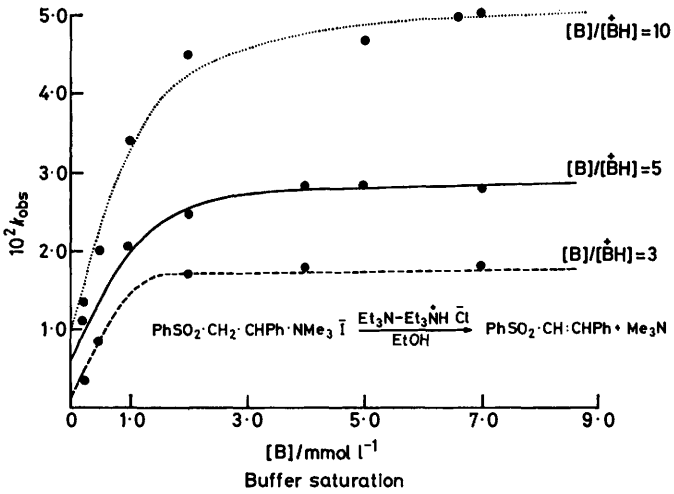


FIGURE 1 Typical buffer saturation plots for elimination in β-sulphonyl ammonium salts in triethylamine buffers (at 25 °C).

obtained by nucleophilic addition of the appropriate amine to the αβ-unsaturated sulphone or nitrile, with subsequent quaternisation of the amine, usually with methyl iodide. Sulphonium salts were obtained by alkylation at sulphur with methyl fluorosulphate, of appropriate sulphides. Details are in Tables 5—9. 2-Phenylethylammonium salts were obtained by alkylation of arylamines with 2-phenylethyl bromide and quaternisation of the resulting amines. Details are in Table 9.

Products of all eliminations were obtained from preparative scale reactions, and u.v. spectrophotometric examination of the products was an additional check on the stoicheiometry.

*Kinetics.*—In most cases, elimination in the salts was followed spectroscopically by appearance of the alkene and/or the (aromatic) amine. Substrate concentrations were typically $10^{-4}$ mol $l^{-1}$ and in all cases except for substrates in Tables 3 and 9 reactions were in triethylamine–triethylamine hydrochloride buffers. In some cases, for which neither amine nor alkene had appropriate spectroscopic properties, conductometric or g.l.c. procedures were

TABLE 1

Rates of elimination in sulphone and cyano-'onium salts

| | Salt | $10^2 k_1$ / l mol$^{-1}$ s$^{-1}$ | $10^4 k_2/k_{-1}$ / mol l$^{-1}$ | $10^3 k_{obs}$ / s$^{-1}$ |
|---|---|---|---|---|
| (2) | $PhSO_2\cdot[CH_2]_2\cdot{}^+NMe_3$ | 86 | 12 | 1.04 |
| (3) | $PhSO_2\cdot[CH_2]_2\cdot{}^+NEt_2Me$ | 53 | 96 | 1.02 |
| (4) | $PhSO_2\cdot[CH_2]_2\cdot{}^+NMe_2Ph$ | 160 | 18 | 1.89 |
| (5) | $PhSO_2\cdot CH_2\cdot CHPh\cdot{}^+NMe_3$ | 850 | 7 | 5.95 |
| (6) | $PhSO_2\cdot CHPh\cdot CH_2\cdot{}^+NMe_3$ | 24 | 10 | 0.24 |
| (7) | $PhSO_2\cdot CHPh\cdot CH_2\cdot{}^+NEt_2Me$ | 7 | 19 | 0.13 |
| (8) | $PhSO_2\cdot[CH_2]_2\cdot{}^+SPhMe$ | 260 | 520 | 135 |
| (9) | $PhSO_2\cdot CH_2\cdot CHPh\cdot{}^+SPhMe$ | 445 | 740 | 333 |
| (10) | $PhSO_2\cdot CH_2\cdot CHMe\cdot{}^+SPhMe$ | 104 | 270 | 28.2 |
| (11) | $PhSO_2\cdot CH_2\cdot CMe_2\cdot{}^+SPhMe$ | 90 | 140 | 12.6 |
| (12) | $CN\cdot[CH_2]_2\cdot{}^+NMe_2Ph$ | 322 | 164 | 52.8 |
| (13) | $CN\cdot CH_2\cdot CHPh\cdot{}^+NMe_3$ | 100 | 300 | 30.0 |
| (14) | $CN\cdot CHPh\cdot CH_2{}^+NMe_3$ | 73 000 | 37 | 2 700 |

TABLE 2

Dependence of elimination rates on leaving group in cyano-'onium salts [a] $CN\cdot CH_2\cdot CH_2\cdot{}^+NMe_2Ar$

| Substituent in Ar | $k_1$ / l mol$^{-1}$ s$^{-1}$ | $10^2 k_2/k_{-1}$ / mol l$^{-1}$ |
|---|---|---|
| *m*-Me | 2.55 | 1.7 |
| None | 3.22 | 1.64 |
| *m*-OMe | 3.2 | 1.64 |
| *m*-Cl | 6.3 | 2.1 |
| *m*-$NO_2$ | 11.9 | 1.8 |
| | ρ = 0.84 | ρ = 0 |

[a] Triethylamine buffers in ethanol at 25 °C.

TABLE 3

Rates of elimination in 2-phenylethylammonium salts [a] ($PhCH_2\cdot CH_2\cdot{}^+NMe_2Ar$)

| Substituent in Ar | $10^4 k_2$ / l mol$^{-1}$ s$^{-1}$ |
|---|---|
| *m*-$NO_2$ | 78.0 |
| *m*-Cl | 22.6 |
| None | 7.85 |
| *m*-OMe | 7.22 |
| *m*-Me | 6.80 |
| | ρ = 1.3 |

[a] $EtO^-$–EtOH at 25 °C.

employed, and higher substrate concentrations were used. Reactions were investigated both by variation of buffer ratio and by variation of buffer concentration at fixed buffer ratio. The buffer ratio [B] : [$\overset{+}{H}$B] was varied from 10 : 1 to 1 : 1. Ionic strengths were maintained at 0.05M.

The systems chosen were reactive enough to undergo elimination in buffer systems, and, because [B] and [$\overset{+}{H}$B] can be controlled, the relative magnitudes of $k_{-1}$[$\overset{+}{H}$B] and $k_2$ can also be controlled [equation (1)]. At low magnitudes of $k_{-1}$[$\overset{+}{H}$B], the rate expression simplifies to $k_{obs} = k_1$, the ionisation rate constant. At high concentrations of buffer acid, $k_{-1}$[$\overset{+}{H}$B] exceeds $k_2$ and the rate expression is then $k_{obs} = k_1k_2$[B]/$k_{-1}$[$\overset{+}{H}$B].

Changeover from base-dependent rate-determining ionisation at low base concentrations to a base-independent rate constant at high base concentrations is an example of

buffer saturation (Figure 1) and shows, unequivocally, that the reaction has two stages with the balance between loss of the leaving group from the carbanion and its reprotonation. From the rate constants obtained by varying buffer base concentration at fixed buffer ratio, a double reciprocal plot of $1/k_{obs}$ *vs.* $1/[B]$ gives a rectilinear plot with slope $1/k_1$ and intercept $k_{-1}[BH]/k_1k_2[B]$. As the apparent ionisation rate $k_1$ is directly evaluable, $k_2 : k_{-1}$ can also be obtained. Results are in Tables 1, 2, and 4.

TABLE 4

Elimination in α-aryl sulphone ammonium salts ($PhSO_2 \cdot CH_2 \cdot CHAr \cdot NMe_3I$)

| Substituent in Ar | $10^2 k_{obs}$ / $s^{-1}$ |
|---|---|
| *m*-$NO_2$ | 9.50 |
| *m*-Cl | 5.40 |
| *p*-Cl | 3.75 |
| *m*-OMe | 3.30 |
| None | 2.95 |
| $\rho\ k_1k_2/k_{-1} = 0.7$ | |

[a] In triethylamine buffer; $[Et_3N] = 10^{-1}$ mol $l^{-1}$, $[Et_3\overset{+}{N}H] = 10^{-2}$ mol $l^{-1}$; in EtOH at 25 °C.

## DISCUSSION

The kinetic analysis of reactions in buffer systems yields two separate pieces of information: $k_1$, the ionisation rate constant, and $k_2 : k_{-1}$ the ratio of the rate constants for departure of the leaving group from the intermediate carbanion and the reprotonation of the carbanion. We shall discuss separately the factors which effect ionisation rate and $k_2 : k_{-1}$.

*Ionisation Rates.*—In conditions under which solvent and base are kept constant, three structural features of the substrate would be expected to effect the ionisation rate: the activating group G, the leaving group Z, and substituents at $C_\alpha$ and $C_\beta$.

*The activating group.* Nitriles bearing 'onium leaving groups (Table 1) ionise more slowly than the related sulphones,[13,14] and this is consistent with Taft plots [15] for the detritiation of β-substituted sulphones and nitriles in ethanolic ethoxide. The plots intersect at $\sigma^* = 1.05$ and above this value sulphones ionise the more rapidly.

*The leaving group.* Variation in the structure of the 'onium leaving group has rather little effect on ionisation rate. Over the range of unsubstituted sulphones (2)—(4) and (8), variation in $k_1$ is less than $10^1$. The sulphonium sulphone (8) ionises appreciably faster than the ammonium sulphones (2)—(4). The greater value of $k_1$ for (4) than for (2) is due to the greater inductive effect of Ph as compared with Me,[16] and the slightly lower value for (3) than for (2) is possibly steric in origin. It is magnified when steric effects are exacerbated (below).

Variation in the polar effect of the leaving group undoubtedly does affect $k_1$ as shown by the Hammett ρ value (0.84) for the arylammonium nitriles (Table 2). The small value of ρ reflects the attenuation of the effect of substituents by the two-atom separation between the aryl group and the site of ionisation, notwithstanding the relatively high sensitivity of nitrile ionisation to polar effects.

*Substituent effects. β-Phenyl substitution.* Comparison of substrates (2) and (3) with substrates (6) and (7) shows that, for sulphones, β-phenyl substitution actually depresses ionisation rate. Such substitution lowers the $pK_a$ values of the sulphones although the effect is very variable. For monosulphones in dimethyl sulphoxide,[17] $\Delta pK_a$ is *ca.* 5 units but in cyclic α-bis-sulphones, $\Delta pK_a$ is *ca.* 0.1 unit.[18] A phenyl group at $C_\beta$ improves delocalisation of the developing negative charge which is increased by coplanarity of the three bonds to the carbanion centre. A specific conformation of the sulphonyl group is probably required for [19] maximum stability of the carbanion. Failure of even the inductive effect of the phenyl group to be manifested in an increased ionisation rate is, however, to be attributed to steric inhibition of the approach of the base to the (solvated) substrate or to steric inhibition of coplanarity in the derived carbanion. This phenomenon has previously been described by Hibbert [18] in α-disulphones, in which phenyl substitution adjacent to the sulphonyl group slightly lowers the $pK_a$ in the phenyl substituted compound but depresses the ionisation rate, as measured by detritiation, fifteen-fold. Two further comparisons strengthen these views. First, increase in the size of the leaving group increases the inhibitory effect of the substituent at $C_\beta$. In comparison of substrates (2) and (3) with (6) and (7), the ratio of $k_1$ values for the former pair is less than that for the latter. The sulphonyl group is large [20] and in this system steric effects are particularly emphasised. Secondly, when the carbanion stabilising group is small, *e.g.* for nitriles, steric restraints on ionisation should be much reduced and essentially the full effect of the stabilising phenyl group should be felt. This is dramatically shown in comparisons between substrates (12) and (14) in which phenyl substitution at $C_\beta$ produces an acceleration of 422-fold when allowance is made for the change of leaving group by using the ratio of $k_1$ values for substrates (2) and (4). The difference between the sulphone and the nitrile systems is clearly shown in models (Figure 2).

The depressive effect on ionisation rate of phenyl substitution at $C_\beta$ accounts for the behaviour found earlier in β-phenoxy- and -phenylthio-sulphones.[10,21]

[13] R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439.
[14] J. R. Jones, 'The Ionisation of Carbon Acids,' Academic Press, London, 1973, ch. 2.
[15] P. J. Thomas and C. J. M. Stirling, accompanying paper (Part 31).
[16] 'Steric Effects in Organic Chemistry' ed. M. S. Newman, Wiley, New York, 1956.
[17] W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, R. J. McCallum, C. J. McCollumn, and N. R. Vanier, *J. Amer. Chem. Soc.*, 1975, **97**, 7006.
[18] F. Hibbert, *J.C.S. Perkin II*, 1973, 1289.
[19] L. A. Paquette, J. P. Freeman, and M. J. Wyvratt, *J. Amer. Chem. Soc.*, 1971, **93**, 346.
[20] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, 'Conformational Analysis,' Wiley, New York, 1965.
[21] C. J. M. Stirling, *Internat. J. Sulfur Chem.*, 1971, **6**, 41.

Insertion of a phenyl group at $C_\beta$ in the nitrile (1; G = CN, Z = SPh) [22] raises $k_{obs}$ for reaction in ethanolic sodium ethoxide by a factor of $10^5$. For the sulphone (1; G = $SO_2Ph$, Z = SPh), however, the accelerative effect is only 45-fold.[10]

*α-Methyl substitution.* This produces rate depression entirely consistently with the results of ionisation rate studies of *e.g.* nitro-compounds [23] and sulphones.[15] For sulphones (1; G = $PhSO_2$, Z = H) substitution of α-Me for α-H produced a three-fold depression of ionisation rate in ethoxide–ethanol. This is in good agreement with the rate ratio for substrates (8) and (10). The depressive effect may be polar and/or a steric effect on the solvation of the ion.[24] It is, therefore, rather surprising, on either interpretation, that the effect of two methyl groups at $C_\alpha$ is not greater [*cf.* substrates (10) and (11)]. *E*l mechanisms are known for

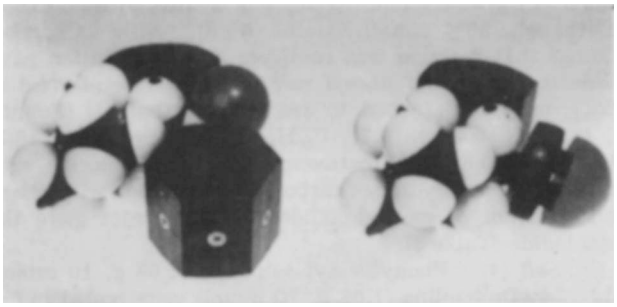

FIGURE 2 Space-filling (Courtauld) models of the sulphone ammonium salt (6) (left) and the cyano ammonium salt (14) (right); the β-proton which is removed is marked with a dot.

tertiary sulphonium salts [25] but this possibility is excluded for salt (11) by the lack of reaction in the absence of base.

*α-Phenyl substitution.* In all combinations of activating and 'onium leaving group systems so far studied, α-phenyl substitution accelerates ionisation. This is seen in the comparisons of substrates (2) with (5) (ratio 9.9), (8) with (9) (ratio 2.5), and (12) with (13) (ratio *ca.* 4). These results are not in accord with direct determination of ionisation rates in sulphones [15] and nitro-compounds.[23] In these systems, two bulky groups fail to produce an effect on the ionisation rate commensurate with the summation of the σ* values of the two α-substituents. Thus for $PhSO_2{\cdot}CH_2{\cdot}CHPh{\cdot}OEt$, the ionisation rate constant is 25 times smaller than the value predicted from the Taft plot and for $NO_2{\cdot}CH_2{\cdot}CHPh_2$ is 2.4 times smaller. In the sulphone (1; G = $PhSO_2$) exchange of Z = H for Z = Ph produced a 20-fold acceleration of ionisation rate, and it appears that for ammonium and sulphonium salts, the balance between inductive acceleration and steric depression is more favourable than for oxygen or aryl substituents.

*Ratio of Elimination to Protonation; $k_2 : k_{-1}$ Values.—Effect of the leaving group.* For substrates with the same type of activating group, *e.g.* $PhSO_2$, and leaving group, *e.g.* $\overset{+}{N}R_3$, the most striking feature is the constancy of this function. In substrates (2)—(7) there is less than a ten-fold variation irrespective of change of leaving group 'stability'; *cf.* substrates (2) and (4) where the species eliminated differ in basicity by 7 powers of 10. It may be argued that the inverse of carbon nucleophilicity could be regarded as a more relevant criterion of leaving group ability. This criterion is certainly not applicable to a series of leaving groups connected by different atoms [26] but for a series of ammonium salts it might reasonably be applied. Carbon nucleophilicity, as measured by relative rates of reaction of triethylamine and dimethylaniline with methyl iodide [27] [$k_{rel}(Et_3N : PhNMe_2) = 10.6$], suggests that the differences should be small. Nucleophilicities of aromatic and aliphatic amines towards electrophilic alkenes are, however, extremely different,* and this emphasises the insensitivity of $k_2 : k_{-1}$ to structural changes. This insensitivity suggests that there is a low degree of C–Z bond cleavage in the elimination transition state and a correspondingly low degree of carbon–carbon double bond character. This conclusion is also supported by the composite value of ρ (*ca.* 0) for $k_2 : k_{-1}$ as a function of the leaving group in the nitrile ammonium series. The value of $k_{-1}$ is very large [28] (*ca.* $10^8$) and is likely, therefore, to be rather little affected by minor perturbations due to remote substituents in the leaving group. The fact that the differentials in $k_2 : k_{-1}$ are also very small suggests that the effect on $k_2$ is also small and this is consistent only with a small degree of C–Z bond cleavage in the transition state.

The lack of response of $k_2 : k_{-1}$ in these carbanionic eliminations is in direct contrast with the effect of leaving group variation on a concerted elimination involving expulsion of ammonium leaving groups. We have determined the Hammett ρ value for elimination in the 2-phenylethyl series, $PhCH_2{\cdot}CH_2{\cdot}{}^+NMe_2Ar$, in ethoxide–ethanol (Table 3). The ρ value of 1.3 is substantial for this much investigated system,[29] whose degree of carbanion character at $C_\beta$ in the transition state is regarded as high and the degree of $C_\alpha$–Z bond cleavage correspondingly low.

* Data which would allow quantitative comparison are not available. In cyanoethylation of diethylamine, a 93% yield is obtained in 0.5 h at 55 °C; for *N*-methylaniline, 4 h at 180 °C is required for a 25% yield (H. A. Bruson, *Org. Reactions*, 1949, **5**, 116). The experimental section of this paper also emphasises the difference in conditions required for additions of alkyl- and aryl-amines to αβ-unsaturated sulphones.

[22] P. J. Thomas and C. J. M. Stirling, in preparation.
[23] P. F. Cann and C. J. M. Stirling, *J.C.S. Perkin II*, 1974, 817.
[24] J. Shorter, in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, London, 1972, ch. 2.
[25] D. Darwish, Sai Hong Hui, and R. Tomilson, *J. Amer. Chem. Soc.*, 1968, **90**, 5631.
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[28] J. Hine, J. C. Philips, and J. I. Maxwell, *J. Org. Chem.*, 1970, **35**, 3943.
[29] W. H. Saunders and A. F. Cockerill, 'Mechanisms of Elimination Reactions,' Wiley–Interscience, New York, 1973, ch. 2.

*Effects of α- and β-substituents.* Within the ammonium series, variation of substituents at $C_\alpha$ and $C_\beta$ again produces remarkably little response in $k_2 : k_{-1}$. This is particularly notable in the results for the sulphones (2), (5), and (6) and for the nitriles (12)—(14). α-Substitution in the substrates (5), (9), and (13) produces little change in $k_2 : k_{-1}$ for these carbanion processes. By contrast, in a concerted process involving elimination of a sulphonium leaving group, phenyl substitution at $C_\alpha$ accelerates 100-fold.[10] To the extent that partial double bond formation is present in the transition state, interaction with an α-phenyl group should preferentially reduce the activation energy for expulsion of the leaving group. This is clearly unimportant in the expulsion of the 'onium leaving groups from the carbanions in these systems, and it must be concluded that the degree of development of double bond character in the transition states is low. Presumably, the bond to the leaving group is also little extended in the transition state. This behaviour is, in general, characteristic of carbanion eliminations. In β-aryloxy-sulphones,[30] ρ for the leaving group is less than half of the value for the ionisation of phenols in the same solvent medium. This is consistent with the lack of variation in $k_2 : k_{-1}$ for the sulphone and nitrile ammonium systems in the present work.

The transition state for the elimination process has also been examined by insertion of a series of substituted α-phenyl groups in the sulphone ammonium series (Table 4). It was not possible to observe general base catalysis (*i.e.* $k_{-1}[^+BH] < k_2$) for the substituents with the larger σ values and it is concluded, therefore, that $\rho(k_{-1}) > \rho(k_2)$. However, $\rho(k_{-1})$ is expected to be small (and negative) and as $\rho(k_{obs}) = +0.71 = \rho(k_1) + \rho(k_2) - \rho(k_{-1})$, it is clear that the overwhelming effect of substitution in the α-phenyl group is on $\rho(k_1)$. The situation is to be contrasted with that for concerted elimination in the α-phenylethyl ammonium series[31] for which $\rho = +0.95$.

Phenyl substitution at $C_\beta$ similarly evokes rather little response in $k_2 : k_{-1}$. One might expect that, because $k_{-1}$ is very large, the internal nucleophilicity of the carbanion (reflected in $k_2$) would be reduced relative to the $k_{-1}$ value, causing a reduction of $k_2 : k_{-1}$. In the nitriles a substantial decrease [substrates (12) and (14)] is observed but in the sulphone series [substrates (2) and (6)] a negligible effect is seen. We have no present explanation for this behaviour.

## EXPERIMENTAL

Ethanol was dried by the magnesium–iodine method[32] and triethylamine was purified by addition of 10% w/w benzoyl chloride, double distillation, and storage over sodium. Buffer solutions were kept at constant ionic strength (0.05M) by addition of sodium perchlorate. Extractions were performed with $CH_2Cl_2$ and extracts were dried over $Na_2SO_4$.

*Kinetics.*—Most reactions were followed spectrophotometrically using a Unicam SP800 spectrophotometer whose cell block was maintained at 25.0 ± 0.1 °C by circulation of water from a thermostat. For fast reactions, a Durrum–Gibson stopped-flow spectrophotometer was used, the photomultiplier output being relayed *via* an analogue-digital converter to a Northern NS-600 ECON multichannel analyser linked to a teletype, which provided punched tape output suitable for a standard Fortran computer program. When spectrophotometric methods were not appropriate, a conductometric technique using a Wayne–Kerr Autobalance Universal Bridge B642 connected to an external recorder was used, with temperature control to within ±0.02 °C.

Pseudo-unimolecular rate constant values at each buffer concentration are means of three or more determinations. A plot of $1/k_{obs}$ *vs.* 1/[B] gave slope $1/k_1$ and intercept $k_{-1}[\overset{+}{B}H]/k_1k_2[B]$.

*Substrates; Preparation of Intermediates.*—(a) *Sulphone ammonium salts.* (i) *Salt* (2). 2-Chloroethyl phenyl sulphone (4.1 g) in ethanol (50 ml) was treated with an excess of ethanolic 30% dimethylamine (5 ml). After 24 h, t.l.c. showed that reaction was complete and evaporation gave 2-*dimethylaminoethyl phenyl sulphone hydrochloride* (4.6 g, 92%), m.p. 176° [raised to 184° (from ethanol)] (Found: C, 48.0; H, 6.4; N, 5.7. $C_{10}H_{16}ClNO_2S$ requires C, 48.1; H, 6.5; N, 5.6%). Treatment of the hydrochloride with aqueous sodium hydrogen carbonate, extraction with ether, and addition of methyl iodide to the extract gave the methiodide (Table 5).

(ii) *Salt* (4). Phenyl vinyl sulphone (1.68 g, 10 mmol) and *N*-methylaniline (1.08 g, 10 mmol) were boiled under reflux in toluene (30 ml) under nitrogen for 3 days. Evaporation gave a black oil which on extraction with di-isopropyl ether gave 2-(*N-methylanilino*)*ethyl phenyl sulphone* (1.2 g, 43%), m.p. 58° [raised to 71° (from methanol)] (Found: C, 65.6; H, 6.2; N, 5.2. $C_{15}H_{17}NO_2S$ requires C, 65.5; H, 6.2; N, 5.1%). Treatment with methyl iodide gave the methiodide (Table 5).

(iii) *Salt* (5). Phenyl styryl sulphone[33] (2.4 g) in ethanol (25 ml) was treated with aqueous 30% dimethylamine (20 ml). After 3 h, t.l.c. showed complete reaction and addition of water precipitated 2-*dimethylamino*-2-*phenylethyl phenyl sulphone* (93%), m.p. 130° [raised to 134° (from di-isopropyl ether)] (Found: C, 66.5; H, 6.6; N, 4.8. $C_{16}H_{20}NO_2S$ requires C, 66.4; H, 6.6; N, 4.9%).

(iv) *Salt* (6). 2-Phenyl-2-phenylsulphonylethanol (0.78 g, 3 mmol) was refluxed in toluene (50 ml) with acetyl chloride (10 mmol) and one drop of *NN*-dimethylaniline for 1 h. The mixture was washed with brine; evaporation gave the *acetate* (0.7 g, 78%), m.p. 91° [raised to 103° (from di-isopropyl ether)] (Found: C, 63.2; H, 5.2. $C_{16}H_{16}O_4S$ requires C, 63.1; H, 5.3%). The acetate (0.7 g) in methanol (30 ml) was treated with an excess of aqueous 20% dimethylamine (4 ml). After 24 h, the mixture was poured into saturated brine and extraction gave 2-*dimethylamino*-1-*phenylethyl phenyl sulphone* (0.6 g, 95%), m.p. 126° [raised to 138° (from ethanol)] (Found: C, 66.6; H, 6.7; N, 4.5. $C_{16}H_{19}O_2NS$, C, 66.5; H, 6.6; N, 4.9%). Treatment of the amine with methyl iodide in methanol gave the salt (Table 5).

The procedure for product analysis in the sulphone

[30] J. Crosby and C. J. M. Stirling, *J. Chem. Soc. B*, 1970, 671.
[31] P. J. Smith and S. K. Tsui, *Tetrahedron Letters* 1972, 917.
[32] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 1956.
[33] L. Field, *J. Amer. Chem. Soc.*, 1952, **74**, 3919.

ammonium series is typified by that for the salt (4). The methiodide (0.83 g, 2 mmol) in ethanol (30 ml) was treated with triethylamine (2.02 g, 20 mmol). After 12 h, the mixture was neutralised with aqueous 2M-hydrochloric acid and extraction with toluene gave phenyl vinyl sulphone (0.30 g, 89%), m.p. 68° (raised to 72° on admixture with an authentic specimen). Neutralisation of the aqueous acidic extracts with sodium hydroxide and extraction gave *NN*-dimethylaniline (0.21 g, 87%), identical (i.r. and n.m.r. spectra) with an authentic specimen.

(b) *Sulphone sulphonium salts.* Preparation and product analysis are typified by those of the salt (11). Methyl fluorosulphate (1.14 g, 10 mmol) was added to 2-phenyl-1-phenylsulphonyl-2-phenylthioethane (1.77 g, 5 mmol) in anhydrous dichloromethane (50 ml). After 12 h at 20 °C, dry ether was added and the precipitated oil was washed

TABLE 5

Sulphone ammonium salts [a]

| Salt | M.p. (°C) [b] | Yield (%) | Found (%) | Formula | Reqd. (%) | Products (%) |
|---|---|---|---|---|---|---|
| (2) $PhSO_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3I$ | 201 | 96 | C, 37.2; H, 5.1; N, 4.1 | $C_{11}H_{18}INO_3S$ | C, 37.2; H, 5.1; N, 3.9 | $PhSO_2{\cdot}CH{:}CH_2$ (100) |
| (3) $PhSO_2{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2MeI$ [c] | 172 | 88 | C, 41.2; H, 5.8; N, 3.7 | $C_{13}H_{22}INO_2S$ | C, 40.7; H, 5.75; N, 3.7 | |
| (4) $PhSO_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2PhI$ | 145 | 58 | C, 45.5; H, 4.8; N, 3.2 | $C_{16}H_{20}INO_2S$ | C, 46.0; H, 4.8; N, 3.4 | $PhSO_2{\cdot}CH{:}CH_2$ (89) $PhNMe_2$ (87) |
| (5) $PhSO_2{\cdot}CH_2{\cdot}CHPh{\cdot}NMe_3I$ | 184 | 98 | C, 47.3; H, 5.2; N, 3.2 | $C_{17}H_{22}INO_2S$ | C, 47.3; H, 5.15; N, 3.3 | $PhSO_2{\cdot}CH{:}CHPh$ (94) |
| (6) $PhSO_2{\cdot}CHPh{\cdot}CH_2{\cdot}NMe_3I$ | 199 | 90 | C, 47.4; H, 5.2; N, 3.2 | $C_{17}H_{22}INO_2S$ | C, 47.3; H, 5.15; N, 3.3 | $PhSO_2{\cdot}CPh{:}CH_2$ (94) |
| (7) $PhSO_2{\cdot}CHPh{\cdot}CH_2{\cdot}NEt_2MeI$ [c] | 188 | 35 | C, 50.0; H, 5.8; N, 2.9 | $C_{19}H_{26}INO_2S$ | C, 49.5; H, 5.7; N, 3.0 | |

[a] Prepared by methylation of free amine (see text) with methyl iodide in methanol. [b] From ethanol. [c] Amine precursor (not characterised) obtained by addition of amine to αβ-unsaturated sulphone.

TABLE 6

Sulphone sulphonium salts [a]

| Salt | M.p. (°C) | Yield (%) | Found (%) | Formula | Reqd. (%) | Products |
|---|---|---|---|---|---|---|
| (8) $PhSO_2{\cdot}CH_2{\cdot}CH_2{\cdot}SMePh(OSO_2F)$ | 105 | 98 | C, 45.7; H, 4.4 | $C_{15}H_{17}FO_5N_3$ | C, 46.0; H. 4.3 | $PhSO_2{\cdot}CH{:}CH_2$, [b] PhSMe [b] |
| (9) $PhSO_2CH_2{\cdot}CHMe{\cdot}SMePh(OSO_2F)$ | 76 | 55 | C, 44.4; H, 5.1 | $C_{16}H_{19}FS_3O_5$ [d] | C, 47.1; H, 4.7 | $PhSO_2{\cdot}CH{:}CHMe$, [b] PhSMe [b] |
| (10) $PhSO_2{\cdot}CH_2{\cdot}CMe_2{\cdot}SMePh(OSO_2F)$ | 59 | 95 | C, 46.4; H, 5.2 | $C_{17}H_{21}FO_5S_3$ | C, 46.6; H, 4.8 | $PhSO_2{\cdot}CH{:}CHMe$, [e] PhSMe [b] |
| (11) $PhSO_2{\cdot}CH_2{\cdot}CHPh{\cdot}SMePh(OSO_2F)$ | 74 | 71 | C, 51.7; H, 4.7 | $C_{21}H_{21}FO_5S_3$ | C, 52.0; H, 4.4 | $PhSO_2{\cdot}CH{:}CHPh$ (70%) [e] PhSMe (92%) [c] |

[a] From sulphide and methyl fluorosulphate in ether; details of sulphides to be given in a later paper (R. P. Redman, Ph.D. Thesis, London University, 1970). [b] 100 ± 5% by g.l.c. [c] Isolated and compared with authentic specimen. [d] This compound was very deliquescent; analysis suggests 1.8 $H_2O$. [e] 95 ± 15% by g.l.c.

TABLE 7

Cyano-'onium salts [a]

| Salt | M.p. (°C) [a] | Yield (%) | Found (%) | Formula | Reqd. (%) | Products |
|---|---|---|---|---|---|---|
| (12) $(CN)CH_2{\cdot}CH_2{\cdot}NMe_2PhI$ | 132 [b] | 78 | C, 42.9; H, 5.15; N, 9.2 | $C_{11}H_{15}IN_2$ | C, 43.7; H, 5.0; N, 9.3 | $PhNMe_2$ (84%) |
| (13) $(CN)CH_2{\cdot}CHPh{\cdot}NMe_3I$ | 136 [b] | 72 | C, 45.3; H, 5.7; N, 9.0 | $C_{12}H_{17}IN_2$ | C, 45.5; H, 5.4; N, 8.9 | $(CN)CH_2{:}CHPh$ (97%) |
| (14) $(CN)CHPh{\cdot}CH_2{\cdot}NMe_3I$ | 166 [c] | 23 | C, 45.5; H, 5.5; N, 8.9 | $C_{12}H_{17}IN_2$ | C, 45.5; H, 5.4; N, 8.9 | *f* |
| $(CN)CH_2{\cdot}CH_2{\cdot}NMe_2{\cdot}C_6H_4Me$-*m*I | 135 [b] | 97 | C, 45.3; H, 5.3; N, 8.8 | $C_{12}H_{17}IN_2$ | C, 45.5; H, 5.4; N, 8.9 | *f* |
| $(CN)CH_2{\cdot}CH_2{\cdot}NMe_2{\cdot}C_6H_4{\cdot}OMe$-*m*I | 149 [b] | 85 | C, 43.0; H, 5.1; N, 8.4 | $C_{12}H_{17}IN_2O$ | C, 43.4; H, 5.1; N, 8.4 | *f* |
| $(CN)CH_2{\cdot}CH_2{\cdot}NMe_2{\cdot}C_6H_4Cl$-*m*I | 165 [b] | 32 | C, 39.6; H, 4.4; N, 8.3 | $C_{11}C_{14}ClIN_2$ | C, 39.4; H, 4.2; N, 8.3 | *m*-$ClC_6H_4{\cdot}NMe_2$ (88%) |
| $(CN)CH_2{\cdot}CH_2{\cdot}NMe_2{\cdot}C_6H_4{\cdot}NO_2$-*m*Cl | 120 [d] | *e* | C, 49.9; [d] H, 5.7; [d] N, 15.9 [d] | $C_{11}H_{14}ClN_3O_2$ | C, 51.9; H, 5.5; N, 16.5 | *f* |

[a] By methylation with methyl iodide in ether or methanol of the cyano-amine obtained by addition of the amine to acrylonitrile. [b] From ethanol. [c] From ethanol–ether. [d] Approximate; very deliquescent. [e] *Amine* (69%), m.p. 93 °C (from ethanol–water) (Found: C, 58.4; H, 5.4; N, 21.3. $C_{10}H_{11}N_3O_2$ requires C, 58.5; H, 5.4; N, 20.5%). [f] Comparison of u.v. spectra with those of authentic mixtures.

with ether and recrystallised from ethanol–ether (Table 6). The salt (1.35 g, 3 mmol) in ethanol (30 ml) was treated with triethylamine (3.0 g, 30 mmol). After 1 h at 20 °C, the mixture was poured into acidified (HCl) brine; extraction gave methyl phenyl sulphide (0.34 g, 92%), b.p. 79° at 15 mmHg, identical (i.r. and n.m.r.) with an authentic specimen. The residue on crystallisation from propan-2-ol gave phenyl styryl sulphone (0.51 g, 70%), m.p. and mixed m.p. 72°.

(c) *Cyano-'onium salts.* Preparation and product analysis are typified by those for the salt (13). Cinnamonitrile (1.29 g, 10 mmol) in methanol (30 ml) was treated with aqueous 30% dimethylamine (10 ml). After 24 h at 20 °C, the mixture was poured into brine; extraction gave the amine (1.41 g, 81%), which decomposed on attempted distillation and was treated directly with methyl iodide (8 molar excess) in methanol (30 ml). After 24 h at 20 °C, addition of dry ether gave the methiodide (Table 7). The salt (1.58 g, 5 mmol) was treated with triethylamine (5.05 g, 50 mmol) in ethanol (30 ml). After 12 h at 20 °C, the mixture was poured into acidified brine; extraction gave cinnamonitrile (0.63 g, 97%), $n_D^{22}$ 1.5836.

α-*Aryl sulphone ammonium salts* (*Table* 8). Synthesis and product analysis are typified by those for the *m*-chloro-derivative.

Methyl phenyl sulphone (8.3 g, 53 mmol) was added to

TABLE 8

α-Aryl sulphone ammonium salts [a]

| $PhSO_2{\cdot}CH_2{\cdot}CHAr{\cdot}NMe_3I$ | M.p. (°C) | Yield (%) | Found (%) | Formula | Required (%) |
|---|---|---|---|---|---|
| Ar = *m*-MeO·$C_6H_4$ | 175 [b] | 82 | C, 46.4; H, 5.2; N, 3.1 | $C_{18}H_{24}INO_3S$ | C, 46.5; H, 5.2; N, 3.0 |
| Ar = *m*-$ClC_6H_4$ | 186 | 98 | C, 44.0; H, 4.5; N, 3.0 | $C_{17}H_{21}ClINO_2S$ | C, 44.0; H, 4.6; N, 2.8 |
| Ar = *p*-$ClC_6H_4$ [c] | 172 | 93 | C, 44.2; H, 4.6; N, 2.9 | $C_{17}H_{21}ClINO_2S$ | C, 44.0; H, 4.6; N, 2.8 |
| Ar = *m*-$NO_2{\cdot}C_6H_4$ | 203 [d] | 86 | C, 42.8; H, 4.6; N, 5.8 | $C_{12}H_{21}IN_2O_4S$ | C, 42.8; H, 4.6; N, 5.9 |

[a] Obtained by the sequence $ArCHO \xrightarrow{PhSO_2CH_2^-} ArCHOH{\cdot}CH_2SO_2Ph \xrightarrow{H_3PO_4} ArCH{:}CH{\cdot}SO_2Ph \xrightarrow{Me_2NH} ArCH(NMe_2){\cdot}CH_2{\cdot}SO_2Ph \xrightarrow{MeI} ArCH(^+NMe_3){\cdot}CH_2{\cdot}SO_2PhI^-$. [b] From ethanol. [c] Product alkene (96%). [d] Product alkene (88%).

| $PhSO_2{\cdot}CH_2{\cdot}CHAr{\cdot}NMe_2$ | | | | | |
|---|---|---|---|---|---|
| Ar = *m*-MeO·$C_6H_4$ | 95 [a] | 91 | C, 64.0; H, 6.7; N, 4.2 | $C_{17}H_{21}NO_3S$ | C, 64.0; H, 6.6; N, 4.4 |
| Ar = *m*-$ClC_6H_4$ | 93 [b] | 97 | C, 59.3; H, 5.7 | $C_{16}H_{18}ClNO_2S$ | C, 59.5; H, 5.6 |
| Ar = *p*-$ClC_6H_4$ | 115 [b] | 93 | C, 61.0; H, 4.0 | $C_{16}H_{18}ClNO_2S$ | C, 59.5; H, 5.6 |
| Ar = *m*-$NO_2{\cdot}C_6H_4$ | 118 | 80 | C, 57.5; H, 5.7; N, 8.3 | $C_{16}H_{18}N_2O_4S$ | C, 57.5; H, 5.4; N, 8.3 |

[a] From methanol. [b] From ethanol.

| $PhSO_2{\cdot}CH{:}CHAr$ | | | | | |
|---|---|---|---|---|---|
| Ar = *m*-MeO·$C_6H_4$ | 127 [a] | 52 | C, 65.9; H, 5.0 | $C_{15}H_{14}O_3S$ | C, 65.6; H, 5.1 |
| Ar = *m*-$ClC_6H_4$ | 95 [b] | 51 | C, 61.0; H, 3.9 | $C_{14}H_{11}ClO_2S$ | C, 61.0; H, 4.0 |
| Ar = *p*-$ClC_6H_4$ | 127 [c] | 56 | C, 61.0; H, 4.0 | $C_{14}H_{11}ClO_2S$ | C, 61.0; H, 4.0 |
| Ar = *m*-$NO_2{\cdot}C_6H_4$ | 142 [b] | 51 | C, 58.0; H, 3.8; N, 4.9 | $C_{14}H_{11}NO_4S$ | C, 58.0; H, 3.8; N, 4.8 |

[a] From di-isopropyl ether. [b] From ethanol–water. [c] From toluene.

| $PhSO_2{\cdot}CH_2{\cdot}CH(OH)Ar$ | | | | | |
|---|---|---|---|---|---|
| Ar = *m*-MeO·$C_6H_4$ | 83 [a] | 76 | C, 61.6; H, 5.5 | $C_{15}H_{16}O_4S$ | C, 61.6; H, 5.5 |
| Ar = *m*-$ClC_6H_4$ | 80 [b] | 91 | C, 56.8; H, 4.4 | $C_{14}H_{13}ClO_3S$ | C, 56.7; H, 4.4 |
| Ar = *p*-$ClC_6H_4$ | 104 [b] | 79 | C, 56.9; H, 4.4 | $C_{14}H_{13}ClO_3S$ | C, 56.7; H, 4.4 |
| Ar = *m*-$NO_2{\cdot}C_6H_4$ | 108 [a] | 59 | C, 54.8; H, 4.4; N, 4.4 | $C_{14}H_{13}NO_5S$ | C, 54.8; H, 4.2; N, 4.6 |

[a] From ethanol. [b] From di-isopropyl ether.

TABLE 9

2-Phenylethylammonium salts [a] and 2-phenylethylamines [b]

| Salt | M.p. (°C) | Yield (%) | Found (%) | Formula | Required (%) |
|---|---|---|---|---|---|
| $PhCH_2{\cdot}CH_2{\cdot}NMe_2PhI$ | 135 [c] | 91 | C, 54.5; H, 5.7; N, 3.9 | $C_{16}H_{20}IN$ | C, 54.5; H, 5.6; N, 3.9 |
| $PhCH_2{\cdot}CH_2NMe_2(C_6H_4{\cdot}OMe\text{-}m)I$ | 121 [c] | 79 | C, 53.5; H, 5.9; N, 3.6 | $C_{17}H_{22}INO$ | C, 53.0; H, 5.7; N, 3.6 |
| $PhCH_2{\cdot}CH_2{\cdot}NMe_2(C_6H_4Me\text{-}m)I$ | 136 [c] | 71 | C, 58.0; H, 6.3; N, 3.9 | $C_{17}H_{22}IN$ | C, 58.1; H, 6.3; N, 4.0 |
| $PhCH_2{\cdot}CH_2{\cdot}NMe_2(C_6H_4Cl\text{-}m)I$ | 131 [d] | 30 | C, 49.6; H, 4.9; N, 3.6 | $C_{16}H_{19}ClIN$ | C, 49.9; H, 4.9; N, 3.6 |
| $PhCH_2{\cdot}CH_2{\cdot}NMe_2(C_6H_4{\cdot}NO_2\text{-}m)(OSO_2OMe)$ | 127 [e,f] | 33 | C, 52.9; H, 5.9; N, 7.2 | $C_{17}H_{22}O_6N_2S$ | C, 53.4; H, 5.8; N, 7.3 |

| Amine | B.p. (°C; mmHg) | | | | |
|---|---|---|---|---|---|
| $PhCH_2{\cdot}CH_2{\cdot}NMePh$ | 121; 0.1 | 60 | (Lit.,[g] b.p. 124; 0.1) | | |
| $PhCH_2{\cdot}CH_2{\cdot}NMe(C_6H_4{\cdot}OMe\text{-}m)$ | 150; 0.1 | 71 | C, 80.1; H, 7.9; N, 5.8 | $C_{16}H_{19}NO$ | C, 80.0; H, 7.9; N, 5.8 |
| $PhCH_2{\cdot}CH_2{\cdot}NMe(C_6H_4Me\text{-}m)$ | 130; 0.1 | 66 | C, 85.2; H, 8.5; N, 6.3 | $C_{16}H_{19}N$ | C, 85.0; H, 8.5; N, 6.2 |
| $PhCH_2{\cdot}CH_2{\cdot}NMe(C_6H_4Cl\text{-}m)$ | 131; 0.1 | 62 | C, 73.4; H, 6.5; N, 5.6 | $C_{15}H_{16}ClN$ | C, 73.5; H, 6.5; N, 5.7 |
| $PhCH_2{\cdot}CH_2{\cdot}NMe(C_6H_4{\cdot}NO_2\text{-}m)$ | (86 [g,h]) | 34 | C, 69.5; H, 5.3; N, 11.4 | $C_{14}H_{14}N_2O_2$ | C, 69.4; H, 5.8; N, 11.2 |

[a] By methylation of amine with methyl iodide. [b] By reaction of *N*-methylarylamine with 2-phenylethyl bromide. [c] From ethanol. [d] From ethanol–water. [e] From dichloromethane. [f] Methylation with dimethyl sulphate. [g] L. J. Steffa and E. R. Thornton, *J. Amer. Chem. Soc.*, 1963, **85**, 2680. [h] M.p. (°C) from ether–petroleum.

the Grignard reagent from bromoethane (60 mmol) and magnesium (60 mg atom) in ether (70 ml). *m*-Chlorobenzaldehyde (53 mmol) in dry tetrahydrofuran (30 ml) was added and the mixture was boiled under reflux for 30 min. Addition of saturated aqueous ammonium chloride and extraction gave the alcohol (91%), m.p. 80° (from di-isopropyl ether).

The preceding alcohol (9 g) was boiled under reflux with phosphoric acid (30 ml) for 30 min and the cold mixture was diluted with water. Extraction gave the styryl sulphone (51%), m.p. 95° (from ethanol–water).

The alkene (3 g) in ethanol (50 ml) was kept with an excess of aqueous 30% dimethylamine at 20 °C for 12 h. Evaporation gave the dimethylamino-α-aryl sulphone (97%), m.p. 93° (from ethanol).

The amine (3.24 g) in ethanol (80 ml) was treated with methyl iodide (3 ml). After 1 h, evaporation gave the methiodide (98%), m.p. 186° (from ethanol).

We thank the S.R.C. for equipment and a studentship (to K. N. B.).

[6/2361 *Received*, 30*th December*, 1976]