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REACTION BETWEEN ALKYL PHENYL SULPHIDES AND BROMINE IN AQUEOUS ACETIC ACID.

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The reactivity[1] of ethers, ArOR, in electrophilic aromatic substitution reactions invariably increases, R = $Pr^i > Et > Me$. This sequence contrasts with that now reported for alkyl phenyl sulphides, PhSR. From the second order rate constants (TABLE), the reactivity of PhSR towards bromine in 95% (w/w) aqueous acetic acid is R = $Me > Et > Pr^i$. While the rate ratios for PhSMe and PhSEt are fairly constant ($k_{PhSMe} : k_{PhSEt} = 1.1$) and independent of the bromine ion concentration, the ratios involving $PhSPr^i$, e.g. $k_{PhSMe} : k_{PhSPr^i}$, are not constant but vary with $[Br^-]$. None of the plots of $(k_2)^{-1}$ against $[Br^-]$ were linear, although that for $PhSPr^i$ became so at higher $[Br^-]$. The effect of $[Br^-]$ on the rates is clearly more than a simple retardation arising from tribromide ion formation.[2] The <u>relative</u> reactivities of PhOR in an analogous study were all independent of $[Br^-]$; the rates however showed more than a single dependence[3] on $[Br^-]$; ($k_{PhOMe} : k_{PhOEt} : k_{PhOPr^i} = 1 : 2.3 : 4.4$).

The products of the $PhSR/Br_2$ reactions, in 95% aqueous acetic acid, were the alkyl bromophenyl sulphides, as found in 100% acetic acid,[4] and in trifluoroacetic acid.[5] No <u>meta</u> isomers were detected and the <u>para</u> isomers predominated; for R = Me, Et, Pr^i, % <u>para</u> isomers were 99.3, 98.9 and 98.6 respectively. The absence of the oxidation products, Ph-S(O)-R, the major products of bromination in aqueous methanol[6] as well as in 70% aqueous acetic acid in the presence of base[7 a,b] was also shown. All product analyses were by VPC (2<u>m</u> x 3<u>mm</u> column packed with D.G.S. 10% on chromosorb W).

TABLE

Second order rate constants, k_2, for the bromination of PhSR in 95% w/w aq. acetic acid at 15 ± 0.10° C, in the presence of sodium perchlorate and bromide.[8]

k_2 = average of at least two values with reproducibility ± 3%

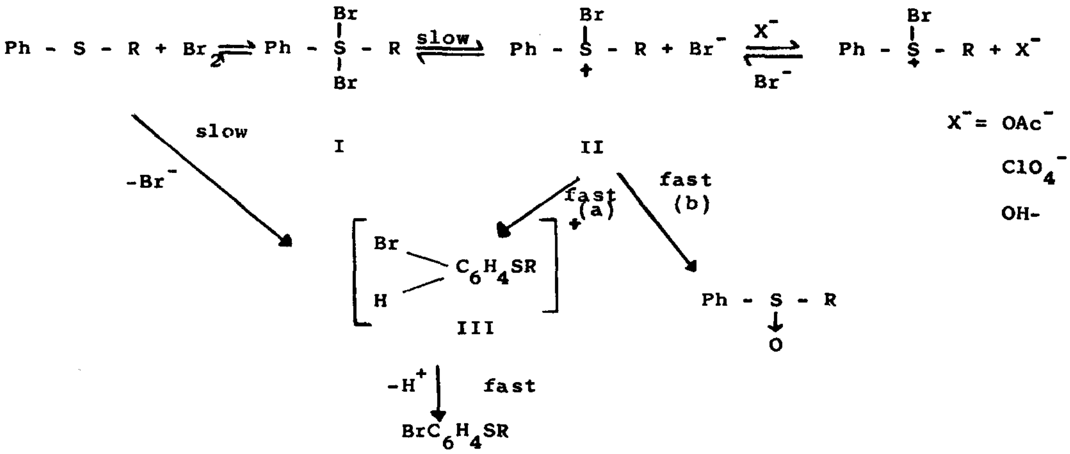
$[PhSR] = 2 \times 10^{-3}$ to 7×10^{-2} M : $[Br_2] \simeq 10^{-4}$ M

[NaBr]	$[NaClO_4]$	PhSMe	PhSEt	$PhSPr^i$	PhS-⬡
M		$k_2 \times 10^2$ l/mole			
0.10	-	20.0	18.3	0.890	1.41
0.15	-	13.4	12.6	0.653	1.10
0.20	-	10.2	9.25	0.594	1.00
0.15	0.05	19.2	16.8	0.803	1.40
0.10	0.10	31.8	30.3	1.22	2.06
0.05	0.15	97.7	93.2	3.03	4.08

The similarity in the rate ratios of PhSMe and $PhSPr^i$ with Br_2 in aq. methanol and in 95% aq. acetic acid solutions is striking despite the differences in the products. These ratios ($k_{PhSMe} : k_{PhSPr^i}$) are 18:1 (aq. MeOH) and between 22:1 and 32:1 (aq. AcOH). One possibility is that common intermediates are formed slowly in both solvent systems and whose further reactions are fast and solvent dependent. Complexes, I, (SCHEME) are well established[9] and were considered with the sulphonium ions, II, to be important in aq. MeOH.[6] These or possibly I and ion-pairs containing II are now also thought important in aq. AcOH solution. The rearrangement of II to the σ complex, III, could either be intramolecular within an ion pair or brought about by nucleophilic attack of Br^- on a carbon of II with release of another Br^- from sulphur. Migration of halogen into the ring from addition complexes, such as I, has been established.[9] A direct route for substitution is also considered.

The sequence, R = Me, Et, Pr^i, represents (a) increasing steric hinderance in I and (b) increasing electron releasing ability of R and so stabilisation of II. These factors would give rise to opposing reactivity orders. Our results for PhSR suggest that steric effects are the more important of the two in the

SCHEME

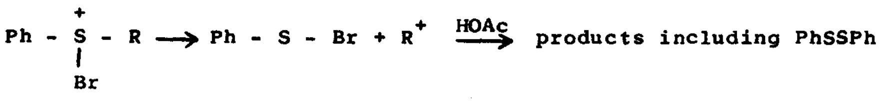


(a) in 95% aq. HOAc ; 100% HOAc and 100% CF_3CO_2H.

(b) in aq. MeOH and 70% aq. HOAc + pyridine

mechanism through I and II. The direct route leading to para substitution (that is to the major substitution products) would be influenced, mainly if not solely, by the inductive effects of the R groups. In the bromination of PhOR, which leads to predominately para substitution and in which the direct route should be the only significant one, such an influence is apparent.[3]

In the Table, some results for cyclopentyl phenyl sulphide are included for comparison. $PhSBu^t$ was also studied. The other PhSR compounds all gave good pseudo-first rate plots for at least three half-lives, but those obtained for $PhSBu^t$ were linear for less than one half-life with the apparent pseudo-first order rate thereafter increasing with time. The product isolated from the reaction between $PhSBu^t$ and bromine was diphenyl disulphide and only minor amounts of bromophenyl t-butyl sulphides were detected by VPC. No reaction of $PhSBu^t$ occured in aq. acetic acid in the absence of Br_2. Bromination of the sterically hindered sulphide, $PhS.CPh_3$, in 70% aq. acetic acid has also been shown to give the disulphide.[7b] Cleavage of benzyl phenyl sulphide by chlorine in acetic acid also leads to diphenyl disulphide.[10] In all these sulphide cleavage reactions, the alkyl or aralkyl group in the sulphide gives particularly stable carbonium ions, suggesting the following mechanism:



$$\mathrm{Ph-\overset{+}{\underset{Br}{S}}-R \longrightarrow Ph-S-Br + R^{+} \xrightarrow{HOAc}}\ \text{products including PhSSPh}$$

II

The five PhSR compounds were prepared by standard means,[11] and were repeatedly distilled (using either a spinning-band column or a 1 m. column of glass helices) until VPC indicated one compound.

REFERENCES AND NOTES

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