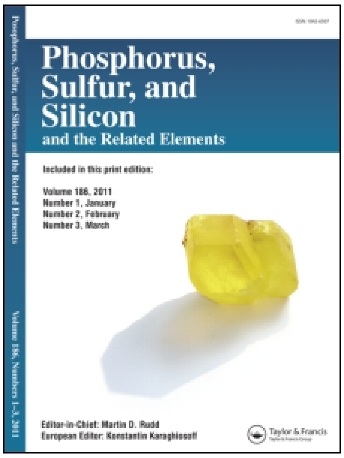

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New Six-Coordinate Phosphorus Compounds. Synthesis and Stereochemistry

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NEW SIX-COORDINATE PHOSPHORUS COMPOUNDS. SYNTHESIS AND STEREOCHEMISTRY

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Abstract Synthesis and stereochemistry of several new six-coordinate organophosphorus compounds are discussed.

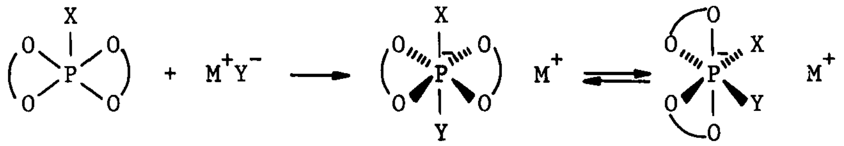
INTRODUCTION

A growing number of six-coordinate organophosphorus compounds including intermediates in the associative nucleophilic displacement at five-coordinate phosphorus atom has been described.[1,2] It has been recently demonstrated that the nucleophilic attack on some phosphoranes yielded initially the less stable isomeric six-coordinate phosphorus anions, which subsequently were transformed to thermodynamically more stable isomers.[3-5] However, data on more such reactions are needed before rationalization is possible.

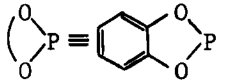
Our present work is a continuation of investigations devoted to the nucleophilic displacement reactions at P(V) atom. Reactions of selected bicyclic and acyclic five-coordinate phosphorus compounds with various nucleophiles are discussed.

RESULTS AND DISCUSSION

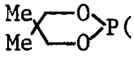
Thorough investigations of the reactions of bicyclic phosphoranes with nucleophiles were performed on spirophosphoranes 1 in which phosphorus is attached to five heteroatoms each having lone pairs of electrons. Monitoring the reactions of 1 with a variety of nucleophiles by ^{31}P NMR spectroscopy over a large temperature range revealed that two isomeric six-coordinate anions 2a and 2b are formed. At lower temperatures the less stable anions 2a were observed either as a unique species or together with small amounts of 2b. Anions 2a rearrange gradually at higher temperatures to anions 2b. Six-coordinate structure of 2a and 2b is evident from their chemical shift values. In most cases, the structure of 2a and 2b was additionally confirmed by coupling between P(VI) atom and methine proton of $(CF_3)_2CH$ group, or phosphoryl atom, or fluorine atom.



1 2a 2b



$R_f=(CF_3)_2CH$; $M^+=R_4N, R_3NH, Cs$

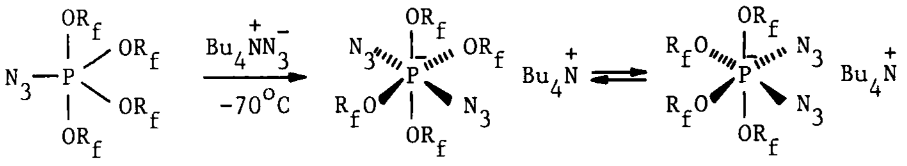
X,Y=PhO[4]; X,Y=R_fO[4]; X,Y=Pr^iO; X,Y=$(EtO)_2P(O)O$[4];
X,Y= P(O)O; X=R_fO, Y=PhO[4]; X=R_fO, Y=N_3;
X=R_fO, Y=CN; X=R_fO, Y=F; X=F, Y=R_fO

Cis configurations of more stable anions 2b could be determined taking an advantage of chirality of these compounds. Using brucine as a chiral base the anions 2b have been obtained. Their ^{31}P NMR spectra showed two separate signals attributed to two diastereoisomeric salts.

In order to obtained more information about the isomerization process, the kinetics of the reaction of the spirophosphorane 1 (X=PhO) with phenoxide anion in methylene chloride in the range of -72°C to -45°C by ^{31}P NMR spectroscopy was investigated. Analysis of the preliminary results has shown that fast nucleophilic attack on 1 results in the irreversible formation of thermodynamically less stable trans anion 2a. Isomerization 2a ⟶ 2b is described by first order kinetics. The $\Delta G^{\ddagger}$ value is 44 kJ mol^{-1}. Doubling the concentration of 1 neither affect the first order rate constants, nor the addition of phenoxide ion. These observations rule out an associative isomerization mechanism involving a seven-coordinate intermediate or transition state. Further kinetic investigations are in progress.

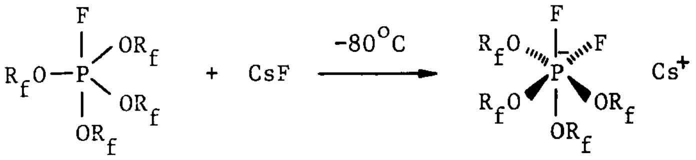
Little information is available concerning the stereochemistry of acyclic six-coordinate organophosphorus compounds. We have therefore examined the reactions of acyclic phosphoranes with nucleophiles using two model compounds 3 and 6.

The phosphorane 3 reacts with tetra-butylammonium azide at -70°C to give a mixture of two six-coordinate compounds 4a and 4b in a ratio 8:2 (trans:cis). At higher temperature the ratio changes and then remains constant being 4:6. The cis isomer 4b is again the favoured under thermodynamic conditions. However, substancial amount of trans 4a are still present in the equillibrium mixture. Configurations of 4a and 4b were determined on the basis of ^{31}P and ^{19}F NMR data.



3 4a 4b

When the phosphorane 5 is subjected to the substitution with cesium fluoride the spectra reveal that only one product 6 is produce at the temperature range from -80°C to +30°C.



5 6

The compound 6 is unaffected by prolonged heating at 120°. We presently favour the interpretation of ^{31}P and ^{19}F spectra in terms of cis configuration of 6. It is noteworthy that chemical shift values 4a, 4b and 6 are in line with those predicted by the pairwise interactions method.[6] ($\delta^{31}P$: 4a -157.5 qu exp., -157.5 calc. for trans isomer; 4b -159.95 m exp., -158.95 calc. for cis isomer; 6 -143.02 t qu exp., -143.83 calc. for cis isomer, -141.96 calc. for trans isomer).

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