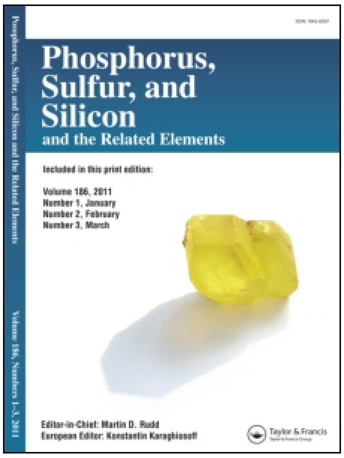

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CYCLIC OXYPHOSPHORANES WITH SIX- AND SEVEN-MEMBERED RINGS

K. C. KUMARA SWAMY, SARAH D. BURTON, JOAN M. HOLMES, ROBERTA O. DAY, AND ROBERT R. HOLMES+

Abstract X-ray and variable temperature NMR investigations of cyclic pentaoxyphosphoranes reveal a preference of six- and seven-membered rings for apical-equatorial orientations of trigonal bipyramids. Saturated six-membered rings prefer a boat conformation. Apical-equatorial ring pseudorotations are more facile for five-membered rings, whereas ligand exchange via diequatorial ring placement is more facile for the larger rings. Application to enzymatic reactions of cyclic AMP is emphasized.

INTRODUCTION

Although an abundance of structural studies[1] of phosphoranes containing five-membered rings have been performed, little is known about larger rings. In the area of pentaoxyphosphoranes, only one structural study exists. This concerns an X-ray study recently reported by D. Schomburg and coworkers[2] of a cyclic derivative containing a six-membered ring.

What we report here are X-ray and NMR studies of a series of related cyclic pentaoxyphosphoranes containing ring sizes from five- to seven-membered. The studies were undertaken to determine ring site preferences and solution state exchange processes, the knowledge of which should prove useful in interpreting mechanisms of nucleophilic displacement reactions of cyclic phosphorus compounds.

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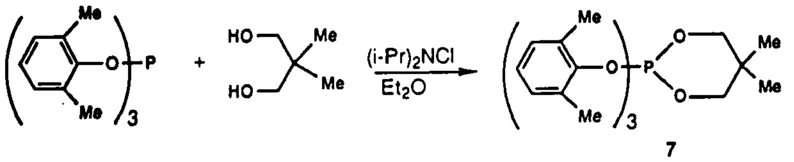
RESULTS AND DISCUSSION

Synthesis

Monocyclic and bicyclic pentaoxyphosphoranes, including two thio derivatives, for which X-ray structures have been obtained are listed in Table I. All of these derivatives were synthesized by oxidative additions of quinones to phosphites or oxidative coupling of diols with phosphites in the presence of chloro diisopropylamine, e.g. the synthesis of **7**, eq 1. In general, yields varied from 40% to 80%.



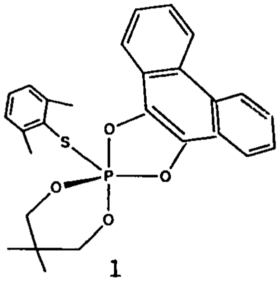
(1)

X-Ray Structures

The dithiaphosphorinane ring compound, **5** and **6**, is the first example of a phosphorane structure containing a six-membered ring with the ring sulfur atoms bonded to phosphorus. It is obtained in two crystallographically distinct forms. Each form exhibits an apical-equatorial orientation for the sulfur containing ring. The expected structure would place the more electronegative oxygen atoms in apical positions leaving the sulfur ring atoms in equatorial sites with the ring in a chair conformation. A further feature of the sulfur derivative, which is found in the structures of all of the phosphoranes reported here that contain saturated six-membered rings, is the existence of these rings in a boat conformation of the type discussed by Trippett[3] occupying apical-equatorial sites of a trigonal bipyramid.

The apical sulfur atom and methylene carbon atom bonded to the equatorial sulfur atom comprise the bow and stern positions of the boat conformation and is the one that allows lone pairs of the equatorial atoms bonded to phosphorus to be placed near the equatorial plane for effective back-bonding.[3]

TABLE I Cyclic oxyphosphoranes studied by X-ray diffraction.



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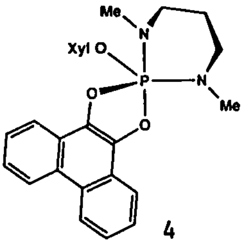

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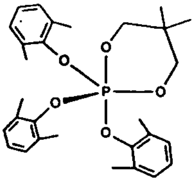

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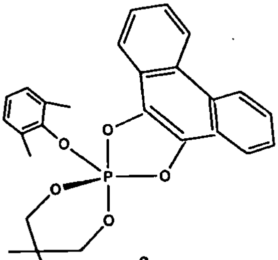

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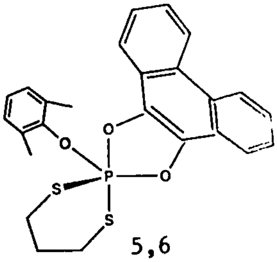
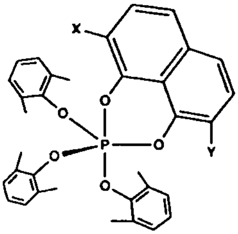


5,6

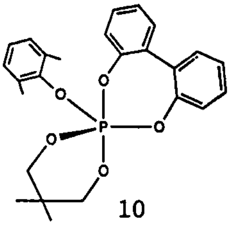


8

X = Y = H

X = Y = Cl

X = H, Y = Cl



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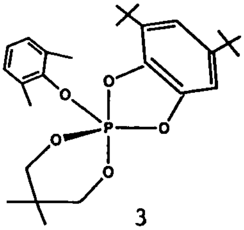

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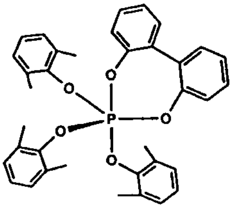

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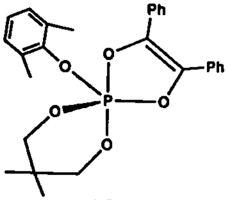

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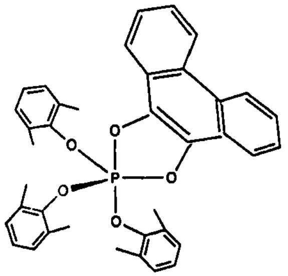
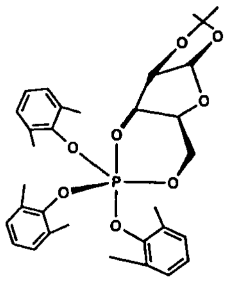
^{1}H NMR Studies

Analysis of the variable temperature ^{1}H NMR spectra of the cyclic pentaoxyphosphoranes of Table I as well as **11** and **13** shown here indicates



11



13

that the solid state structures are retained in solution. For example, the ^{1}H NMR spectrum of the monocyclic phosphorinane derivative, **7**, shows at 19°C a single resonance at 0.50 ppm, a singlet at 2.40 ppm and a doublet at 3.60 ppm. These peaks are assignable to the methyl protons of the phosphorinane ring, the methyl protons of the xylyl groups, and the methylene protons of the phosphorinane ring, respectively. The latter doublet results from phosphorus coupling, $^3J_{P\text{-}\underline{H}}$ = 18.3 Hz. The ^{31}P shift at -77.5 ppm confirms that the compound is pentacoordinated.

The equivalence of the phosphorinane ring methyls, the xylyl methyls, and methylene protons indicated at 19°C, changes to a more complex pattern at -70°C. As an approximation, two types of each of these units are indicated. The spectral changes are consistent with the presence of an apical-equatorial ring placement at -70°C, as found for the solid state structure, and the onset of pseudorotation to give the higher temperature spectrum at 20°C where pseudorotation maintains the ring in an apical-equatorial position. Accompanying pseudorotation, a rapid interchange of boat forms, must occur.

In contrast to the monocyclic pentaoxyphosphoranes, where ^{1}H NMR indicates that Berry pseudorotation is "stopped" at reduced temperatures for six- and seven-membered ring derivatives (but not for five-membered ring compound, **11**), interpretation of ^{1}H spectra for bicyclic derivatives indicates two intramolecular exchange processes occurring at phosphorus. A Berry pseudorotation process appears to operate down to the lowest temperatures studied. At higher temperatures, a trigonal bipyramid with apical-equatorial ring orientations is indicated to undergo exchange via a higher energy trigonal bipyramid that has a six-membered ring in a diequatorial position.

The principal conclusion of the work presented here is that six-membered rings of oxyphosphoranes, like that previously known for five-membered ring derivatives, have an apical-equatorial site preference in a trigonal bipyramid. The preferred ring conformation of saturated six-membered rings is that of a boat. The apical-equatorial site preference also seems to apply to phosphoranes with seven-membered rings. The NMR data suggest that diequatorial ring placement becomes easier for the larger sized rings.

Our study lends credence to the theoretical investigation by van Ool and Buck[4] who conclude that hydrolysis of cAMP with phosphodiesterase proceeding by way of a trigonal bipyramidal intermediate must have the intermediate with an apical-equatorial ring orientation and the 3'-oxygen atom positioned at the apical site, cf. **13**.

We may anticipate that additional studies focusing on six-membered ring systems in oxyphosphoranes and their sulfur analogs will yield further insight that should prove useful in constructing mechanistic pathways for enzymatic and nonenzymatic nucleophilic displacement reactions of phosphorus.[5]

ACKNOWLEDGMENT

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