

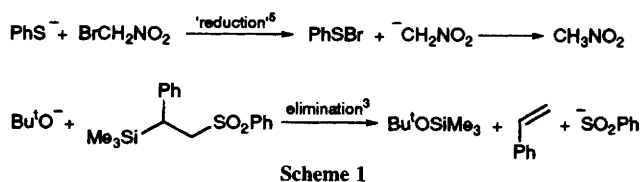
Reactivity in Z-Philic Displacements in α -Halogenosulfones

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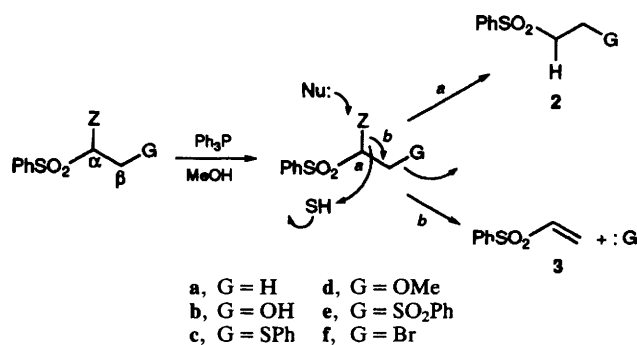
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Rates of Z-philic reactions in β -substituted α -bromosulfones have been measured; for displacement-protonation $\rho^* = 2.9$, and isotope fractionation factors close to 2.4 demonstrate extensive C-protonation in the transition structure.

Attack by nucleophiles at hetero-atoms, Z, such as halogen in preference to their displacement in, for example, nucleophilic substitution, is a familiar but poorly quantified process.¹ Such Z-philic processes are common (Scheme 1) when, for example, Z is halogen² but also when Z is silicon,³ or sulfur.⁴ Attack on the heteroatom may lead to 'reduction', *i.e.* replacement of Z by H, or may be coupled with another process such as elimination (Scheme 1). We now present quantitative results on Z-philic reactions involving a carbon-halogen bond.⁶ Reactions of triphenylphosphine with α -halogenosulfones 1,



bearing β -groups (G), have been studied with attention being focused on the effect of the β -groups on the reaction pathway (Scheme 2).



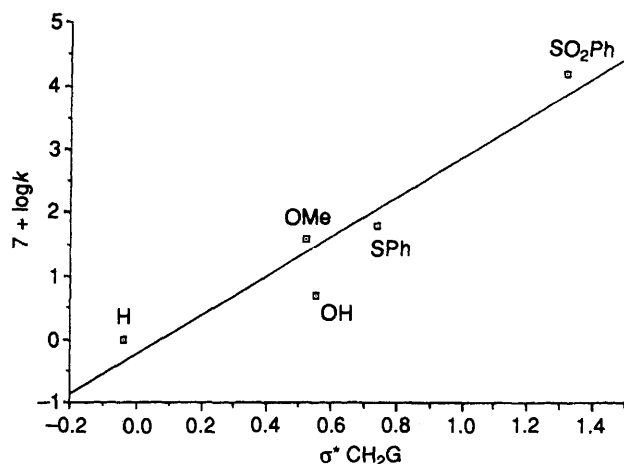


Fig. 1 Plot of $\log k_{\text{reduction}}$ vs. $\sigma^*\text{CH}_2\text{G}$ for reactions of α -bromosulfones with triphenylphosphine in methanol at 25 °C

The questions we have now addressed for this system are (i) how is the rate of Z-philic displacement affected by β -groups? (ii) What is the competition between displacement-protonation (pathway *a*) giving **2** on the one hand, and displacement-elimination (pathway *b*)⁶ giving **3**, on the other? (iii) How is reactivity affected by the nature of the electrophilic atom, Z? (iv) What is the timing of the proton transfer yielding products **2**, and how is this affected by the β -substituent, G?

Rate constants for reactions of triphenylphosphine with α -bromosulfones **1** in methanol are in Table 1. Reactions at a number of temperatures were followed by HPLC and comparison of rate constants at 25 °C was made using values obtained by extrapolation of Arrhenius plots. The accompanying product in each case is triphenylphosphine oxide derived in high yield from solvolysis of the initially formed bromotriphenylphosphonium bromide. We have also measured the isotopic fractionation factor⁷ for 'reduction' (reaction *a*) at the middle and each extreme of the reactivity range.

Table 1 shows first the sharp division between the elimination and 'reduction' modes concurrent with Z-philic attack. Only with G = Br is elimination observed and reaction is much more rapid than for the 'reduction' pathways followed with other groups, G. For these groups which span a range for $\sigma^*\text{CH}_2\text{G}$ ⁸ of 1.4, a linear relationship is found between $\log k_{\text{reduction}}$ and $\sigma^*\text{CH}_2\text{G}$ with $\rho^* = 2.95$. When G = OH, a considerably deviant point is obtained (Fig. 1). Attack of the Z-ophile at bromine is clearly considerably influenced by change of electron density at bromine. The ρ^* value is comparable with that found for deprotonations to give sulfonyl-stabilised carbanions bearing β -substituents.⁹ For these bromides, the electrophilic atom is large and polarisable. When the electrophilic atom is smaller and much less polarisable, as in dichloride **1g** (Z = G = Cl) (Table 1), reaction is very sluggish even with a strongly inductive β -group.

Activation parameters for such processes (Table 1) have been derived for the first time. Entropies are very negative suggesting substantial solvent restriction at the transition structure. This is consistent with a substantial extent of P-Br bond formation. Values for **1e** are clearly out of line and we have no explanation at present.

Pathway (*a*) leading to 'reduction' products permits evaluation of the isotope fractionation factor (IFF). For **1e** the value for 1:1 MeOH:MeOD is 2.38, clearly inconsistent with formation of a stabilised carbanion and it approaches values found¹⁰ for eliminative fission of strained rings in which carbon-carbon cleavage is concerted with protonation at carbon. The

Table 1 Reactions of α -bromosulfones with triphenylphosphine

1	Z	G	% 2 ^a	<i>k</i> ^b	$\Delta H^{\ddagger c}$	$\Delta S^{\ddagger d}$	IFF ^e
a	Br	H	78	1.0×10^{-7}	58	-183	2.35
b	Br	OH	91	5.3×10^{-7}	58	-170	—
c	Br	OMe	82	3.9×10^{-6}	48	-186	2.28
d	Br	SPh	85	6.8×10^{-6}	44	-196	—
e	Br	SO ₂ Ph	80	1.5×10^{-3}	93	+13	2.38
f	Br	Br	92 ^f	$\sim 1 \times 10^{6g}$	—	—	—
g	Cl	Cl	<i>h</i>	—	—	—	—

^a % Conversion to **2** (isolated). ^b Units; $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ for formation of **2**. ^c kJ mol^{-1} . ^d $\text{J mol}^{-1} \text{K}^{-1}$. ^e Isotope fractionation factor. ^f % Yield of **3**. ^g Estimated for formation of **3**. ^h 88% of recovery of starting material after 5 days at 65 °C in MeOH with 2 mol Ph₃P (0.2 mol dm^{-3}).

IFF values for **1a** and **1d** are remarkably similar and little affected by considerable variation of the β -substituent. The evidence points to comparable extents of C-H bond formation in the transition structures.

The rate constant for elimination (pathway *b*) in dibromide **1f** is considerably greater than for any of the 'reduction' reactions. This implies that there is considerable concertedness between formation of the P-Br bond and cleavage of the β -C-Br bond.

We thank the SERC for a studentship (to A. V.) and the Universities of Sheffield and Wales, Bangor for support.

Received, 15th July 1993; Com. 3/04152B

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