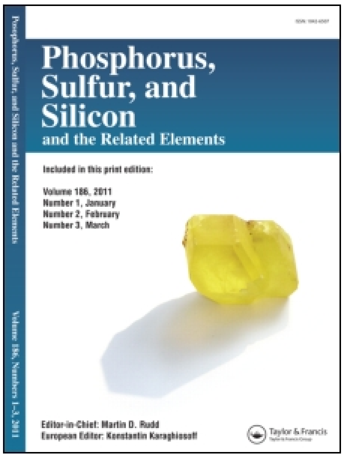

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Concerning the Formation, Hydrolysis and Thermolysis of Acyclic Phosphoranes

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CONCERNING THE FORMATION, HYDROLYSIS AND THERMOLYSIS OF ACYCLIC PHOSPHORANES

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Abstract Kinetic data on the formation, hydrolysis and thermolysis of acyclic phosphoranes is reported and the mechanism of each reaction is discussed.

INTRODUCTION

The reaction of trico-ordinate phosphorus compounds (1) with sulphenate esters (2) is now a well-established route to a wide range of phosphoranes (3 and 4)[1]. There is however, relatively little quantitative data to support the proposed mechanism of biphilic insertion of (1) into the S-O link of (2)[2]. This paper reports kinetic studies of each step of the reaction in an attempt to refine the mechanistic picture.

$$\underset{(1),\ R = CH_2CF_3,\ n = 0\text{-}3}{Ar_nP(OR)_{3-n}} + \underset{(2)}{Ar'SOR} \longrightarrow \underset{(3)}{Ar_n(RO)_{4-n}PSAr'} \qquad (1)$$

$$(3) + (2) \longrightarrow \underset{(4)}{Ar_nP(OR)_{5-n}} + Ar'_2S_2 \qquad (2)$$

The mechanism of hydrolysis of phosphoranes is a topic which has also attracted considerable attention[3,4] and the ready availability of a range of acyclic oxyphosphoranes by the sulphenate ester route prompted a mechanistic study in an effort to extend the results obtained by Westheimer and Janzen.

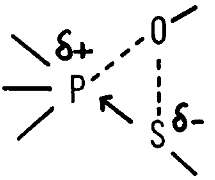
Finally, relatively little information has been published on the thermal stability of phosphoranes and hence a mechanistic study of the thermal decomposition of acyclic phosphoranes was initiated.

RESULTS AND DISCUSSION

Formation of Acyclic Phosphoranes

The reactions of (1) with (2) were carried out in toluene with the initial mixing at -78^oC. With a 1:1 molar ratio of reactants (Ar = Ar' = Ph, R = CH_2CF_3) and n = 0, the thiophosphorane was found to be stable at room temperature. Under the same conditions, with n = 1, the thiophosphorane (3) was stable at -78^o but disproportionated to (1, n = 1) and (4, n = 1) at 30^oC. With n = 2, the thiophosphorane was detectable at -78^o but disproportionated rapidly to (1) and (4) and with n = 3 only the oxyphosphorane (4) was observed by ^{31}P nmr. Thus a kinetic study of the formation of (3) was restricted to n = 0 and n = 1.

For n = 0, Ar, Ar' = Ph and R = CH_2CF_3 as followed by ^{31}P nmr, the reaction was first order in both (1) and (2) and the activation parameters (E_A = + 7.4 kcal mol^{-1} and $\Delta S^{\neq}$ = -38 cal K^{-1} mol^{-1}) were entirely consistent with a bimolecular transition state. Varying the substituents in Ar' (for n = 0) and in both Ar' and Ar (for n = 1) gave Hammett ρ-values of + 1.5, + 1.3 and -1.8 respectively. These results are consistent with only a moderate degree of charge developing on sulphur and phosphorus despite the implication from the activation parameters of highly ordered transition states. The paradox may be explained by a degree of back donation from sulphur to phosphorus equivalent to a biphilic transition state (5) with some ionic character.



(5)

The disproportionation of (3, n = 1) to (4) in toluene at 50^oC was shown to be first order in (3) implying rate-limiting ionization of the thiophosphorane (eqn. 3).

$$(CF_3CH_2O)_3PhPSAr' \xrightarrow{r.l.s.} (CF_3CH_2O)_3\overset{+}{P}Ph \cdots \overset{-}{S}Ar \qquad (3)$$

Likewise, with n = 0, the reaction of (3) with (2) to form (4) as defined by eqn. (2) was first-order in (3) but zero-order in (2). The Hammett ρ value varying Ar' in (3) in toluene at 30°C was + 2.1 (± 0.2) consistent with the development of negative charge on sulphur in the T.S. whereas variation of Ar' in (2) had virtually no effect on the rate as required by rate-limiting ionization. The relative rates of reaction for $PhP(OCH_2CF_3)_3SPh$: $P(OCH_2CF_3)_4SPh$ of ca 100:1 are a reflection of the anticipated stabilities of the respective phosphonium ions which also suggests rate-limiting ionization.

Hydrolysis of acyclic phosphoranes

The hydrolysis of the oxyphosphoranes (eqn. 4) was followed in toluene 19% acetonitrile at 31°C by ^{31}P nmr. In all cases using $H_2{}^{18}O$ the labelled oxygen appeared in the phosphoryl group as

$$Ar_nP(OR)_{5-n} + H_2{}^{18}O \longrightarrow Ar_n\overset{^{18}O}{\overset{\|}{P}}(OR)_{3-n} + 2\ ROH \qquad (4)$$

$n = 0\text{-}3$

determined by isotope shifts on the ^{31}P nmr signal of the oxide with no ^{18}O detected in the alcohol (by gc/m.s.). Hence the hydrolysis must involve either an associative, S_N2P, or dissociative, S_N1P, mechanism. The relative rates (Table 1) suggested a change in mechanism across the series and this was confirmed by steric retardation for n = 0 (S_N2P) and steric acceleration for n = 1-3 (S_N1P). Hammett ρ values of -1.0 (for n=3) and -1.3 (n=1) also denoted dissociative mechanisms for these phosphoranes and hence a duality of mechanism was established[5] entirely analogous

TABLE 1. Relative rates of hydrolysis of $Ph_nP(OCH_2CF_3)_{5-n}$ at 31°C

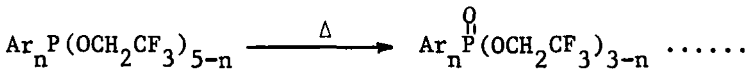
n	0	1	2	3
Relative rate	23	1	2	16

n.b. For n = 1, $k_{obs} = 1.2 \times 10^{-3}\ s^{-1}$ [first-order in $PhP(OCH_2CF_3)_4$]

to the duality of mechanism established some fifty years ago for the hydrolysis of alkyl halides[6].

Thermolysis of acyclic phosphoranes

The thermal decomposition of the oxyphosphoranes (4) was followed in decalin or mesitylene by ^{31}P nmr and gave the corresponding oxides as the major (and sometimes exclusive) phosphorus products (eqn. 5). The disappearance of (4) was first-order and the activation parameters supported the concept of rate-limiting ionization with relative rates corresponding to the stabilities of the respective phosphonium ions. Deuterium isotope effects using $Ar_nP(OCD_2CF_3)_{5-n}$ also indicated rate-limiting ionization.



$$Ar_nP(OCH_2CF_3)_{5-n} \xrightarrow{\Delta} Ar_n\overset{O}{\overset{\|}{P}}(OCH_2CF_3)_{3-n} \quad \cdots\cdots \quad (5)$$

(4) n = 0 - 3

Hammett plots gave ρ values (at 180°C) of -0.67 (for n = 1) and -0.3 (for n = 2) which denotes only a low degree of positive charge developing on phosphorus and suggests dissociation to ion-pairs rather than solvent-separated ions prior to the formation of oxide. This hypothesis is supported by the observation of a weak solvent effect with increasing polarity. The reaction pathway for collapse of the ion-pairs will be discussed.

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