Pseudomolecular Rearrangement of *O*-Ethyl *N*-Methyl Toluene-4-sulphonimidate to *N*-Ethyl-*N*-methyltoluene-4-sulphonamide and its Relevance to the Nucleophilic Properties of Neutral Sulphonamides

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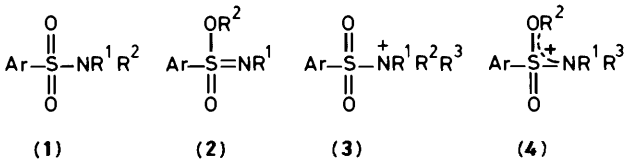
Kinetic studies are reported for the pseudo-molecular rearrangement of *O*-ethyl *N*-methyl toluene-4-sulphonimidate to *N*-ethyl-*N*-methyltoluene-4-sulphonamide in organic solvents at 34—100 °C. Without catalysts, the rearrangement follows the equation rate = k_{rearr} [substrate]^2, which is indicative of an intermolecular S_N2 transalkylation *via* an ion-pair intermediate: it is accompanied by concurrent *E*2 elimination to *N*-methyltoluene-4-sulphonamide. The rearrangement is catalysed by electrophilic reagents such as alkyl halides, ZnI_2, and HBr where rate = k_2 [substrate][catalyst]. For alkyl halides, a two-step mechanism *via* an ionic intermediate applies in which formation of the intermediate by an S_N2 reaction between the substrate and alkyl halide is rate limiting. Other catalysts effect rearrangement by forming alkyl halides in an initial rapid reaction with the substrate. The results are discussed in relation to the ambident nucleophilic properties of sulphonamides. It is suggested that, like carboxylic acid amides and phosphinylamides, alkylation occurs most readily at the O-atom of neutral sulphonamides to give a sulphonimidate (kinetic product), which then rearranges in the presence of electrophilic catalysts to give an *N*-substituted sulphonamide (thermodynamic product). Rearrangement is normally too fast for the isolation of *O*-alkyl sulphonimidates, but *O*-aryl analogues can be obtained.

The pseudomolecular imidate–amide[1] and phosphorimidate–phosphoramide[2] rearrangements have given insight to the ambident nucleophilic properties of amides and phosphoramidates. Sulphonamides (**1**) are another class of compounds that, in principle, are potential [1,3]-ambident nucleophiles. Thus, the alkylation of neutral sulphonamides might be expected to give the *O*-substituted sulphonimidate (**2**) as the kinetic product and the thermodynamically more stable sulphonamide (**1**) by subsequent rearrangement of (**2**). There are few reports in which sulphonamides act as nucleophiles. It is known, however, that at 150 °C tertiary sulphonamides react with alkyl halides to give S–N cleavage products arising from *N*-alkylation.[3] At lower temperatures, tertiary sulphonamides react with more reactive alkylating agents, *e.g.*, $MeSO_3F$ [4] and $(MeO)_2\overset{+}{C}HSbCl_6^-$,[5] to give salts assigned the structure (**3**) on the basis of ^1H n.m.r. spectra, independent synthesis, and hydrolysis. In contrast, arylation of tertiary sulphonamides by aryldiazonium hexafluorophosphates[6,7] is considered to give the cations (**4**), products of *O*-substitution. Neither alkylation nor arylation of neutral primary or secondary sulphonamides has been studied. However, silylation of these compounds is effected using trimethylsilyl chloride in the presence of a tertiary amide;[8,9] both *N*-silylation and a mixture of *O*- and *N*-silylation are reported to occur. Since it is known that sulphonimidates (**2**) rearrange at *ca.* 100 °C to the corresponding sulphonamide (**1**) and that reaction of sulphonimidates (**2**) with methyl iodide generates *N*-methylsulphonamides (**1**; R^2 = Me),[10] it is possible that the product orientation outlined above is a manifestation of kinetic *versus* thermodynamic control. We have therefore investigated the kinetics of the reaction between (**2**; Ar = MeC_6H_4, R^1 = Me, R^2 = Et or Ph) and several electrophilic agents to define the reaction mechanism and to establish whether the conversion of (**2**) into (**1**) occurs under conditions where *N*-alkylated products are usually obtained from (**1**).



(**1**) (**2**) (**3**) (**4**)

a; Ar = 4-MeC_6H_4, R^1 = Me, R^2 = Et
b; Ar = 4-MeC_6H_4, R^1 = Me, R^2 = Ph
c; Ar = 4-MeC_6H_4, R^1 = Me, R^2 = H
d; Ar = 4-MeC_6H_4, R^1 = R^2 = Me
e; Ar = Ph, R^1 = Me, R^2 = Ph
f; Ar = Ph, R^1 = H, R^2 = Me
g; Ar = Ph, R^1 = R^2 = Me

Experimental

Substrates and Products.—Both sulphonimidates (**2a** and **b**) were prepared by literature procedures.[10] (**2a**) gave b.p. 45—50 °C at 3 × 10^{-5} Torr, $\nu_{max.}$ 1 292 and 1 178 (O=S=N) cm^{-1} (Found: C, 56.1; H, 7.2; N, 6.0. Calc. for $C_{10}H_{15}NO_2S$: C, 56.3; H, 7.1; N, 6.6%), and (**2b**) gave m.p. 63—65 °C, $\nu_{max.}$ 1 300 and 1 185 (O=S=N) cm^{-1} (Found: C, 64.5; H, 5.8; N, 5.3. Calc. for $C_{14}H_{15}NO_2S$: C, 64.3; H, 5.8; N, 5.4%). ^1H N.m.r. absorptions of both compounds are given in Table 1. *N*-Methyl-*N*-phenyl-, *N*-methyl-, and *N*,*N*-dimethyl-toluene-4-sulphonamide (**1b—d**) and *N*-methyl-*N*-phenyl- and *N*-methylbenzenesulphonamide (**1e** and **f**) were synthesized using the Schotten–Baumann procedure.[11] *N*-Ethyl-*N*-methyltoluene-4-sulphonamide (**1a**) was prepared by refluxing (**1c**), ethyl iodide, and silver oxide together in ether for 24 h. (**1a**) gave m.p. 25—26 °C, $\nu_{max.}$ 1 340 and 1 160 (SO_2) cm^{-1}, (**1b**) gave m.p. 93—95 °C, $\nu_{max.}$ 1 342 and 1 170 (SO_2) cm^{-1}, (**1c**) gave m.p. 77—79 °C, $\nu_{max.}$ 3 270 (N–H), 1 323, and 1 160 (SO_2) cm^{-1}, (**1d**) gave m.p. 80—81 °C, $\nu_{max.}$ 1 335 and 1 164 (SO_2) cm^{-1}, (**1e**) gave m.p. 78—79 °C, $\nu_{max.}$ 1 348 and 1 174 (SO_2) cm^{-1}, and (**1f**) gave $\nu_{max.}$ 3 295 (N–H), 1 315 and 1 161 (SO_2) cm^{-1}. ^1H N.m.r. chemical shifts of the sulphonamides (**1a—f**) are included in Table 1. *N*-Chloro-*N*-methyltoluene-4-sulphonamide was prepared from (**1c**) and sodium hypochlorite in a two-phase system employing

Table 1. ^{1}H N.m.r. chemical shifts (δ) relative to $SiMe_4$ for sulphonimidate reactants and sulphonamide products in [$^2H_3$]acetonitrile solutions[a]

Compound	Ar	$ArCH_3$	OCH_2(Ph)	NCH_2(Ph)	OCH_2CH_3	NCH_2CH_3	NCH_3	NH
(**2a**)	7.20—7.97[b]	2.39 (s)	3.90 (q)[c]		1.13 (t)[c]		2.81 (s)	
(**2b**)	7.27—8.10[b]	2.43 (s)	7.17 (m)				3.10 (s)	
(**1a**)	7.27—7.87[b]	2.41 (s)		3.06 (q)[d]		1.07 (t)[d]	2.67 (s)	
(**1b**)	8.13—7.70[b]	2.43 (s)		7.33 (s)			3.19 (s)	
(**1c**)	7.20—7.90[b]	2.40 (s)					2.49 (d)[e]	5.33 (br)
(**1d**)	7.31—7.89[b]	2.44 (s)					2.64 (s)	
(**1e**)	6.97—7.50			7.53 (s)			3.17 (s)	
(**1f**)	7.27—8.13						2.41 (d)[f]	5.27 (br)

[a] 0.2M solutions. [b] AA'BB'. [c] J_{CHCH} = 7.5 Hz. [d] J_{CHCH} = 7.0 Hz. [e] J_{NHCH} = 6.0 Hz. [f] J_{NHCH} = 4.5 Hz.

Table 2. Second-order rate coefficients (k_2) for the reaction of *O*-ethyl and *O*-phenyl *N*-methyl toluene-4-sulphonimidates (**2a** and **b**) with alkyl halides corrected for the thermal reaction: initial [(**2**)] = 0.15M; [alkyl halide] = 0.1—0.5M

Sulphonimidate	Alkyl halides	*t*/°C	10^6k_2/l mol^{-1} s^{-1}
(**2a**)	MeI	100	853
	EtI	100	52.1
	EtI	86	21.3
	EtI	73.5	10.8
	EtI[a]	100	29
	EtI[b]	100	4.7
	EtBr	100	10
	EtCl	100	3.8[c]
	$EtNO_3$	100	1.1
	EtI–$AgNO_3$	100	4.5
	Pr^iI	100	11.5
	$MeSO_3F$[d]	34	*ca.* 2000
	None	100	3.8
(**2b**)	MeI	100	66[e]
	$MeSO_3F$[f]	34	5930
	None	100	0

[a] In [$^2H_6$]acetone. [b] In CCl_4. [c] $k_2 = k_{rearr}$; $k_{dealk} = 5.14 \times 10^{-7}$ l mol^{-1}. [d] In CCl_4; 0.25 mol equiv., formation of $MeC_6H_4SO_2NMe_2$ and $EtSO_3F$ over 10 min, followed by formation of $MeC_6H_4SO_2NMeEt$. [e] See text. [f] In [$^2H_3$]nitromethane.

methylene dichloride and acetic acid; m.p. 76—78 °C, $\nu_{max.}$ 1 355 and 1 175 cm^{-1}, δ($CDCl_3$) 2.50 (3 H, s), 3.11 (3 H, s), and 7.37—8.07 (4 H, AA'BB'). 1-Methyl-1-(-*p*-tolylsulphonyl)-3-phenyltriazene[12] was prepared from the anion of (**1c**) and benzenediazonium fluoroborate in either ether or THF; $\nu_{max.}$ 1 372 and 1 172 (SO_2) cm^{-1}, δ($CDCl_3$) 2.37 (3 H, s), 3.33 (3 H, s), and 7.20—8.10 (9 H, m).

Reagents and Solvents.—All chlorinated solvents were washed with $NaHCO_3$ solution, then water, dried ($CaCl_2$), distilled and stored over 4A molecular sieves. [$^2H_3$]Acetonitrile, [$^2H_3$]nitromethane, and [$^2H_6$]acetone were stored over 4A molecular sieves and used as supplied. Alkyl halides were redistilled and stored over mercury. Methyl fluorosulphonate was used as supplied by Aldrich. Fluorosulphonic acid was redistilled from calcium fluoride. Zinc iodide was purified as described previously.[2]

Kinetics.—The reactions of (**2a** and **b**) with various electrophiles in [$^2H_3$]acetonitrile, [$^2H_6$]acetone, [$^2H_3$]nitromethane, or CCl_4 and of (**1c**—**f**) with methyl fluorosulphonate were monitored by ^{1}H n.m.r. spectroscopy. Usually the measurements were carried out on a solution of the sulphonimidate (*ca.* 0.15M) and the electrophile (*ca.* 0.01—0.1M) in 0.5 ml of solvent in a sealed n.m.r. tube. Reactions were followed using either the decrease in the *O*-CH_2 and *N*-Me signals of (**2a**) or the *N*-Me signals of (**2b**). Each spectrum was integrated three times and an average taken. Signals were normalised internally using the total aromatic signal of the starting material and products. For the reactions employing ethyl halides, pseudo-first-order rate coefficients, rate = k_o[(**2a**)], were obtained from equation (1),

$$k_o = 2.303 \log(2x/a)/t \quad (1)$$

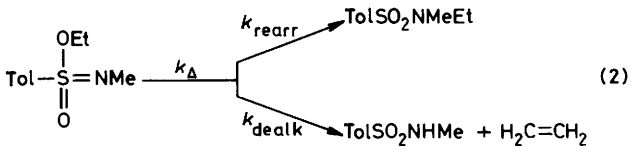
where x = area of the *O*-CH_2 signal for the substrate and a = total area of the aromatic signal. Plots were linear up to *ca.* 85% reaction and rate coefficients were reproducible to ±15%. For reactions involving MeI and $MeSO_3F$, second-order rate coefficients were obtained from the usual integrated rate equation where $[MeX]_o \neq [(\mathbf{2a})]_o$.

Product Analysis.—Products were usually identifiable *in situ* by comparison of their ^{1}H n.m.r. spectra with authentic materials.

In most cases, however, the products were also isolated and identified by m.p., t.l.c., i.r., ^{1}H n.m.r., and mass spectroscopy. The formation of ethylene was evident from the singlet in the ^{1}H n.m.r. spectrum at δ 5.48 p.p.m.

Results and Discussion

On heating alone at 100 °C in either [$^2H_3$]acetonitrile or [$^2H_6$]acetone, *O*-ethyl *N*-methyl toluene-4-sulphonimidate (**2a**) was slowly converted ($t_{\frac{1}{2}}$ *ca.* 20 days) into a mixture of *N*-ethyl-*N*-methyltoluene-4-sulphonamide (**1a**) and *N*-methyltoluene-4-sulphonamide [equation (2)]. The ethylene co-product of



(2)

dealkylation was observable in the ^{1}H n.m.r. spectrum of the reaction solution, and by comparison with the aromatic signals the extent of dealkylation in [$^2H_3$]acetonitrile was estimated to be 12% (±3). The integrated rate equation showed the overall thermal reaction (k_Δ) had a second-order dependence on [(**2a**)] [equation (3)], which was confirmed by a 5-fold increase in the overall initial rate on increasing the initial [(**2a**)] by 2.26. Values of k_Δ were solvent dependent, being twice as large in acetonitrile as in acetone. Individual rate coefficients for the thermal rearrangement and dealkylation (k_{rearr} and k_{dealk}), calculated in the usual way from equation (3) and the product

$$\text{Rate} = k_\Delta[(\mathbf{2a})]^2 = (k_{rearr} + k_{dealk})[(\mathbf{2a})]^2 \quad (3)$$

ratios, are given in Table 2. In contrast to (**2a**), the sulphonimidate (**2b**) was stable at temperatures up to 150 °C.

Above this temperature, decomposition to unidentified products other than (**1b**) occurred. Thus the Chapman rearrangement,[13] *i.e.*, intramolecular *O*- to *N*-phenyl migration, appears to be restricted to the imidate–amide system.

The rearrangement of (**2a**) to (**1a**) occurred more readily in the presence of ethyl halides, the rates showing a solvent dependence decreasing in the order $[^2H_3]$acetonitrile > $[^2H_6]$acetone > CCl_4 by factors of 1.8 and 6.2, respectively (see Table 2). This suggests that the rearrangement involves an ionic intermediate. From practical considerations, acetonitrile was the most suitable solvent and most of the following results refer to this. The rates of conversion of (**2a**) into (**1a**) in the presence of ethyl halides (except EtCl, where catalysis was negligible) followed equation (4), and with appropriate ethyl

$$\text{Rate} = k_o[(\mathbf{2a})] \quad (4)$$

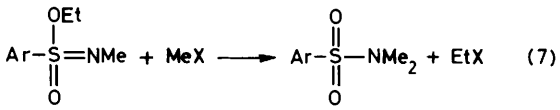
halide concentrations a much faster rearrangement than by heating alone was obtained. The k_o coefficients varied linearly with [EtHal] so these reactions are bimolecular and governed by equation (5). Values of k_2 for various ethyl halides are listed

$$\text{Rate} = k_2[(\mathbf{2a})][\text{alkyl halide}] \quad (5)$$

in Table 2. For methyl iodide, the rate of reaction was much faster than with ethyl iodide, but it also followed second-order kinetics and k_2 was obtained from equation (6). The product of this reaction was *N*,*N*-dimethyltoluene-4-sulphonamide (**1d**).

$$k_2 = \frac{\ln\{[\text{MeI}]_o[(\mathbf{2a})]_t/[\text{MeI}]_t[(\mathbf{2a})]_o\}}{t\{[\text{MeI}]_o - [(\mathbf{2a})]_o\}} \quad (6)$$

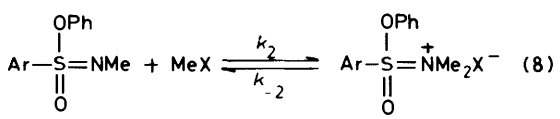
When less than one equivalent of methylating agent (*e.g.*, MeI, $MeSO_3F$) was used, a corresponding amount of (**1d**) and ethylating agent was produced first [equation (7)]. The latter then brought about rearrangement of (**2a**) to (**1a**) in the usual way. For isopropyl iodide plots of $\log(2x/a)$ *versus* t were curved becoming steeper as the reaction proceeded. This arose from a reaction similar to equation (7), giving rise to *N*-isopropyl-



(7)

N-methyltoluene-4-sulphonamide, and the more reactive ethyl iodide. The value of k_2 for isopropyl iodide is that obtained from the initial reaction.

In contrast, (**2b**) did not form sulphonamides on reaction with alkylating agents. However, reaction of (**2b**) with methyl iodide in $[^2H_3]$acetonitrile at 100 °C gave rise to two new CH_3 signals at δ 2.60 and 3.27 p.p.m. (in a ratio of 1:2) both downfield from the sulphonimidate at δ 2.43 and 3.10 p.p.m. (ratio 1:1). These new signals are consistent with formation of the sulphonimidonium ion (**4b**; R^3 = Me).[6,7] The reaction [equation (8)] appeared to stop at 20% completion, which may be evidence that an equilibrium is established.



(8)

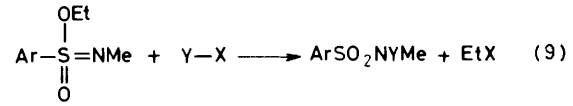
The second-order rate constant, k_2, for the forward reaction was calculated by the initial-rate method and is given in Table 2. With methyl fluorosulphonate in $[^2H_3]$nitromethane (**2b**) gave the cation (**4b**; R^3 = Me)[7] in 100% yield. Significantly, heating (**4b**; R^3 = Me, $X = FSO_3^-$) in the presence of $Et_4N^+I^-$ in $[^2H_3]$nitromethane at 100 °C gave (**2b**) and MeI, *i.e.*, the reverse reaction of equation (8), in 75% yield after 48 h. Johnson and Wambsgans[14] have attempted, without success, to form aryl iodides by heating the salts (**4**) with sodium iodide. Obviously, *N*-dealkylation of (**4**) is favoured over *O*-dearylation.

The effect of other electrophiles on the rearrangement of (**2a**) to (**1a**) was also examined and these results are listed in Table 3. It is apparent that ZnI_2 behaves much like EtI and that HBr (0.33 equivalents) is similar to EtBr. These observations can be explained by initial formation of the ethyl halide and a sulphonamide derivative [equation (9)] followed by the usual

Table 3. Second-order rate coefficients (k_2) for the conversion of (**2a**) into (**1a**) with electrophilic catalysts in $[^2H_3]$acetonitrile

Catalyst	t/°C	10^6k_2/l mol^{-1} s^{-1}
ZnI_2 (0.1 equiv.)	100	55.3
HBr (0.33 equiv.)	100	12.2
HBr (1 equiv.)	25	*a*
HSO_3F (1 equiv.)	25	*a*

[a] No rearrangement but quantitative formation of sulphonamide (**1c**) and EtX (X = Br or SO_3F) immediately.



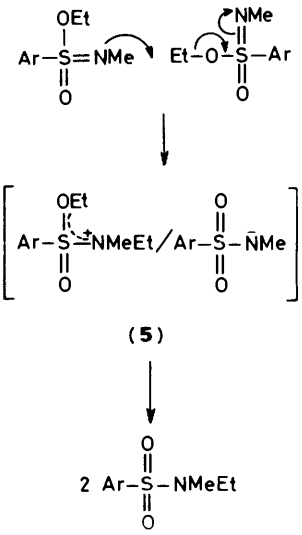
(9)

ethyl halide-catalysed rearrangement. In support of this conclusion, ^1H n.m.r. absorption signals characteristic of the ethyl halides were observed after addition of the electrophile of an intensity proportional to the amount added. Thus, one equivalent of HBr brought about quantitative dealkylation yielding *N*-methyltoluene-4-sulphonamide and ethyl bromide whilst 0.33 equivalents of HBr brought about dealkylation followed by rearrangement as noted above.

The results in Table 2 show that $EtNO_3$ is some 50 times less effective than EtI at promoting the rearrangement of (**2a**) to (**1a**). Addition of silver nitrate ought therefore to inhibit the alkyl halide-catalysed rearrangement as noted in earlier investigations.[1,2] Indeed, addition of an equimolar amount of $AgNO_3$ to a solution of (**2a**) and EtI brought about immediate precipitation of AgI and the formation of $EtNO_3$ was apparent in the ^1H n.m.r. spectrum. At 100 °C the rate of rearrangement was reduced but not by the factor of 50 anticipated. The effect was not examined further but has been observed previously.[2]

The effect of temperature on the reaction of (**2a**) with EtI was also examined. The data in Table 2 lead to values of $E_a^{\neq}$ 64.5 ± 3 kJ mol^{-1} and $\Delta S^{\neq}$ −164 ± 5 J K^{-1} mol^{-1}.

Mechanism of the Rearrangement Reaction.—An earlier investigation of the thermal rearrangement of (**2a**) to (**1a**) concluded that the reaction was first order and therefore involved an intramolecular 1,3-alkyl shift.[10a] However, the reactions were carried out in the absence of solvent and were only followed to *ca.* 30% completion. Our results show that the reaction is bimolecular and solvent dependent. The most likely pathway is alkylation of one sulphonimidate *N*-atom by a second sulphonimidate molecule to give the ion pair (**5**) followed by transalkylation of the sulphonamide anion (Scheme 1). Given the strong alkylating ability of the sulphonimidonium cation (*vide infra*) and the nucleophilicity of the sulphonamide anion, the formation of (**5**) is presumably rate determining. The concurrent dealkylation under thermal conditions represents



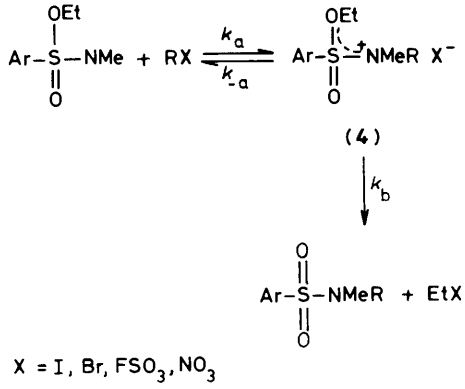
Scheme 1. Bimolecular mechanism for the thermal rearrangement of *O*-ethyl *N*-methyl toluene-4-sulphonimidate to *N*-ethyl-*N*-methyltoluene-4-sulphonamide

the usual competitive *E*2 pathway to S_N2 reactions. It probably involves proton abstraction by the sulphonamide anion from either the sulphonimidonium ion or neutral sulphonimidate.

Comparison of the thermal rearrangement rates for the sulphonimidate (**2a**) and the analogous imidate (no detectable rearrangement even at 138 °C [1]) shows that (**2a**) is much more labile. This may relate to the greater nucleophilicity of the *N*-atom and/or the greater alkylating ability of the sulphonimidates. The relative reactivities of the two towards EtI at 138 °C (k_2 = 1 540 × 10^{-6} and 350 × 10^{-6} l mol^{-1} s^{-1} for the imidate and sulphonimidate, respectively) determines that the greater lability of sulphonimidates arises from their better alkylating ability. This parallels the corresponding alkylating ability of sulphonates and esters.

The alkyl halide-promoted conversion of (**2a**) into (**1a**) is markedly dependent on solvent polarity (Table 2), which implies charge development in the transition state and ionic intermediates. Bimolecular kinetics, the decrease in rate along the series EtI ≫ EtBr ≫ EtCl, and the rate reduction on increased steric hindrance in the reagent (MeI > EtI > PrI) are good evidence for an S_N2 pathway (Scheme 2). This involves the rate-limiting attack by the sulphonimidate on the alkyl halide (step k_a) to give an ionic intermediate (**4**) followed by rapid removal of the *O*-ethyl group (step k_b) by X^- to give the sulphonamide. As noted above, the equilibrium k_a/k_{-a} can be observed for the corresponding *O*-phenyl sulphonimidate (**2b**) and in this case the corresponding cation (**4b**) can be isolated.

Ambident Nucleophilic Properties of Sulphonamides.—The potential energy diagram for the reaction of the sulphonimidate (**2a**) with both RX and HX is illustrated in the Figure. This is also the energy profile for the alkylation at the O-atom of neutral sulphonamides, which suggests that the explanation proposed for the apparent ambident nucleophilic properties of amides [1] and phosphylamides [2] can be extended to sulphonamides. Briefly, this requires that electrophilic substitution of neutral sulphonamides takes place most readily at the O-atom, with *N*-substitution arising from subsequent rearrangement. Thus, *O*-alkyl sulphonimidates are kinetic products whilst *N*-alkylsulphonamides are thermodynamic products. The only observation of *O*-substitution is for the arylation of tertiary sulphonamides by aryldiazonium hexafluorophosphates [6,7] but



Scheme 2. S_N2 Mechanisms for the conversion of sulphonimidates into sulphonamides by the alkylating agents RX

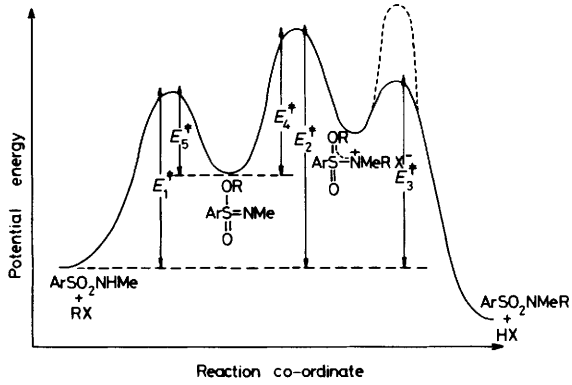
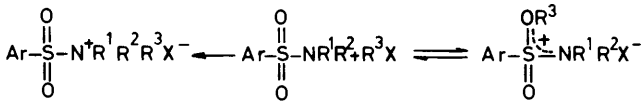


Figure. Potential-energy diagram for the alkylation of sulphonamides

we have shown above that *O*-arylsulphonimidonium cations are more stable than the corresponding *O*-alkyl analogues. The inability to observe products of *O*-alkylation with alkyl halides is not surprising given the high temperatures involved. Our results show that under these reaction conditions the sulphonimidate intermediate would quickly rearrange to the *N*-substituted product. More difficult to explain is the observation of *N*-substitution of tertiary sulphonamides at low temperatures by $MeSO_3F$ [4] and $(MeO)_2CH^+SbCl_6^-$ [5]. However, *O*-alkylation by both reagents [equation (10)] will give the salt (**4**)



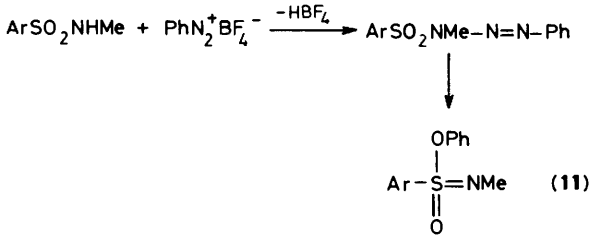
(**3**) (**4**)

$X = SbCl_6^-, FSO_3^-$ (10)

which, for $X = FSO_3^-$ at least, we have shown to dealkylate extremely rapidly. One inference here is that the cation (**4**) is a stronger alkylating agent than $MeSO_3F$ itself. This allows competitive formation of the thermodynamic product (**3**) by direct attack at the N-atom.

The potential-energy diagram (Figure) reinforces our conclusions. The inequality $E_3^{\neq} < E_2^{\neq}$ is a consequence of k_a (Scheme 2) being rate limiting for alkyl halides. That $E_5^{\neq} < E_4^{\neq}$ results from the rapid, quantitative dealkylation of (**2a**) on addition of equimolar HBr or HSO_3F without con-

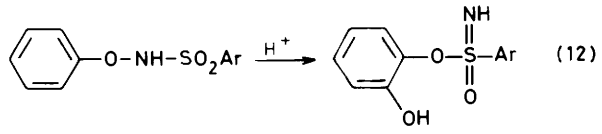
current rearrangement to (**1a**). Dealkylation is therefore faster than rearrangement, *i.e.*, $E_5^{\neq} < E_4^{\neq}$. Further, $E_4^{\neq} < E_1^{\neq}$ because rearrangement by EtBr and $EtSO_3F$ occurs much faster than alkylation of the sulphonamide under the same conditions. This leads to $E_1^{\neq} < E_2^{\neq}$, which is the condition for kinetic *versus* thermodynamic product control. Formation of the sulphonamide product arises from decomposition of the ionic intermediate (**4**) (step k_b). The salient factor in the successful *O*-arylation of tertiary sulphonamides must be the increase in $E_3^{\neq}$ indicated by the dotted line in the Figure. It follows that secondary sulphonamides should form *O*-aryl sulphonimidates directly on reaction with arenediazonium ions. This expectation was realised by treating the sulphonamides (**1c** and **f**) with benzenediazonium fluoroborate at 80 °C to give, after washing with NaOH solution and chromatography, the sulphonimidates (**2b** and **e**), respectively, in *ca.* 25% yield. No *N*-substituted products were formed. Nonetheless, it is possible that (**2b**) and (**2e**) arise from decomposition of a triazene formed by coupling of the sulphonamides and diazonium ion [equation (11)]. Both triazenes were synthesized independently [12] but they



(11)

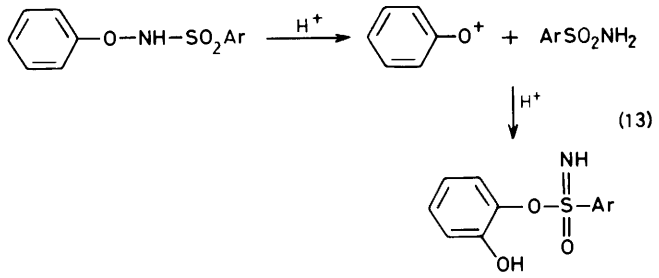
decomposed to give the parent sulphonamides (**1c** and **f**) rather than *O*-phenyl sulphonimidates or *N*-phenylsulphonamides. We therefore conclude that arylation of sulphonamides takes place directly at the O-atom.

Recently, the formation of *O*-(2-hydroxyphenyl) toluene-4-sulphonimidate from *O*-phenyl-*N*-(*p*-tolyl-sulphonyl)hydroxylamine in strong acid solution was interpreted as a [3,3]-rearrangement of the protonated hydroxylamine [equation (12)].[15] However, in the light of our findings the sulphonimidate



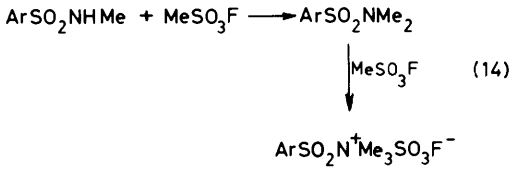
(12)

could arise from the *O*-arylation of toluene-4-sulphonamide by phenoxonium ion, a known intermediate in this reaction [equation (13)].



(13)

In contrast, the sulphonamides (**1c**, **d**, and **f**) did not react with methyl iodide at 100 °C after 7 days. In the presence of Ag_2O, (**1c**) was cleanly converted into (**1d**) with MeI and (**1a**) with EtI. It is conceivable that direct *N*-alkylation results from reaction *via* the sulphonamide anion. With $MeSO_3F$, (**1c**) was converted into a mixture of (**1d**) and (**3d**; R^3 = Me) and (**1f**) into (**1g**) and (**3g**; R^3 = Me) [equation (14)]. The *NN*-



(14)

dimethylsulphonamides are formed first, and these react with $MeSO_3F$ further to yield the salts (**3**). Since sulphonimidates react extremely rapidly with either HSO_3F or $MeSO_3F$ they are unlikely to be isolable under the conditions of the experiment. We therefore conclude that *O*-alkyl sulphonimidates are unlikely to be synthesized by direct *O*-substitution.

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References

1 B. C. Challis and A. D. Frenkel, *J. Chem. Soc., Perkin Trans. 2*, 1978, 192.
2 B. C. Challis, J. A. Challis, and J. N. Iley, *J. Chem. Soc., Perkin Trans. 2*, 1978, 813.
3 S. Searles and S. Nukina, *Chem. Rev.*, 1959, **59**, 1077.
4 J. F. King and J. R. DuManoir, *J. Am. Chem. Soc.*, 1975, **97**, 2566.
5 T. Oishi, K. Kamata, and Y. Ban, *Chem. Commun.*, 1970, 777.
6 G. R. Chalkey, D. J. Snodin, G. Stevens, and M. C. Whiting, *J. Chem. Soc. C*, 1970, 682.
7 G. R. Chalkey, D. J. Snodin, G. Stevens, and M. C. Whiting, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1580.
8 W. Maringgele and A. Meller, *Z. Naturforsch., Teil B*, 1979, **34**, 969.
9 L. Golebiowski and Z. Lasocki, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1976, **24**, 439.
10 E. S. Levchenko, L. N. Markovskii, and A. V. Kirsanov, *Zh. Org. Khim.*, 1967, **3**, (*a*) 1481; (*b*) 1273.
11 A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 4th edn., 1978.
12 R. Kreher and R. Halpaap, *Tetrahedron Lett.*, 1977, 3147.
13 C. G. McCarty and L. A. Garner, in 'The Chemistry of Amidines and Imidates,' ed. S. Patai, Wiley, London, 1975, ch. 2.
14 C. R. Johnson and A. Wambsgans, *J. Org. Chem.*, 1979, **44**, 2278.
15 Y. Endo, K. Shudo, and T. Okamoto, *J. Am. Chem. Soc.*, 1982, **104**, 6393.

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