

Ambident Electrophilic Character of Thioxophosphoranesulphenyl Bromides $=P(S)SBr$. A Novel Observation of Electrophilic Addition to a Carbon–Carbon Double Bond

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The thioxophosphoranesulphenyl bromides (**1**) act as ambident electrophiles towards alkenes and react, depending on the structure of the alkene, to give either the normal addition products $-SC(R^1)(R^2)CR^3(R^4)(Br)$ or 1,2-dibromides and -disulphides.

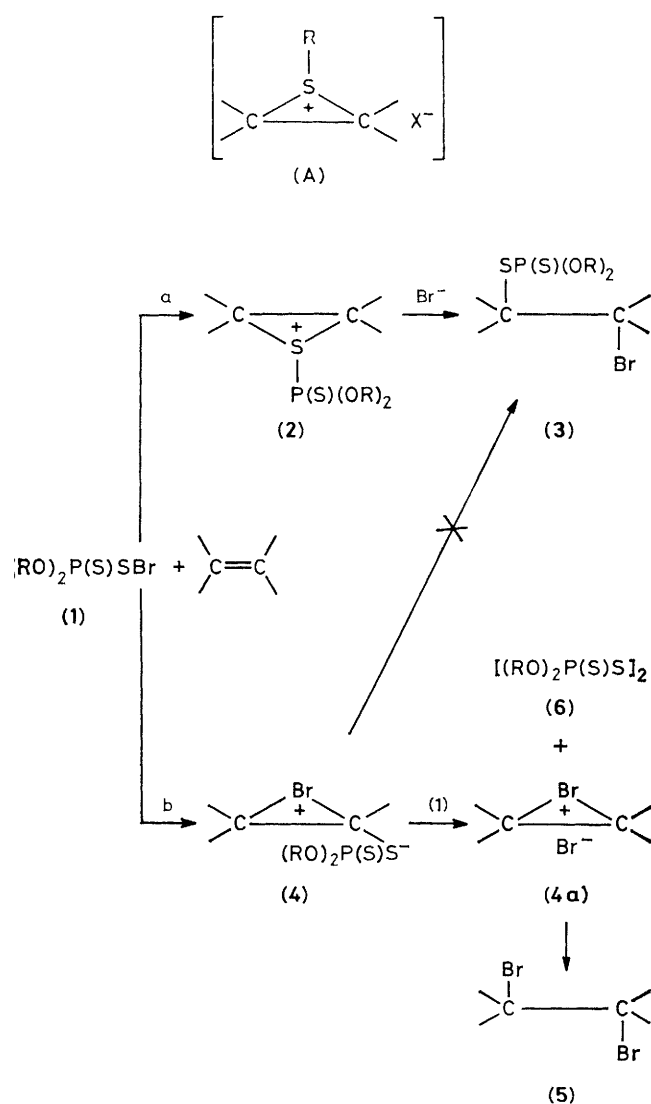
The Ad_E reactions of sulphenyl halides RSX including oxophosphoranesulphenyl chlorides¹ with alkenes have been extensively studied and it is generally accepted that this reaction proceeds *via* the formation of an episulphonium

intermediate (A).² Recently a new class of sulphenyl halides dialkoxithioxophosphoranesulphenyl bromides (**1**) has been synthesized in this laboratory.³ Sulphenyl bromides (**1**) exhibit a pronounced reactivity towards C, N, O, S, and P

Table 1. Results of the reaction of di(neopentyloxy)thioxophosphoranesulphenyl bromide with alkenes.

R	Alkene RR ¹ C=CHR ² R ¹ R ²	Adduct	Yield, % Disulphide	B.p. of adducts ^a °C (mmHg)	³¹ P n.m.r. δ/p.p.m.	¹ H n.m.r. ^b δ	Structure of adducts R ³ = (Bu ^t CH ₂ O) ₂ P(S)S
H	H OEt	100	0	87—90 (0.01)	94.46 {	s 1.35; t 1.65; m 3.6—4.5; t 6.4	R ³ CH ₂ CH(Br)OEt ^c (7)
H	H Me ₃ Si	97	3	107—109 (0.01)	91.31 {	s 1.35; t 1.65; m 3.6—4.5; m 5.7	BrCH ₂ CH(R ³)(OEt) (8)
H	—[CH ₂] ₄ —	95	5	105—108 (0.01)	98.88 {	s 0.61; s 1.35; t 3.96; m 4.1—4.6	R ³ CH ₂ CH(Br)(SiMe ₃)
Me	Me H	75	25	108—110 (0.02)	92.16 {	s 0.8; m 1.2—2.2; m 2.95; ^d m 3.6	R ³ CH[CH ₂] ₄ CH(Br)
H	H OCOMe	65	35	100—102 (0.01)	94.87 {	s 1.55; s 2.42; d 3.95; m 4.38—4.20	R ³ CH ₂ CMe ₂ (Br)
H	H H	3	97	81—83 (0.05)	92.46 {	s 1.87; s 3.0; q 4.35; m 4.61—4.75; t 7.65	R ³ CH ₂ CH(OCOMe)(Br)
H	H CN	0	100		93.1 {	s 1.68; dt 3.85; t 4.35; m 4.51—4.65	R ³ CH ₂ CH ₂ (Br)
H	H SiCl ₃	0	100				

^a All adducts gave satisfactory elemental analysis (C, H, S, P). ^b The adducts were analysed, using a Perkin R 12 B, ca. 50% solutions in CCl₄ with tetramethylsilane as an external standard. ^c Kinetically controlled adduct (7) rearranged gradually to (8). ^d This ¹H n.m.r. spectrum was run on a Tesla 80 with tetramethylsilane as an internal standard.

**Scheme 1**

nucleophiles resembling other classes of sulphenyl halides. It is known that in some reactions sulphenyl bromides may act as halogenating agents.⁴ We report the discovery of the ambident electrophilic reactivity of sulphenyl bromides (1) towards ethylenic systems.

The course of the reaction between (1) and the alkene depends to a large extent on the structure of the latter and only slightly on the reaction conditions. The reaction is stereospecifically *trans* with respect to the attack by both positive sulphur and positive bromine. For this reason it would seem likely that we have encountered $E_{\pi}B^{+}$ type processes leading to the intermediate episulphonium and epibromonium ions.

Reaction pathway a in Scheme 1 is typical for all classes of sulphenyl halides whereas route b has, to our knowledge, never been described before. In pathway b two moles of sulphenyl bromide are consumed. This is a straightforward consequence of the very high S-nucleophilicity of the anion $(RO)_2P(S)S^{-}$ towards the electropositive divalent sulphur and it is reasonable to suppose that the rate of disulphide (6) formation will be much higher than that of decomposition of the ion pair (4) into the normal addition product (3). The epibromonium ion pair (4a) undergoes attack by the bromide anion from the back in a manner generally accepted for the addition of the elemental bromine to the ethylenic double bond. Variation of alkyl groups in (1) does not change the qualitative picture of the addition reaction. For this reason, for more quantitative studies the neopentyl ester (1; R = Bu^tCH₂) was chosen. Bromides (1; R = Bu^tCH₂) react smoothly with alkenes in toluene solution at 0—15 °C. The reaction course was followed by Fourier transform ³¹P and ¹H n.m.r. spectroscopy and no products other than those expected from the reaction scheme were observed. In all cases analytically pure adducts could be isolated in high total yield by distillation. Experimental data are given in Table 1. Addition reactions obey *trans*-stereochemistry and both Markovnikov and anti-Markovnikov adducts were observed.

The reaction picture presented above can be rationalised by employing the F.M.O. approach. In accordance with the π -complex model proposed by Dewar⁵ forward and backward co-ordination should be of special importance in the episulphonium and epibromonium structure formation since both sulphur and bromine atoms have filled p A.O.s.

The relatively low difference in the electronegativity between S and Br atoms is presumably due to the electron attracting thiophosphoryl group attached directly to the sulphenyl sulphur atom. For this reason the preference for the formation of episulphonium or epibromonium structures depends on the difference of energy levels between alkenic F.M.O. and the corresponding electrophilic centres. According to the theory of perturbation⁶ the high value of this difference causes the reaction to favour the bromine atom as an apical group in the π -complex because of its higher electronegativity in comparison with the sulphur atom. Such a situation occurs in the case of ethylene and alkenes bearing electron-attracting groups. On the other hand small differences in the F.M.O. energy of the reagents favours the orbital controlled reaction with the sulphur atom being the apical group in the π -complex (2). This is the case for alkenes bearing electron-donating groups.

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