Elimination and Addition Reactions. Part 39.[1,2]† Variation of Nucleofugality with Transition State Structure – 1,3- and 1,2-Eliminations from Carbanions Compared

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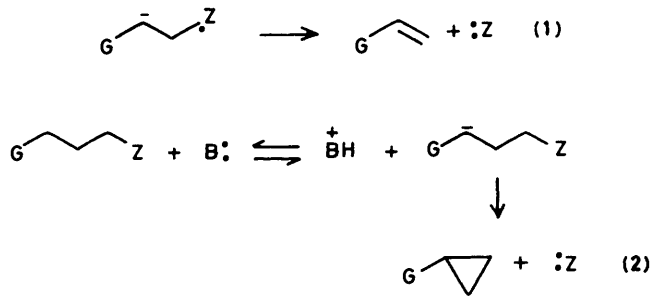
Phenylsulphonyl-activated 1,3-eliminations have been investigated with the objective of determining nucleofugalities of six leaving groups. In cyclohexane-1,3-diyl and propane-1,3-diyl systems unactivated 1,2-elimination of 'poor' leaving groups occurs faster than 1,3-elimination. In 2,2-dimethylpropane-1,3-diyl substrates, however, quantitative 1,3-eliminations occur and the nucleofugalities of Br, Cl, OTs, $PhSO_2$, PhS, PhO, have been determined. In a linear free energy relationship extending over 15 pK_a units and 12 rank units, an excellent correlation of nucleofugality with the pK_a of the conjugate acid of the leaving group is found. It is concluded from the comparison with 1,2-eliminations previously studied that 1,3-elimination involves considerable leaving group separation and ring formation in the transition state. With bromide as leaving group, the 2,2-dimethylpropane-1,3-diyl system is 10^3 times more reactive in cyclopropane formation than the propane-1,3-diyl system; this is the first quantitation of the Thorpe–Ingold effect in homocyclic ring formation. With chloride and tosylate leaving groups, smaller accelerations are observed.

Part of the recent work on elimination reactions from these laboratories has been addressed to the problem of nucleofugality: the tendency of leaving groups to depart bearing the connecting electron pair.[3] The problem is not a straightforward one because separation of the process in which the leaving group departs from others which may be concerted with it is required if the data obtained are to be meaningful. Indeed it is this failure to separate such processes which has delayed the definitive assignments of nucleofugalities despite the fundamental importance of such quantities. Unfortunately, most qualitative generalisations about nucleofugality derive from data on nucleophilic substitution at sp^3 carbon by the S_N2 mechanism and have led to the precarious notion that nucleofugality is related to the acidity of the conjugate acid. Nucleophilic substitution at saturated carbon is in fact a very poor basis on which to develop generalisations of this sort because reactivity is well known to be nucleophile variable[4] and the range of leaving groups which can be displaced is extremely limited. Furthermore, those leaving groups that *can* be studied, halogens, sulphonates, and so on, have poorly defined relative basicities because the acidities of such strong acids are difficult to measure accurately.[5] More subtle points, such as the very large and differential variations of acidity which can occur with change of solvent[6] and the fact that when a leaving group is charged, reactivity is differentially changed, are widely ignored. The fact that alkylammonium salts, sulphonium salts, and chlorides all have roughly comparable reactivities for the same alkyl group notwithstanding the basicity variation of not less than 10^{17} between chloride and trialkylammonium, illustrates the difficulties. Entirely appropriate reservations about generalisations relating to nucleofugality are well made in both advanced[4] and introductory[7] texts.

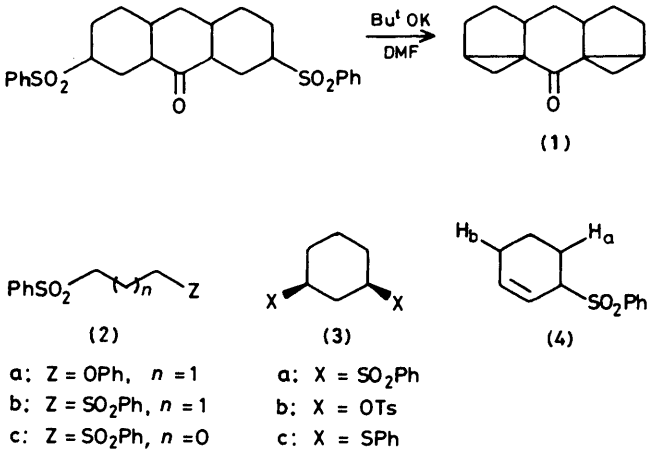
All data from which nucleofugalities can be extracted are derived either from S_N1 processes[8] or elimination[9] reactions. In the case of elimination reactions some data are available from the decomposition of the tetrahedral intermediates of acyl transfer reactions[9-12] and related structures, but most have become available from alkene-forming eliminations from carbanions[13] together with sulphene-[14] and ketene-forming[15-17] reactions. It was clear from alkene-forming reactions studied earlier that the leaving group ranks (= nucleofugalities) obtained related to that specific process. There was no evidence to suggest that the data were generally applicable to other types of reactions, or even to other elimination reactions; such a generalisation would be absurd because it is clear that nucleofugality is a composite of bond polarisation (accounting for high nucleofugalities of positively charged groups and conversely of negatively charged ones) together with bond strength, to say nothing of leaving group solvation which must vary with the degree of bond cleavage to the nucleofuge at the transition state. It was clear, however, that for the process of equation (1), nucleofugalities were little dependent upon considerable differences in the structure of the carbanion from which the nucleofuge was expelled; only minor variations were found in the series G = $PhSO_2$, CN, and PhCO.[13d] Further, for this type of reaction in which the degree of cleavage of the bond to the leaving group is thought to be very small,[13f] substantial changes in medium composition had little effect on reactivities.[13d]

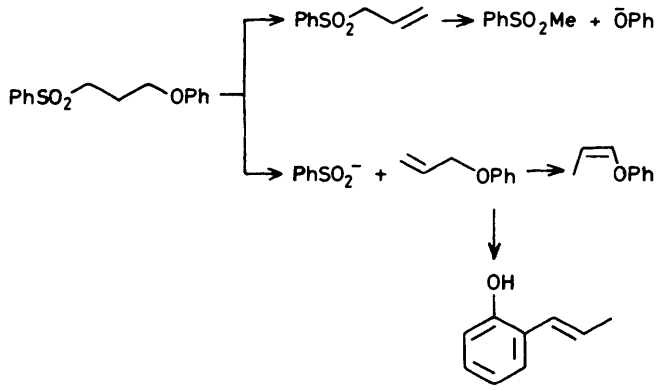


Results and Discussion

Against the background of this work and with an eye to an examination of the generality of nucleofugality data obtained in any one reaction, we have examined nucleofugalities in 1,3-elimination from carbanions [equation (2)]. Such reactions have also received considerable earlier attention in our

† Preliminary accounts of this work have been given by B. Issari and C. J. M. Stirling at the Third International Symposium on Reaction Mechanisms in Solution, University of Kent at Canterbury, 1982; *J. Chem. Soc., Chem. Commun.*, 1982, 684.





Scheme.

laboratories.[18] The most striking feature of these reactions is that of all intramolecular nucleophilic substitutions of carbanions, they are the most successful. Formation of three-membered rings occurs more rapidly than that of any other size up to and including six. This is true even with considerable variations in G.[18a,b] It was concluded from the element effect [18f] that, again surprisingly, ring-formation was well advanced in the transition state and this encouraged simple rationalisation of the rapid formation of a highly strained three-ring in preference, for example, to a four-membered ring of closely similar strain.[18c]

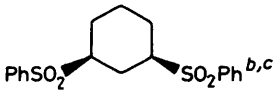
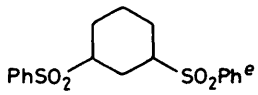
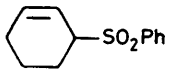
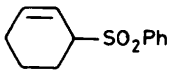
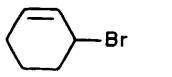
Previous work on 1,3-cyclopropane-forming eliminations had been on systems with ' good ' leaving groups of the type familiar in nucleophilic substitution at saturated carbon, notably chloride,[18b,c] bromide,[18a,b] and sulphonate.[18d] We wished to test the generality of nucleofugality data and required a range of ' poorer ' leaving groups. We were encouraged in this respect by Woodward's observation that benzenesulphinate, a highly ranked nucleofuge in 1,2-elimination from carbanions, could be expelled in 1,3-elimination from a highly structured enolate ion to give (1).[19] Formation of cyclopropanes in intramolecular displacement of arenesulphinate ions by carboxylate-stabilised carbanions has been put to good use by Julia [20] in synthesis of chrysanthemic derivatives. In preliminary work, we examined the reactivities of three simple model systems (2a), (2b), and (3). System (2b) was known to be very poorly reactive towards bases by comparison with (2c) [13b,21] and the products formed [21] are entirely consistent with a more rapid and probably concerted 1,2-elimination leading eventually to phenyl methyl sulphone. No cyclopropane was formed. Similarly (2a), on treatment with ethanolic sodium ethoxide under severe conditions (150 °C), gave products consistent with 1,2-elimination of both phenoxide and benzenesulphinate in roughly comparable proportions (Scheme). Again no cyclopropane was obtained. The two nucleofuges have similar ranks (*n.b. ca.* 8 pK_a units difference in basicity!) in carbanionic 1,2-elimination.[13c] The stereochemistry of the fragments resulting from the residuum after elimination of benzenesulphinate is interesting. Phenyl (*Z*)-prop-1-enyl ether [22] and (*E*)-propenylphenol [23] are obtained in accordance with literature precedent in other systems.

System (3a), modelled on Woodward's compound (1),[19] was straightforwardly obtained from *cis*-cyclohexane-1,3-diol *via* the bis-tosylate (3b) and the bis-sulphide (3c). Treatment under mildly basic conditions (ethanolic 0.1M-sodium ethoxide) at 78° for 3 h caused partial isomerisation of *cis*- to *trans*-isomer. The isomer mixture recovered (90%) contained the *cis*- and *trans*-isomers in the ratio of 8 : 1 in accord with the lower conformational energy of 1,3-*cis*- than 1,3-*trans*-isomers. With strong bases under a variety of harsh conditions, no cyclopropane was formed. Benzenesulphinate was eliminated but no mono-sulphone was detected. Instead the volatile products were found to consist of an equilibrium mixture of cyclohexa-1,3- and -1,4-dienes. Again, formation of these compounds is consistent with a preferential 1,2-elimination to give mono-sulphone (4) which undergoes a second 1,2-elimination to give the cyclohexadienes. The second elimination is more rapid than the first; none of (4) can be isolated from partial reactions and the second elimination is more favourable either because of the formation of a diene (H_a removed) or an allylically activated 1,4-elimination (H_b removed). It was confirmed that (4) disappeared more rapidly in the reaction conditions than (3a), and that under such milder conditions the 1,3-diene was the much preferred kinetic product. Equilibration of cyclohexadienes in a 1 : 3 ratio of 1,3 : 1,4-dienes under such conditions is entirely consistent with earlier work [24] but no disproportionation products were found.[25] Cyclohexyl phenyl sulphone was recovered in high yield from reactions under much harsher conditions demonstrating the activating influence of both a phenylsulphonyl group and a carbon–carbon double bond upon elimination in these systems. Product analyses are summarised in Table 1.

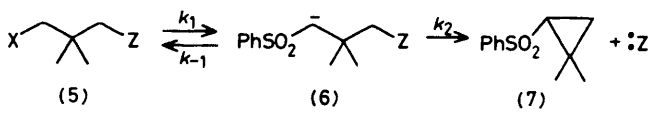
Clearly, it was important on the basis of these results to prevent a more rapid, albeit unactivated, 1,2-elimination in such systems. Our results have therefore been obtained with system (6), in which 1,2-elimination is prevented by *gem*-dimethyl substitution at C-2. Such structural modification turned out to have a double bonus; the Thorpe–Ingold effect [26] operates in favour of 1,3-elimination (below) giving accelerations of up to 10^3. The substrates are, however, more difficult to obtain by nucleophilic substitutions at C-1 and -3 which are neopentylic.[27] Phenylsulphonyl was selected as activating group because of its several advantages. The group does not itself react even under harsh conditions and reprotonation of carbanions stabilised by the group is rapid.[13c] The latter is important because rapid reprotonation permits observation of a wide range of reactions in which, thereby, the slower expulsion of the leaving group is rate determining. This is, of course, essential for studies of nucleofugality. Our earlier nucleofugality studies of 1,2-eliminations had also used phenylsulphonyl group for activation.

Substrates.—The substrates (5) were obtained from diol (5a) which was converted into dibromide (5b) and by treatment with benzenethiolate successively into bromo-sulphide (5c)

Table 1. Products formed in the reaction of the cyclohexyl compounds with base [a]

Substrate	Temp. (°C), Time (h)	Yield (%) of 1,3-Diene	Yield (%) of 1,4-Diene	Yield (%) of $PhSO_2H$	Yield (%) by wt. of diene polymerisation products
	80, 3	*d*			
	180, 18	60	20	91	5
	120, 18	0.2			
	180, 19	66	21	89	10
	120, 19	20	1	*f*	
	180, 18	18	6		
	180, 18	65	22		11
	180, 18	64	21		11
	180, 48	63	21		

[a] Reactions in 1M-EtONa–EtOH. [b] 0.1M-EtONa–EtOH. [c] *cis*. [d] Mixture of *cis* (80%) and *trans* (10%) sulphones recovered. [e] *cis–trans* mixture. [f] Not determined.



(5) (6) (7)

a: X = Z = OH
b: X = Z = Br
c: X = PhS, Z = Br
d: X = Z = PhS
e: X = $PhSO_2$, Z = Br
f: X = Z = $PhSO_2$
g: X = PhS, Z = OPh
h: X = $PhSO_2$, Z = OPh
i: X = Z = Cl
j: X = PhS, Z = Cl
k: X = $PhSO_2$, Z = Cl
l: X = Z = OTs
m: X = PhS, Z = OTs
n: X = $PhSO_2$, Z = OTs
o: X = $PhSO_2$, Z = PhS
p: X = $PhSO_2$, Z = H

and bis-sulphide (5d). Oxidation of each gave sulphones (5e and f).

Treatment of (5c) with phenoxide ion gave (5g), oxidation of which gave (5h). The bis-chloride (5i) was converted *via* sulphide (5j) into sulphone (5k). Similarly, bis-tosylate (5l) was converted *via* sulphide (5 m) into sulphone (5n). Bromide (5e) with benzenethiolate gave sulphide (5o). Neopentyl phenyl sulphone (5p) required for detritiation calibration (below) was obtained conventionally from neopentyl tosylate.

Kinetics.—Cyclisations. Reactions with substrates containing the $PhSO_2$, PhS, and PhO leaving groups were too slow to follow in ethanolic sodium ethoxide, the base–solvent system employed in previous nucleofugality studies. Use of potassium t-butoxide considerably enhanced rate constants [18] undoubtedly by increasing the equilibrium concentration of carbanion. Reactions of substrates with Z = $PhSO_2$, PhS, PhO, and OTs were followed spectrophotometrically; in the case of the first three substrates by determining the extents of reactions in aliquot parts of reaction mixtures. For substrates with Z = Cl and Br, potentiometric titration of aliquot parts against silver nitrate was employed.

In all cases, rate constants for reactions in $KOBu^t$–Bu^tOH were found to be base concentration-dependent at high concentrations of base in the region of 1M. This is not too surprising for concentrated solutions; aggregation is well known to be a feature of strong solutions of this base–solvent system. For the poorer leaving groups rate constants are quoted for concentrations close to 1M. It is recognised that this factor, combined with the need to extrapolate rate constants for the poorly reactive substrates (Figure 1) gives values for individual rate constants at 30 °C whose absolute precision is poor. This work is however concerned with very large reactivity differences.

Table 2. Reactivities and ranks for 1,3- and 1,2-eliminations

Substrate	Z	k_{obs} 30° [a] (1,3)	k_{obs} 25° [a,b] (1,2)	k_{detrit} [a] (1,3)	Rank (1,3)	Rank [c] (1,2)	Yield of cyclopropane (%)
(5e)	Br	6.8	(2 600) [d]	3.3 [e]	11.3 [f]		97
(5k)	Cl	0.2	(780)	2.1 [e]	9.9		91
(5n)	OTs	1.0	(6 700)	4.0 [e]	10.4		98
(5f)	SO_2Ph	1.0×10^{-7} [g]	(1.05)	6.38 (4.65) [h]	3.5	8.7	99 [i]
(5o)	SPh	3.0×10^{-11} [j]	(0.021)	1.17	0.4	8.7	99
(5h)	OPh	5.0×10^{-13} [k]	(0.35)	1.14	−1.4	8.9	99 [i]
(5p)	H			0.11 (0.13) [h]			
$PhSO_2CH_2CH_2CH_3$				0.56			

[a] Units: $dm^3\ mol^{-3}\ s^{-1}$. [b] Reactions in EtONa–EtOH at 25°. [c] log k_{obs} − log k_{detrit} + 11. [d] *E*2 Mechanism. [e] Calculated from Taft plot. [f] Mechanism uncertain. [g] Extrapolated from reactions in range 100—72°. [h] Dedeuteriation. [i] 65% of $PhSO_2^-$ characterised as *p*-nitrobenzyl sulphone. [j] Extrapolated from reactions in range 156—113°. [k] Extrapolated from reactions in range 159—136°. [l] Phenol 42%.

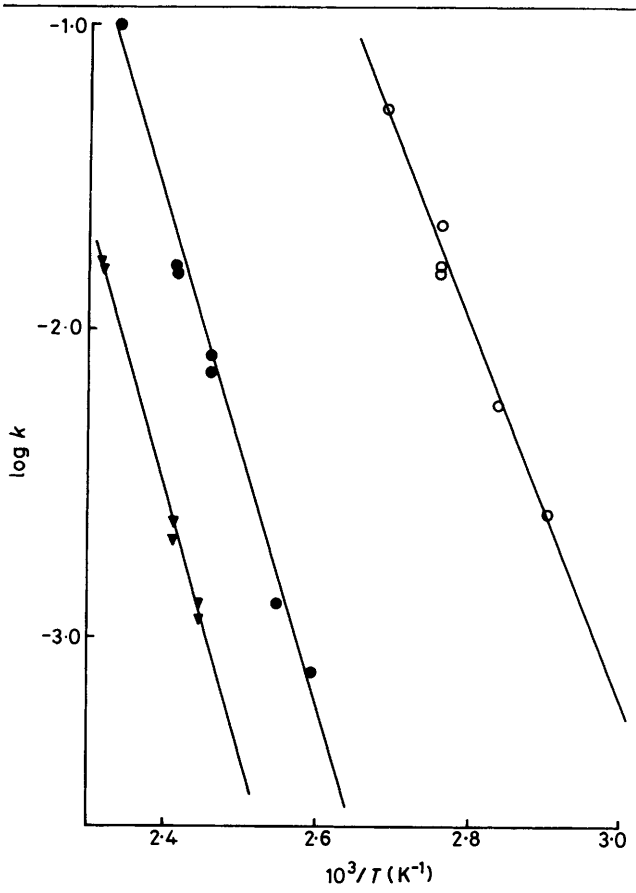


Figure 1. Activation plots for leaving groups (▼ OPh, ● SPh, O SO_2Ph) in reactions of 1-phenylsulphonyl-2,2-dimethylpropyl substrates with KOBu^t–Bu^{t}OH

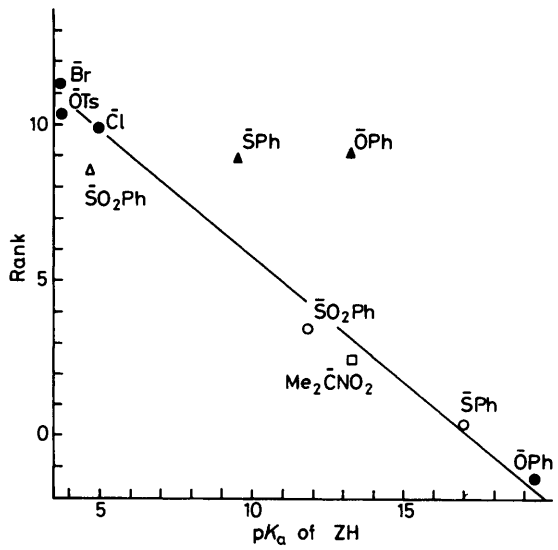


Figure 2. Rank–pK_a^{Z-H} correlations for elimination reactions. ▲ 1,2-Alkene-forming eliminations in EtONa–EtOH (ref. 3*c*); literature values of pK_a^{Z-H} for 95% EtOH–H_2O (G. Schwarzenbach and E. Rudin, *Helv. Chim. Acta*, 1939, **22**, 360); △ value estimated from mean ΔpK_a between 95% EtOH and H_2O for other groups; □ pK_a in methanol (ref. 13*e*); ● 1,3-eliminations (this work) in Bu^{t}OK–Bu^{t}OH; pK_a^{Z-H} values in Bu^{t}OH from ref. 34*a*; O value of pK_a^{Z-H} estimated from mean ΔpK_a^{Z-H} between Bu^{t}OH and H_2O for other groups

Determination of leaving group ranks. The extraction of nucleofugality data from substrate reactivities has been carried out as for 1,2-alkene-forming eliminations.[13c] The overall rate constants, k_{obs}, are a composite of the equilibrium constants k_1/k_{-1}[BH] for carbanion formation and the rate constants, k_2, for their conversion into cyclopropanes. In all cases, except for Z = Br (Table 2), $k_{obs} \ll k_1$ (evaluated as the detritiation rate constant, see below) showing that the rate-determining step is cyclisation (k_2). The case of Z = Br is ambiguous; in half-reactions in Bu^{t}OD both unreacted starting material and product are completely deuteriated adjacent to the sulphonyl group, implying that, *pace* Breslow,[28] the $(E1cB)_R$ mechanism is followed. On the other hand, values of the rate constant for detritiation derived from a Taft plot for other members of the series (Table 2) are *lower* than k_{obs} for cyclopropane formation to *E*2 or $(E1cB)_I$ mechanisms. In addition, rate constants for detritiation of sulphones (5f and p) are comparable with the rate constants for dedeuteriation of these sulphones (Table 2). Such erratic behaviour in respect of primary kinetic isotope effects in the KOBu^t–Bu^{t}OH base-solvent system is also a feature of the reports of earlier workers.[29] Because of these mutually contradictory pieces of evidence, we cannot confidently assign mechanism to reactions with this bromide. Its behaviour (Figure 2) does, however, appear concordant with the other substrates studied.

It is assumed, as before,[13c] that k_{-1} is close to diffusion-controlled; this assumption rests on the quantitative behaviour of localised bis-stabilised carbanions in water. So far as *differences* in rank in this system is concerned, the validity of this assumption is not important. By comparison with 1,2-eliminations giving alkenes, differentials in k_{-1} will depend

much less on variation of the leaving group in these systems as the leaving group is separated from the site of deprotonation by an extra atom.

Rates of detritiation in t-butoxide–t-butyl alcohol under conditions for cyclisation reactions were carried out as before.[30] Rate constants are in Table 2 and we have used these values rather than derived values as before [13c] because kinetic isotope effects for proton transfer are erratic as mentioned above. The rate constant for detritiation of sulphone (5f), for example, was found to be *larger* than dedeuteriation (Table 2). Detritiation rate constants are less sensitive for the cyclopropane-forming system (ρ* 3.1) in Bu^{t}OK–Bu^{t}OH than for the alkene-forming system measured earlier (ρ* 4.89).[30] Leaving group ranks are then evaluated as before; the effect of the leaving group on the pre-equilibrium component of the overall rate constant is allowed for by subtraction of log k_{detrlt}. The reprotonation component is regarded as constant for all leaving groups; it is arbitrarily set at log $k_{-1} = 11$ recognising that the actual values are possibly somewhat smaller and that therefore small leaving group differentials *will* be present. These have been ignored in setting rank = log k_{obs} − log k_{detrlt} + 11.

Discussion

Comparison of 1,2- *and* 1,3-*Eliminations.*—Gross overall comparisons, without reference to mechanism, of 1,3-eliminations from sulphonyl-stabilised carbanions reported here with 1,2-eliminations studied earlier, show very large differences in reactivity. With bromide as nucleofuge, the comparison of the reaction of $PhSO_2CH_2CH_2Br$ with ethoxide and *p*-tolyl-$SO_2CH_2CH_2CH_2Br$ with t-butoxide [18a] shows a ratio of 10^6. For chlorides [18c] the value is 2×10^5. 1,3-Elimination is much more sensitive to change of leaving group; thus for the comparison of $PhSO_2$ and PhO the ratio of k_{obs} for 1,2-elimination is 3 and for 1,3-elimination is 2×10^5 (for extrapolated values; Table 2).

In both of these respects, 1,3-elimination is much more akin to intermolecular nucleophilic substitution for which data for ' poor ' leaving groups have become available from the work of Lewis [31] and his collaborators who used the powerful nucleophiles ArS^- in their studies. We have briefly investigated the intermolecular version of the reactions studied. Treatment of methyl phenyl sulphone with a five molar excess of benzenethiolate in t-butyl alcohol gives a 37% conversion into phenyl methyl sulphide at 170° after 20 h. These conditions are very much more vigorous than those required for quantitative conversion of the bis-sulphone (5f) into the cyclopropane.

The Thorpe–Ingold Effect.—*gem*-Dimethyl substitution was an obligatory feature of the substrates studied, being employed to prevent unactivated 1,2-alkene-forming elimination. It is well known [26] that such substitution can increase the rate constants for cyclisation processes such as that of the conversion of hydroxy halides into cyclic ethers. Accelerations are variable and depend upon the ring size (3 > 4).[26] Curiously, the magnitude of the effect has never been determined for carbocyclic ring formation and our results provide the first values. Comparisons with our earlier work [18a–c] show values of *ca.* 920 for the bromosulphones, 42 for the chlorides, and 12 for tosylates (this work). The origins of the Thorpe–Ingold effect are not clear; [26] evaluation of activation parameters for the ' retro '-Thorpe–Ingold effect in ring *opening* reactions shows that a change in the enthalpy of activation is responsible.[32]

Mechanisms of Reactions.—The substantially higher rate constants for detritiation of substrates than for 1,3-elimination in all cases except for Z = Br points clearly towards rapid formation of the carbanion which sheds the leaving group in a subsequent slow step. In this respect, 1,3-elimination differs from 1,2-elimination for the ' better ' leaving groups Br, OTs, Cl. In such 1,2-eliminations,[13c] rates of elimination are either comparable with or considerably faster than for detritiation. Concerted (*E*2) or rate-determining deprotonation ($E1cB)_I$ mechanisms were assigned. Evidently, in the present cases, the much slower rates of leaving group expulsion coupled with similar rates of carbanion reprotonation permit observation of the $(E1cB)_R$ mechanism.

Leaving Group Ranks.—The ranks, evaluated as described in the previous section, are in Table 2. The striking feature of them, as for the k_{obs} values, is that the differentials are very much greater than for alkene-forming elimination. In the case of phenoxy, there is a substantial reversal of the order of nucleofugalities. Phenoxide is now a substantially poorer leaving group than thiophenoxide but if the pK_a difference is allowed for, in view of the correlation of Figure 2 they become comparable. Douglas and Alborz [17] have studied β-eliminations of phenoxide and thiophenoxide from carbonyl-stabilised carbanions. They find the thio-derivatives to be the more reactive but isobasic plots show phenoxide to be a better leaving group than thiophenoxide in these reactions. It is suggested,[17] however, that special factors may be operating in the case of thiophenoxide which reduce its nucleofugality in the ketene-forming eliminations that were studied.

It is to be noted that the rank order is not affected by the precision of the detritiation data used to evaluate ranks. In this series, all the leaving groups have rather similar inductive-field effects,[33] and the whole range of detritiation rate constants in substrates undergoing cyclisation is embraced by a factor of six. 1,3-Eliminations are particularly interesting in that the ' very good ' leaving groups, familiar in nucleophilic aliphatic (S_N2) reactions, can be directly and quantitatively compared under constant conditions with ' poor ' leaving groups not generally encountered in S_N2 processes.

Correlation of Rank with pK_a *Data.*—As mentioned earlier, there have been frequent attempts to correlate ' leaving group ability ' (note the distinction from rank or quantified nucleofugality) with physicochemical data, notably with pK_a values. It is also, of course, frequently assumed that such leaving group abilities are transferable from reaction to reaction. For 1,2-eliminations there is no correlation (Figure 2) between nucleofugalities and pK_a values, nor is there for that matter with values such as σ_I or the inverse of carbon nucleophilicity as discussed earlier.[3] The situation for 1,3-elimination is quite different. Figure 2 shows the correlation between rank for the six leaving groups studied and their pK_a^{Z-H} values for solvent t-butyl alcohol.[34a] Values not available were estimated from the mean values of pK_a^{Z-H} (Bu^{t}OH) − pK_a^{Z-H} (H_2O) [34b,c] for other groups. The correlation is striking; rectilinearity over 11.8 (log) units of rank and 16 pK_a units (slope −0.8) makes this linear free energy relationship cover one of the wider ranges of reactivity ever studied. Such a correlation speaks of a high degree of reflection of the inherent stability of the leaving group in the transition state for cyclisation. The correlation also suggests a high degree of leaving group bond cleavage in the transition state. If bond order is conserved along the reaction co-ordinate,[35] the corollary is that there is a large degree of ring formation in the transition state.

In the work on β-eliminations,[13c] correlations of rank data with other physicochemical parameters were examined, notably the inverse of carbon nucleophilicity of the leaving group and the inductive effect of the leaving group as indicated

Table 3. Activation parameters for cyclisation of the propyl systems at 30 °C

Substrate		ΔE/kcal mol^{-1}	$\Delta G^{\ddagger}$/kcal mol^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-} K^{-1}
PhO	SO_2Ph	40.6	34.8	40.0	+17
PhS	SO_2Ph	36.3	32.3	35.7	+11
$PhSO_2$	SO_2Ph	29.3	27.5	28.7	+4
TsO	SO_2Ph	17.0	19.2	16.4	−9
Cl	SO_2Ph	21.3	18.9	20.7	+6
TsO	SO_2Ph	28.1	17.8	27.5	+32

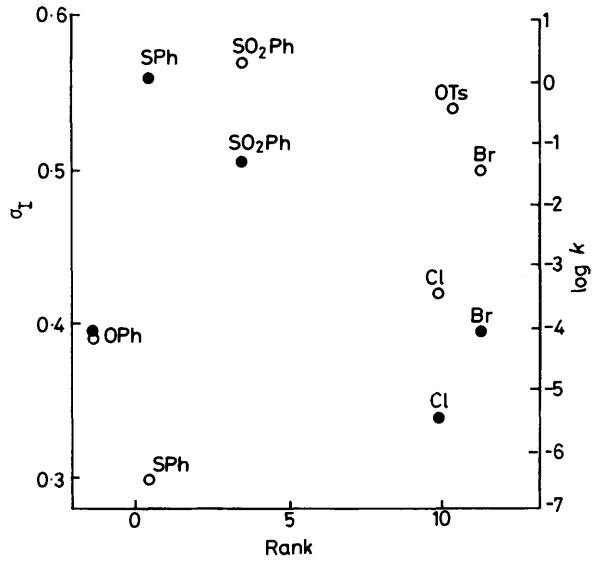


Figure 3. Correlations of ranks of leaving groups, in reactions of 1-phenylsulphonyl-2,2-dimethyl substrates with KOBu^t–Bu^{t}OH, with σ_I, O; with log k for Z: + MeI, ●

by σ_I. Such correlations are shown (Figure 3) for these two criteria; again there is no correlation. In terms of carbon nucleophilicity, it is well known that phenoxide ion in spite of its relatively high basicity and the formation of strong bonds to carbon, is poorly nucleophilic towards sp^3 carbon.[36] Its deviation from the correlation with other groups is striking. Speculation that there might be a relationship between nucleofugality and inverse carbon nucleophilicity is not of course borne out by general experience. Iodide is highly nucleophilic towards sp^3 carbon but is also readily displaced. Cyanide ion is rather weakly nucleophilic towards sp^3 carbon and is very difficult to displace from it.

Activation Parameters.—The very wide range of reactivity in the substrates studied and the consequent need to use widely different reaction temperatures has required extrapolations of activation plots and has hence permitted the evaluation of activation parameters. We stress that the values (Table 3) which are obtained are approximate for the reasons outlined above. What stands out clearly is the trend for the first three leaving groups listed and for which half of the reactivity change occurs, of steady decrease in $\Delta H^{\ddagger}$ and steady decrease in $\Delta S^{\ddagger}$.

Conclusions.—For β-eliminations,[13] the leaving group ranks,[13c] with their striking failure to correlate with pK_a^{Z-H}, suggested a very small degree of bond cleavage in the transition state. This conclusion was amply supported by other characteristics, notably insensitivity to medium [13d] and substituent effects.[13f] By complete contrast, the ranks for leaving groups in γ-eliminations, with their excellent pK_a^{Z-H} correlation, suggest a high degree of bond formation in the transition state, a conclusion supported by other characteristics of the reactions, notably the higher reactivities for three-ring formation when compared with those for other ring sizes. What this work most clearly demonstrates is that, above all, leaving group ability, properly defined as nucleofugality in this and other work, is not a universal property of functions. It depends crucially upon the nature of the transition state and the degree of cleavage of the bond to the leaving group in that transition state. The widely held belief of a universal correlation with pK_a^{Z-H} is never appropriate [37] when leaving groups of different charges are considered. In this respect we entirely endorse the comments of Hoz and his collaborators.[37b] The correlation may be partially appropriate particularly for uncharged groups and when, as in this work, the degree of cleavage of the bond to the leaving group is large.

Experimental

All reactions with thiolates and kinetics of reactions of phenoxy compounds were carried out under dry nitrogen. ^1H and ^{13}C n.m.r. spectra were consistent with the given structures and are detailed only when alternative structures may reasonably be considered.

t-Butyl alcohol was dried by refluxing over sodium and distillation. Solutions of potassium t-butoxide in t-butyl alcohol were prepared by dissolution of clean potassium in dry t-butyl alcohol and standardised against hydrochloric acid using phenolphthalein as indicator. Sodium ethoxide was prepared and standardised similarly. t-Butyl [^2H]alcohol was prepared by Cram and Rickborn's procedure.[38]

Working up of mixtures of products from reactions in

protic solvents were carried out by dilution with acidified, saturated brine and extraction with dichloromethane.

Tritiated compounds were obtained by treatment of the isotopically normal materials with sodium hydroxide in aqueous dioxane containing tritiated water.

Kinetics.—Rates of detritiation were determined by removal of aliquot portions from reaction mixtures which were quenched with acetic acid and evaporated to dryness. In each case the residue was extracted with an appropriate volume of scintillator fluid prepared by dissolution of butyl-PDB (5 g) in toluene (1 l). The solutions were then counted with a Philips liquid scintillation counter. Rates of dedeuteriation were measured similarly, residues from evaporation being extracted with $CDCl_3$ and the ratios of methylene to aryl protons determined by ^1H n.m.r. spectroscopy. Reactions in which halides were liberated were followed by the determination of halide ion concentration potentiometrically in darkened vessels. Non-ionic detergent (Nonex 501; 7 drops) was added to the solutions before insertion of silver indicator electrode and the calomel reference electrode. Reactions for the leaving groups ^-OTs, ^-OPh, $PhSO_2^-$, and PhS^- were followed by spectrometric determination of the ions either continuously or in aliquot parts of the reaction mixtures.

cis-1,3-*Bisphenylsulphonylcyclohexane* (3a).—cis-1,3-Bistosyloxycyclohexane [39] (19.87 g, 0.047 mol) in a mixture of ethanol (100 ml) and water (200 ml) was added to sodium thiophenoxide (0.113 mol) in ethanol (80 ml). The mixture was heated under reflux (N_2) for 10 days when extraction gave crude bis-sulphide (2c) (2.4 g, 13%), b.p. 175° at 0.05 mmHg, which was treated in methanol (30 ml) with 30% aqueous hydrogen peroxide (8 ml) and ammonium molybdate (200 mg) at 20° for 21 h. Filtration yielded the cis-*bis-sulphone* (89%), light m.p. 215° (from chloroform–petroleum) (Found: C, 59.8; H, 5.5. $C_8H_{20}O_4S_2$ requires C, 59.3; H, 5.5%).

When a mixture of *cis*- and *trans*-1,3-bistosyloxycyclohexane obtained directly from the commercial *cis–trans*-mixture was similarly treated, fractional crystallisation from chloroform–light petroleum of the mixture of isomeric sulphones yielded the trans-*bis-sulphone*, m.p. 227° (Found: C, 59.3; H, 5.4%).

When *cis*-sulphone (3a) was heated under reflux with ethanolic 0.1M-sodium ethoxide (50 ml) for 3 h, work-up gave a mixture of (3a) and the *trans*-isomer (94%), fractional crystallisation of which from methanol yielded the *trans*-sulphone (8%), m.p. and mixed m.p. 224°.

A mixture of *cis*- and *trans*-sulphone (3a) (2 g, 5 mmol) in ethanolic M-sodium ethoxide (30 ml) was kept at 180° for 18 h. Ethanol was distilled off and the distillate contained cyclohexa-1,3-diene (60% by u.v.) and cyclohexa-1,4-diene in a 3 : 1 ratio (g.l.c. on SE 30 at 50° identified by peak enhancement with authentic specimens). Extraction of the residue with diethyl ether (3 × 50 ml) gave a product (106 mg) which showed no SO_2 bands in the i.r. spectrum and consisted of diene polymerisation products identical with those obtained by submitting either of the cyclohexadienes to the same conditions. The aqueous extracts were acidified (2M-H_2SO_4) to pH < 1 and extraction with diethyl ether gave benzenesulphinic acid (91%), m.p. 77—81° (lit.,[40a] 84°), characterised as the 4-nitrobenzyl sulphone, m.p. and mixed m.p. 210—211°.[40b]

The bis-sulphide (3c) (above) was recovered (94%) from the same conditions.

3-*Phenylsulphonylcyclohexene* (4).—3-Bromocyclohexene (0.1353 mol) and thiophenol (0.15 mol) were treated with ethanolic 1.5M-sodium ethoxide, (0.15 mol) under nitrogen for 2.5 h. Extraction gave 3-phenylthiocyclohexene (86%), b.p. 142° at 10 mmHg (lit.,[41] 93° at 0.65 mmHg) (^1H n.m.r. identical with that reported [42]). Oxidation of the sulphide with hydrogen peroxide and ammonium molybdate in methanol, as before, gave the *sulphone* (94%), m.p. 43° (from light petroleum) (Found: C, 64.7; H, 6.1. $C_{12}H_{14}O_2S$ requires C, 64.9; H, 6.3%).

The sulphone (3 g) (13.5 mmol) in ethanolic M-sodium ethoxide (30 ml) was kept at 180° for 19 h. Treatment of the reaction mixture as for the bis-sulphone (above) gave cyclohexa-1,3-diene (66% by u.v.) and cyclohexa-1,4-diene in a 3.2 : 1 ratio (g.l.c.). Extraction of the residue gave diene polymerisation products as before and benzenesulphinic acid (89%), m.p. and mixed m.p. 77.5°, was obtained as before. When the reaction was repeated, but at 120°, the yield of cyclohexa-1,3-diene was 20% (by u.v.) and the 1,3 : 1,4 ratio was 20 : 1. When the reaction was repeated at 100° and the time reduced to 3 h, the yield of cyclohexa-1,3-diene was 3% (by u.v.) and no 1,4-diene was detected by g.l.c.

3-Bromocyclohexene in ethanolic M-sodium ethoxide at 180° for 18 h gave an 18% yield of cyclohexa-1,3-diene, together with cyclohexa-1,4-diene in a 3.2 : 1 ratio (g.l.c.).

Cyclohexa-1,3-diene on reaction with ethanolic M-sodium ethoxide at 180° for 18 h gave cyclohexa-1,3-diene (65%; u.v.) and cyclohexa-1,4-diene in a 3 : 1 ratio (g.l.c.). Similarly, cyclohexa-1,4-diene gave the 1,3-diene (64%) mixed with cyclohexa-1,4-diene in a 3 : 1 ratio. The same results were obtained after 48 h in the same conditions.

Cyclohexyl phenyl sulphone [43] was recovered in an 88% yield, m.p. and mixed m.p. 71—72°, after treatment with ethanolic M-sodium ethoxide at 180° for 19 h.

1-*Bromo*-2,2-*dimethyl*-3-*phenylsulphonylpropane* (5e).—1,3-Dibromo-2,2-dimethylpropane [44] (0.19 mol) in dioxane (50 ml) was added to a solution of thiophenol (0.18 mol) in ethanolic M-sodium ethoxide (0.19 mol). The mixture was heated under reflux under nitrogen for 15 h and extraction gave a residue (49 g), distillation of which gave the bromo-sulphide (46%), b.p. 149° at 10 mmHg, n_D^{19} 1.5730 (lit.,[45] b.p. 133° at 2 mmHg, n_D^{26} 1.5714). Oxidation of the bromo-sulphide with a 50% molar excess of hydrogen peroxide in acetic acid at 100° gave the crude sulphone (95%) which after chromatography on silica gel in ether–light petroleum, and distillation, b.p. 135° at 0.05 mmHg, had n_D^{26} 1.5714 (Found: C, 45.5; H, 5.5. Calc. for $C_{11}H_{15}BrO_2S$: C, 45.4; H, 5.2%). The ^1H n.m.r. spectrum of this product agrees with that reported previously.[45]

The bromo-sulphone (0.999 g, 3.43 mmol) in t-butyl alcohol (70 ml) was treated with a solution of potassium t-butoxide in t-butyl alcohol (70 ml), prepared from potassium (0.13 g). After reaction at 30° for 3 h extraction in the usual way gave 2,2-dimethyl-1-phenylsulphonylcyclopropane (0.699 g, 97%), m.p. and mixed m.p. 48—51° (lit.,[45] 47—48°) (Found: C, 63.0; H, 6.5. Calc. for $C_{11}H_{14}O_2$: C, 62.8; H, 6.6%).

The sulphone (42.4 mg, 1.45×10^{-4} mol) in t-butyl [^2H]-alcohol (5 ml) and potassium t-butoxide (7.5×10^{-5} mol) in t-butyl [^2H]alcohol (6 ml) were kept at 20° for 5 min. Extraction gave recovered sulphone mixed with product (37 mg) whose ^1H n.m.r. spectrum showed lack of protons adjacent to the sulphonyl group in both starting material and product.

1-*Chloro*-2,2-*dimethyl*-3-*phenylsulphonylpropane* (5k).—1,3-Dichloro-2,2-dimethylpropane [46] (41 g, 0.3 mol) in dioxane (30 ml) was treated dropwise with a solution of thiophenol (0.336 mol) and potassium hydroxide (0.291 mol) in methanol (60 ml). The mixture was heated under reflux for 20 h and extraction gave a residue (36.4 g), distillation of which afforded crude chloro-sulphide (14.2 g, 23%), b.p. 150° at 10 mmHg. The crude sulphide (12 g) was treated with 30% aqueous

hydrogen peroxide (60 ml) and ammonium molybdate (0.4 g) in methanol (70 ml) at 20° for 48 h. Extraction gave the *sulphone* (12.8 g, 93%), b.p. 150° at 0.5 mmHg (Found: C, 53.3; H, 6.3. $C_{11}H_{15}ClO_2S$ requires C, 53.6; H, 6.1%).

The sulphone (3.1 mmol) was kept with M-potassium t-butoxide in t-butyl alcohol (5 ml) at 30° for 2 h. Extraction gave the sulphonylcyclopropane (91%), m.p. and mixed m.p. 49—50°.

2,2-*Dimethyl*-3-*phenylsulphonyl*-1-*tosyloxypropane* (5n).—Tosyloxy-sulphide (5m) [18d] (3.5 g) was kept with 30% aqueous hydrogen peroxide (20 ml) in methanol (30 ml) containing ammonium molybdate (0.2 g) at 20° for 18 h. Extraction gave the sulphone (4.1 g, 100%), m.p. 59—60° (from methanol) (lit.,[18d] 56—57°).

Treatment of the sulphone-tosylate (0.74 g) in t-butyl alcohol (5 ml) with M-potassium t-butoxide in t-butyl alcohol (30 ml) at 30° for 4 h gave the cyclopropane (98%), m.p. and mixed m.p. 48—50°.

A half-reaction with potassium t-butoxide in t-butyl [^{2}H]-alcohol as for the bromide (above) also showed exchange in both starting material and product.

1,3-*Bisphenylsulphonyl*-2,2-*dimethylpropane* (5f).—Sodium (11.5 g) was allowed to dissolve in methylated spirits (200 ml) and thiophenol (0.5 mol) was added to the solution, which was added dropwise under nitrogen to 1,3-dibromo-2,2-dimethylpropane (0.24 mol) in ethanol (20 ml) at 60°. After being heated under reflux for 52 h, extraction of the mixture gave the crude bis-sulphide (74%), b.p. 150° at 0.05 mmHg, which was added to a 10 molar excess of 30% aqueous hydrogen peroxide and ammonium molybdate (0.3 g) in methanol (200 ml). After 18 h at 20° filtration gave the *bis-sulphone* (60%), m.p. 126° (from methanol) (Found: C, 58.2; H, 5.6. $C_{18}H_{20}O_4S_2$ requires C, 58.0; H, 5.7%).

The bis-sulphone (2 g) was suspended in a solution of sodium (0.147 g) in deuteriomethanol (7 ml) and the mixture was boiled under reflux for 23 h. Removal of the solvent by distillation and extraction of the residue gave deuteriated sulphone (1.8 g, 90%) whose ^{1}H n.m.r. spectrum showed the disappearance of the methylene peak at δ 3.67. Treatment of the bis-sulphone as before with molar potassium t-butoxide in t-butyl alcohol under reflux for 18 h gave the cyclopropane (99%), m.p. and mixed m.p. 51—53°. Extraction of the acidified aqueous layer with dichloromethane gave benzenesulphinic acid (65%) characterised as the 4-nitrobenzyl sulphone (73%), m.p. and mixed m.p. 212—214°.

2,2-*Dimethyl*-1-*phenylsulphonyl*-3-*phenylthiopropane* (5o).—Bromo-sulphone (5e) (2.53 g) in ethanol (30 ml) was added to thiophenol (0.013 mol) containing the solution prepared from sodium hydroxide (0.013 mol), ethanol (40 ml), and water (60 ml). The mixture was boiled under reflux for 4 days, when extraction gave a residue (2.64 g) which t.l.c. showed to consist of two components. Distillation gave a fraction (1.01 g), b.p. 110° at 0.05 mmHg, which on being washed with light petroleum (b.p. 40—60°) left 2,2-dimethyl-1-phenylsulphonylcyclopropane (0.31 g), m.p. 35—43°. The residue from the distillation on extraction with light petroleum gave an extract which, on chromatography on Kiesel Gel with light petroleum–diethyl ether (90 : 10) as eluant, gave the desired sulphide whose i.r., ^{13}C n.m.r., and ^{1}H n.m.r. spectra were all consistent with the assigned structure (Found: C, 66.0; H, 6.2. $C_{17}H_{20}O_2S_2$ requires C, 63.75; H, 6.25%). Repeated purification produced no change in the spectral data but we have been unable to obtain consistent microanalytical figures for this compound. Oxidation with hydrogen peroxide and ammonium molybdate in methanol gave the bis-sulphone (5f) (97%), m.p. and mixed m.p. 125°. Identical material was obtained on similar treatment of the chloro-sulphone (5k).

Treatment of the sulphone sulphide with potassium t-butoxide in t-butyl alcohol as before gave cyclopropylsulphone (99%), m.p. and mixed m.p. 49—51°.

2,2-*Dimethyl*-1-*phenoxy*-3-*phenylsulphonylpropane* (5h).—The bromo-sulphide (5c) (4.0 g) in methylated spirits (30 ml) was added to phenol (5 mol) and ethanolic M-sodium ethoxide (5.5 mol). The mixture was refluxed for 45 days when extraction gave crude phenoxy-sulphide (85%), b.p. 130° at 0.3 mmHg. The crude sulphide was oxidised in methanol with hydrogen peroxide and ammonium molybdate as before to give *phenoxy-sulphone* (3.8 g, 99%), m.p. 76—77° (from methanol) (Found: C, 67.4; H, 6.5. $C_{17}H_{20}O_3S$ requires C, 67.1; H, 6.5%). Treatment of the sulphone with M-potassium t-butoxide in t-butyl alcohol at 140° for 24 h gave cyclopropylsulphone (99%), m.p. and mixed m.p. 48—50°. Acidification of the aqueous layers to pH < 1 and extraction with dichloromethane gave phenol (42%), b.p. 80° at 10 mmHg, m.p. and mixed m.p. 38°.

1-*Phenoxy*-3-*phenylsulphonylpropane* (2a).—The sulphone (0.82 mmol) in M-potassium t-butoxide in t-butyl alcohol (5 ml) was kept at 170° for 0.5 h when t.l.c. showed absence of starting material. Extraction as before gave a small recovery of material which g.l.c. (SE30 at 200°) showed to contain no phenylsulphonylcyclopropane, but an approximately 15% yield of methyl phenyl sulphone.

(With Mr. G. Griffiths). The sulphone was treated with ethanolic 1.5M-sodium ethoxide at 158° for 10 h. The acidic component of the reaction products was phenol (64%) together with (*E*)-propenylphenol (≈9%) (by n.m.r.). The neutrals consisted of phenyl (*Z*)-propenyl ether (43%) and methyl phenyl sulphone (52%) (estimated by g.l.c. on SE30 at 80°).

Stability Test.—Treatment of 2,2-dimethyl-1-phenylsulphonylcyclopropane with a 5.4M excess of ethanolic 0.8M-sodium thiophenoxide at 140° for 5 days gave, after extraction, recovered sulphone (99%) (i.r. identical with authentic specimen).

Neopentyl Phenyl Sulphone (5p).—Treatment of neopentyl tosylate [47] with sodium thiophenoxide in ethanol gave neopentyl phenyl sulphide [47] which on oxidation with hydrogen peroxide in methanol under catalysis with ammonium molybdate gave the sulphone (6g), b.p., 181° at 19 mmHg, m.p. 38—39° (from methanol) (lit.,[47] 38—39°). It was deuteriated as for bis-sulphone (5f).

1-*Tosyloxy*-3-*phenylsulphonylpropane*.—3-Chloropropanol (4.3 g, 0.045 mol) in ethanol (10 ml) reacted with a solution of thiophenol (0.051 mol) in ethanolic sodium ethoxide (0.05 mol). The mixture was heated under reflux for 21 h. Extraction gave 1-hydroxy-3-phenylthiopropane (79%), n_D^{18} 1.5782 (lit.,[48] n_D^{21} 1.5763). Toluene-4-sulphonyl chloride (0.036 mol) was added to the sulphide (0.033 mol) in dry pyridine (40 ml) at −10°, and kept at 20° for 24 h. Extraction gave a residue which on oxidation with hydrogen peroxide in methanol under catalysis with ammonium molybdate gave the sulphone (12%), m.p. 94—95° (from methanol) (lit.,[49] 95—95.5°).

The sulphone (0.29 g, 0.8 mmol) in M-potassium t-butoxide in t-butyl alcohol at 30° for 3 h was centrifuged to give potassium tosylate (70%), structure confirmed by ^{1}H n.m.r. in D_2O. Extraction gave phenylsulphonylcyclopropane (99%), b.p. 130° at 0.8 mmHg, m.p. 31—33° (lit.,[48] b.p. 130—135° at 0.5 mmHg, m.p. 36.7°).

Methyl Phenyl Sulphone.—The sulphone [50] (1.96 g, 12.6 mmol) was added to sodium thiophenoxide (54.5 mmol) in ethanol (30 ml). The mixture was heated at 170° for 20 h. Extraction afforded recovered starting material (39%), methyl phenyl sulphide (37%), b.p. 70° at 12 mmHg (lit.,[40a] 74° at 10 mmHg), and benzenesulphinic acid characterised as the 4-nitrobenzyl sulphone (16%), (m.p. and mixed m.p. 209—211°).[40b]

Acknowledgements

We thank the S.E.R.C. for equipment, Dr. J. Islwyn Davies and the Department of Biochemistry for scintillation counting facilities, and Mr. G. Griffiths for the experiments on 1-phenoxy-3-phenylsulphonylpropane.

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Received 15*th August* 1983; *Paper* 3/1437