The Influence of Ring Strain on the Reactivity of Tervalent Phosphorus Compounds

By R. GREENHALGH, J. E. NEWBERY, R. WOODCOCK, and R. F. HUDSON*
(*Chemical Laboratories, University of Kent at Canterbury, Canterbury, Kent*)

THE enhanced reactivity of cyclic phosphoramidites towards benzaldehyde and phenyl isocyanate[1] was attributed to the release of steric strain on formation of the transition state, by analogy with the hydrolysis of cyclic phosphates.[2] We now find that the heats of alkaline hydrolysis of the cyclic and acyclic compounds are similar (Table); Westheimer[2] has previously reported normal heats of hydrolysis of cyclic phosphites. Moreover, only part of the increase in free energy of activation ($\Delta\Delta F^* \simeq 8{\cdot}5$ kcal./mole) of the hydrolysis of methyl ethylene phosphate is reflected in the increased heat of hydrolysis of the ester ($\Delta\Delta H^h \simeq 5{\cdot}5$ kcal./mole). The difference in these quantities is similar to the difference between the free energies of activation of the reactions of (I) and (II) with phenyl isocyanate ($\Delta\Delta F^* \simeq 3{\cdot}54$ kcal./mole).

Rates of reaction of compounds (I—IV) *with phenyl isocyanate in nitrobenzene at* 33°, *and the corresponding heats of hydrolysis,* ΔH^h, *in alkaline solution.*

	k_2 $\text{M}^{-1}\text{min.}^{-1}$	k_2/k_1	ΔH^h k.cal./mole
(I)	$1{\cdot}12 \times 10^{-3}$	(1·0)	44·5 ± 0·5
(II)	0·38	339	44·0 ± 0·1
(III)	$1{\cdot}9 \times 10^{-3}$	1·73	44·9 ± 0·3
(IV)	0·15	137	[a]

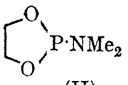
[a] ΔH^h could not be measured owing to rapid polymerisation (see later).

The rate of reaction of $PhP(NMe_2)OMe$ was too low to be measured accurately.

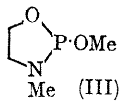
These observations suggest that some factor other than ring strain contributes to the increased reactivity of the cyclic esters. In view of the particular conformation of the ring as shown by the *X*-ray structure of methyl ethylene phosphate,[3] this is assumed to be the greater accessibility of the phosphorus atom to nucleophilic reagents.

$(MeO)_2P{\cdot}NMe_2$

(I)

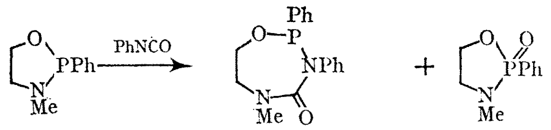


(II)



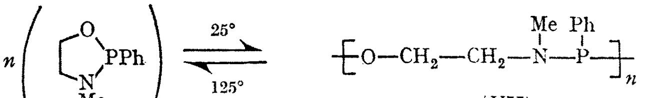
(III)

We now report observations which suggest strongly that release from steric strain on formation of the transition state produces a rate increase. The rate of reaction of (III) with phenyl isocyanate (followed by changes in the intensity of the n.m.r. absorption of the *N*-methyl protons[1]) to give the insertion product[4] is small, possibly because of strain in the bicyclic transition state, whereas the rate of reaction of (IV) is *ca.* 140 times greater. Two products are formed in the latter reaction, one giving a ^1H n.m.r. singlet at τ 7·37 and the other a doublet at τ 7·48 (J 8·2 Hz.) in a ratio of 41 : 59, with corresponding ^{31}P absorptions at −116 and −35·7 p.p.m., respectively, in a ratio of 2 : 3. These products are assumed to be (V) and (VI), reported by Mukaiyama[5] who also obtained a 57% yield of phenyl isonitrile. The ^1H n.m.r. spectrum was almost unchanged after one week, showing that (V) is not a precursor of (VI).

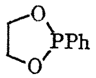


(IV) (V) (VI)

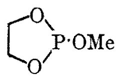
The behaviour of (IV) is interesting. Whereas (II) and (III) are completely stable at room temperature, (IV) slowly polymerises to a solid (VII). The reaction is reversible, as (IV) is regenerated by the action of heat on (VII). According to thermodynamic principles, heat is generated in the polymerisation; this implies appreciable ring strain in (IV), leading to the high rate constant (Table). The phospholan (VIII) polymerises in a similar manner whereas (IX) [like (II)] is completely stable.



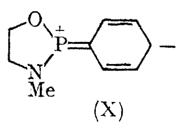
(VII)



(VIII)



(IX)



(X)

We suggest that the greater ring strain leading to polymerisation is due to conjugation between phosphorus and the aromatic group, which changes the hybridisation at phosphorus (X).

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