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ISOLATION OF PENTACOORDINATE SPECIES DURING REACTIONS OF FIVE-MEMBERED CYCLIC PHOSPHATES

—— AN EVIDENCE FOR PENTACOORDINATE INTERMEDIATES ——

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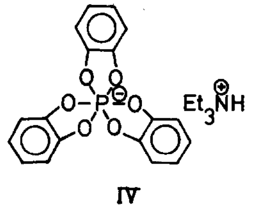
Since Westheimer first proposed the pseudorotation mechanism of pentacoordinate intermediates for the hydrolysis of five-membered cyclic phosphates$^{1)}$, there have been reported many evidences supporting the mechanism. Among those, following facts are considered to be most important: 1) Temperature dependent NMR of phosphoranes$^{2,\ 3)}$, 2) Rate enhancement in the reaction of strained cyclic phosphinates,$^{4)}$ 3) Rate limiting pseudorotation and related phenomenon.$^{5,\ 6)}$ However 1) concerns only with the pseudorotational process of pentacoordinate intermediates if formed, 2) and 3) suggest the pentacoordinate intermediates formation rather indirectly. None of them directly verifies the discrete formation of pentacoordinate intermediates during the displacement reaction of five-membered cyclic phosphates. Therefore, the important question ' Is pentacoordinate intermediate really formed? ' still remains to be solved$^{7)}$. We report here the first clear support for the formation of pentacoordinate intermediate during the displacement reaction of at least some five-membered cyclic phosphates.

During the course of our studies on the phosphorus containing heterocyclic compounds, we found that 2-phenoxy-benzodiazaphosphole-2-oxide$^{8)}$ (I) was easily prepared by the reaction of o-phenylenediamine with phenyl phosphorodichloridate$^{9)}$ and suggested that I was useful for the phosphorylation of alcohols$^{10)}$. In continuation of this study, we undertook the synthesis of 2-phenoxy-benzodioxaphosphole-2-oxide (II) and 2-phenoxy-benzoxazaphosphole-2-oxide (III) by the same procedure and obtained unexpected reaction products.

When catechol was heated with one equivalent of phenyl phosphorodichloridate under the presence of triethylamine in THF, the expected product II was not obtained and instead isolated was crystalline solid (yield 82%) which is insoluble in common organic solvents. The physical data of this solid (IV) are shown in Table I. To our surprise, these data fit quite well with

those of triethylammonium tris(o-phenylenedioxy)phosphate which has been synthesized by Allcock[11] by the reaction of hexachlorocyclotriphosphazene with catechol in the presence of triethylamine and whose structure has been established by X ray analysis quite recently[12].
Thus the structure of the product IV has been confirmed by the direct comparison of IR with that of the compound prepared according to the Allcock's procedure.



IV

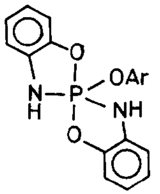
Next o-aminophenol was treated with phenyl phosphorodichloridate under the same condition as above and in this case the expected product III (bp 210°C/10^{-3}mmHg)[13] was obtained along with a small amount of by-products, V and VI. The physical data of V and VI are shown in Table I.

Table I. Physical Properties of IV, V, and VI.

	mp (°C)	Molecular Formula	Mass Spectra (m/e)	IR (ν_{max}^{KBr} cm^{-1})	UV (mμ (logε))
IV	>238	$C_{24}H_{28}NO_6P$	356(M^+), 264	3180, 1600	227(3.78)[a]
			247, 172,156	1490, 1245	280(3.75)
			139, 110	825, 750, 730	284(3.78)
					290(3.68)
V	225(dec.)	$C_{18}H_{16}N_3O_3P$	352(M^+-1)	3390, 3220, 1610	236(4.10)[b]
			244, 137	1580, 1320, 1300	286(3.92)
			107	1225	291(3.88)
VI	206-207	$C_{18}H_{15}N_2O_3P$	337(M^+-1)	3440, 3220, 1615	236(4.19)[b]
			244, 137	1590, 1330, 1230	286(4.11)
			93	690	291(4.06)

a) in acetonitrile b) in dioxane

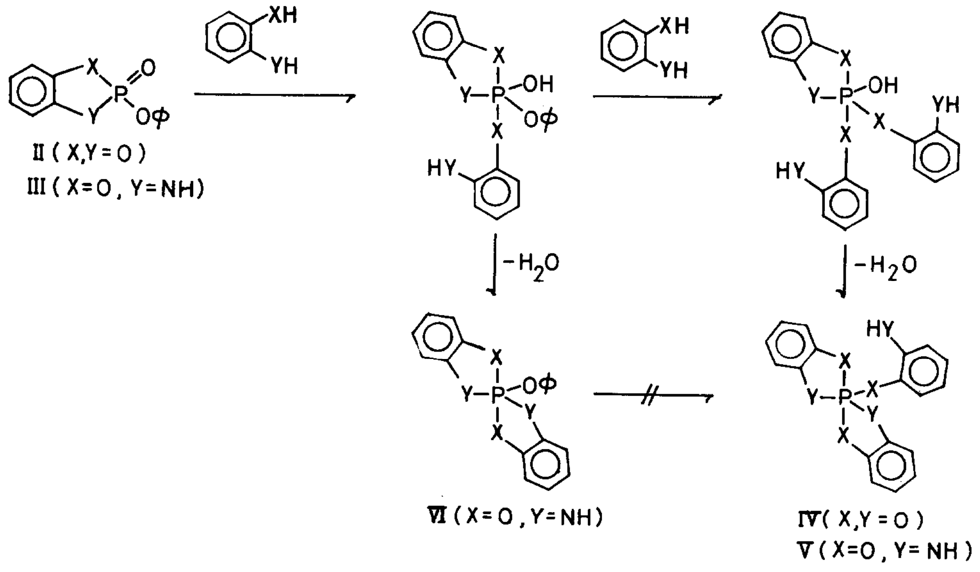
Again the physical properties of V fit well with those of bis-(o-phenyleneoxyamino)-2-aminophenoxy phosphorane[14] which was synthesized by Allcock and Kugel by the reaction of o-aminophenol with hexachlorocyclotriphosphazene. Accordingly, the structure of V was confirmed by comparing mp and IR with those of standard specimen prepared by the Allcock's procedure.
The structure of VI was determined as bis-(o-phenyleneoxyamino)-phenoxy phosphorane by comparison of the physical properties with those of V.



V : Ar = o-NH_2-φ
VI : Ar = φ

Although the formation mechanism of IV, V, and VI in the above reactions may be rather complex, it is a possibility that 2-phenoxy-benzodioxaphosphole-2-oxide II or 2-phenoxy-benzoxazaphosphole-2-oxide III once formed reacts further with catechol or o-aminophenol to give IV, V, and VI. If these are the cases, it should be the first direct evidence to support the pentacoordinate intermediate formation by the displacement reaction of five-membered cyclic phosphates. In order to clarify this possibility, the reaction of II (bp 160°C/0.07mmHg)[15] with catechol in the presence of triethylamine was carried out in refluxing THF. As expected, the compound IV was obtained in 37% yield.[16] The reaction of 2-anilino-benzodioxaphosphole-2-oxide(mp 152-154°C)[15] with catechol also furnished IV in 28% yield. On the other hand, when III was treated with o-aminophenol in THF, V(5%) and VI(trace) have been isolated. These results clearly indicate the formation of the pentacoordinate intermediates during the reactions of II and III with catechol and o-aminophenol under the mild conditions. The reason for this easy formation of the stable pentacoordinate compounds should be attributed to the very stable nature of bicyclic phosphoranes.[2]

Although the mechanism of the formation of IV, V, and VI by the reaction of II and III is considered to be complex and awaits further detailed investigations including kinetics, following mechanism may be a reasonable one.



II (X,Y=O)
III (X=O, Y=NH)

VI (X=O, Y=NH)

IV (X,Y=O)
V (X=O, Y=NH)

The conversion of VI to V during the reaction is unlikely because the reaction of VI with o-aminophenol did not give V under the similar reaction condition. The role of II and III as the dehydrating agents (as well as the substrates) may be the key for this interesting reactions.

References and Notes

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8) 2-phenoxy-1,3-dihydro-2H-1,3,2-benzodiazaphosphole-2-oxide is a formal nomenclature for this compound. In this paper the conventional names are used for this class of compounds.

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12) H. R. Allcock, and E. C. Bissell, J. Amer. Chem. Soc., 95, 3154(1973).

13) Satisfactory elemental analyses and spectral data were obtained on all new compounds.

14) H. R. Allcock, R. L. Kugel, J. Amer. Chem. Soc., 91, 5452(1969). Although it is not certain which of oxygen and nitrogen occupy apical position, the structure with apical oxygen is employed for convenience.

15) II and 2-anilino-benzodioxaphosphole-2-oxide were prepared by the reaction of phenylenephosphorochloridate with phenol or aniline in the presence of triethylamine. These compounds are easily hydrolyzed under mild condition and the mechanism of the hydrolysis is now being investigated.

16) The yield is based on II employed.