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Part I Structural studies of cyclic phosphorus compounds Part II Low-valent transition metal complexes of phosphorus ligands

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PART I. STRUCTURAL STUDIES OF CYCLIC
PHOSPHORUS COMPOUNDS. PART II. LOW-VALENT
TRANSITION METAL COMPLEXES OF PHOSPHORUS LIGANDS.

Iowa State University, Ph.D., 1971
Chemistry, inorganic

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Part I. Structural studies of cyclic
phosphorus compounds

Part II. Low-valent transition metal
complexes of phosphorus ligands

by

Gerald Kent McEwen

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Inorganic Chemistry

Approved:

Signature was redacted for privacy.

~~In Charge of Major Work~~

Signature was redacted for privacy.

~~Head of Major Department~~

Signature was redacted for privacy.

~~Dean of Graduate College~~

Iowa State University
Ames, Iowa

1971

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PART I. STRUCTURAL STUDIES OF CYCLIC
PHOSPHORUS COMPOUNDS

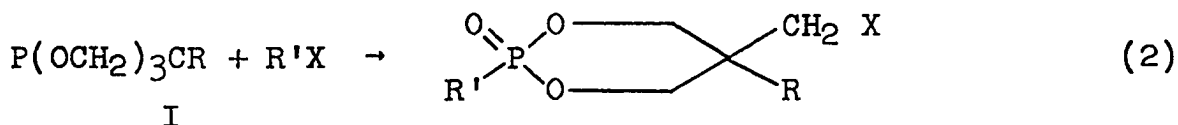
INTRODUCTION

The reaction of an ester of trivalent phosphorus with an alkyl halide to form a pentavalent phosphonate (reaction 1)

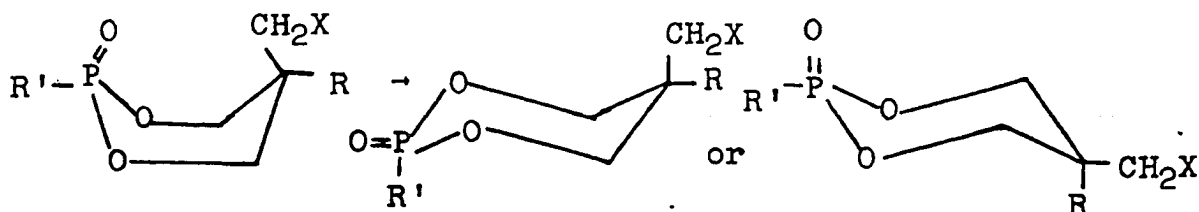
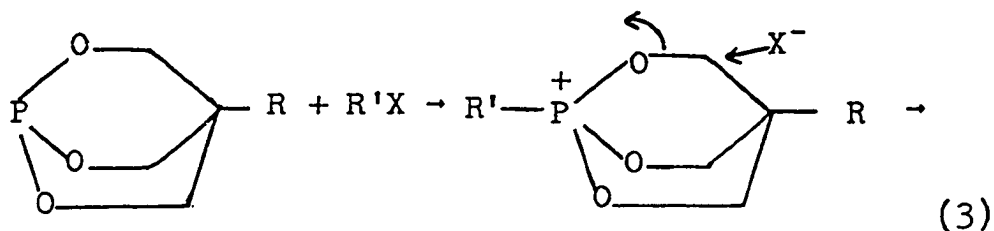


was first discovered by Michaelis and Kaehne (1) and was later investigated more thoroughly by Arbuzov (2). This reaction has been widely used for the formation of carbon-phosphorus bonds in the synthesis of phosphonates, phosphinates, and phosphine oxides. The reaction has come to be known as the Michaelis-Arbuzov reaction and its extensive literature through 1949 has been reviewed by Kosolapoff (3, 4). Harvey and de Sombre (5) have summarized the more recent literature on the reaction. The scope of this reaction has been extended to include virtually any halide capable of undergoing bimolecular nucleophilic displacement. Also, considerable structural variation of the phosphorus reagent is possible. Therefore, only the pertinent points pertaining to this research will be reviewed here.

Wadsworth and Emmons (6) initially showed that bicyclic phosphites are also capable of undergoing a Michaelis-Arbuzov reaction.

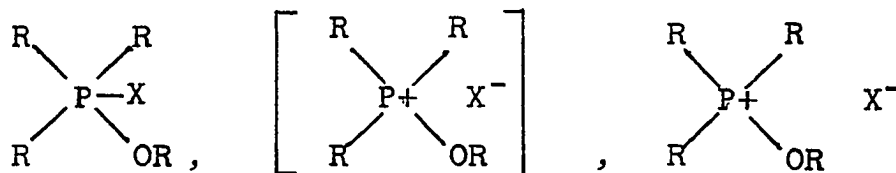


Vapor phase chromatography of the compound where $R = \text{Et}$, $R' = \text{C}_6\text{H}_5\text{CH}_2$, and $X = \text{Cl}$ gave but one peak indicating that bicyclic phosphites give a single isomer. The exocyclic R' and CH_2X groups were assumed to be trans because of the nature of the Michaelis-Arbuzov mechanism (reaction 3).



A chair form of the product was assumed but the conformation was not deduced.

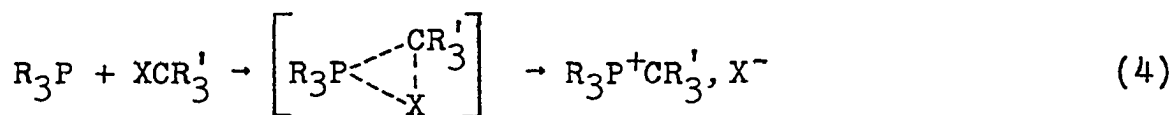
Intermediate structures in the Michaelis-Arbuzov reaction can be considered to be between the extremes of purely ionic or purely covalent bonding.



This uncertainty is reflected in the name "quasi-phosphonium" which frequently appears in the literature. The reaction of I ($R = \text{Et}$) with Br_2 or Cl_2 was described by Wadsworth and Emmons (6) to give intermediates stable

only at low temperatures. No data were obtained on either of the compounds. Abramov et al., (7, 8, 9) obtained noncrystalline adducts from trialkyl phosphites and α , β -dihaloalkyl ethers. Alkyl dialkylphosphinite esters and alkyl halides were found by Razumov and Bonkovskaya (10) to give crystalline 1:1 adducts at low temperatures which were convertible to phosphine oxides upon warming.

The kinetics of the reaction between variously substituted phosphines and alkyl halides was studied by Henderson and Buckler (11). It was shown that while phosphine attack on the alkyl halide was SN_2 , this did not imply that the attack was from the rear with inversion. The possibility of attack on the carbon-halogen bond with configurational retention is present with nucleophiles capable of expanding their valency shells.

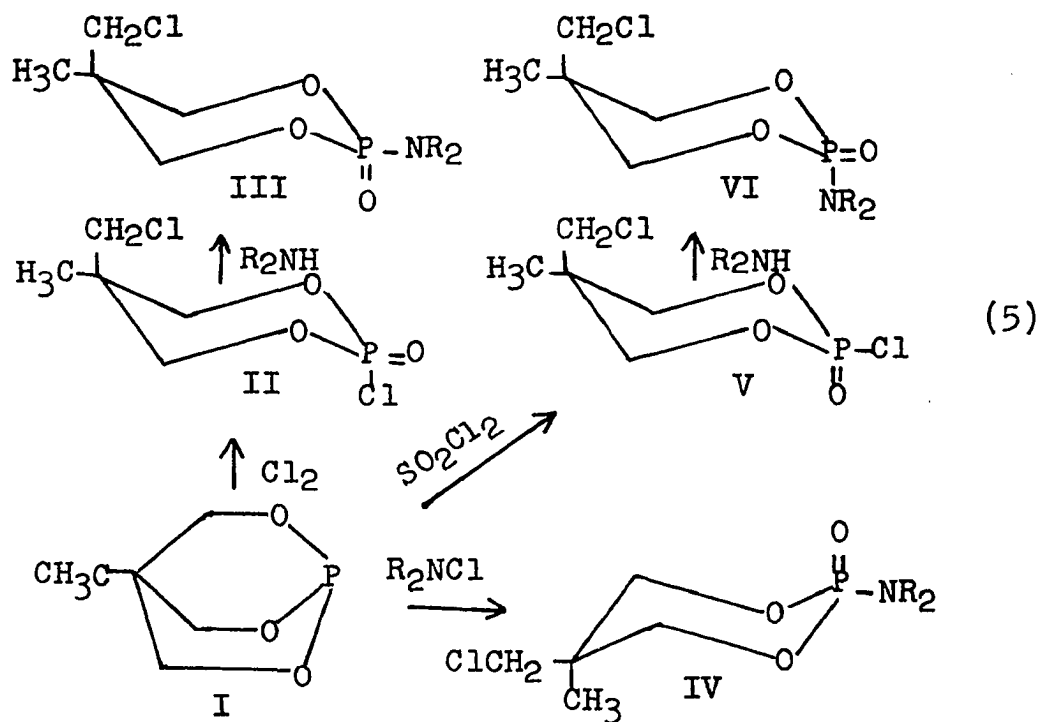


With respect to the second stage of the reaction it was found that valency expansion occurs by nucleophilic attack of the halide on the alkyl carbon of the ester. Using tri-2-octyl-phosphite prepared from (+)-2-octanol, Gerrard and Green (12) found that its reaction with ethyl iodide proceeded with inversion, yielding (-)-2-iodooctane.

The stereochemical aspects of the Michaelis-Arbuzov have seen a more limited investigation. When 2-octyl

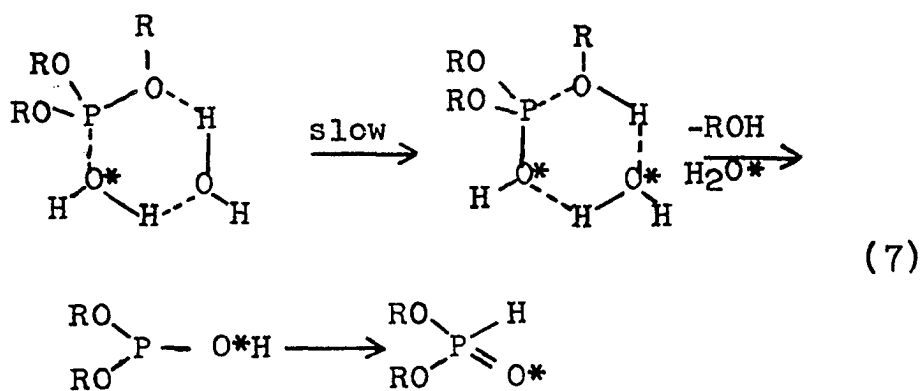
iodide was used, only ambiguous results were obtained since the halide racemized rather than forming the expected phosphonate (12).

Wadsworth (13) concluded that the reaction between the bicyclic phosphite I ($R = Et$) and chloropiperidine gave a six-membered ring Arbuzov product as previously described, whereas if I was first chlorinated and then reacted with piperidine, the product obtained was totally inverted at phosphorus. Furthermore, Wadsworth and Horton (14) recently showed that initial reaction with sulfuryl chloride followed by reaction with piperidine gave yet a third cyclic phosphoroamidate. Their results are summarized in the following reaction scheme.

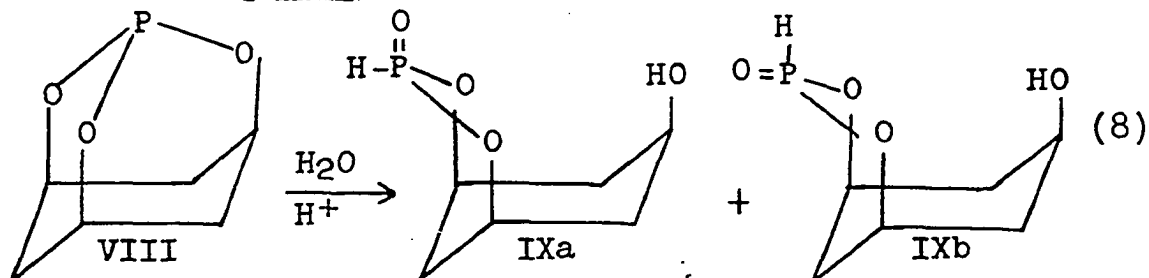


methanol thus attacks from one side only, it was deduced that the methoxy group in VIIa is equatorial since this would represent attack from the least hindered site.

The hydrolysis of phosphite esters has not been as extensively investigated as the Michaelis-Arbuzov reaction. The kinetics of the hydrolysis of tri-n-propyl phosphite was studied by Aksnes and Aksnes (16). The reaction was carried out in acetonitrile using ^{18}O labelled water or deuterium oxide and was found to be third order; first order in phosphite and second order in water. Labelling experiments with 85 percent ^{18}O enriched water caused the phosphoryl stretching frequency of the product dialkyl phosphite to be lowered by 42 cm^{-1} . Also, use of deuterium oxide caused an eightfold decrease at 52° compared to water. This is the order of magnitude of the ratio of the ionization of water in water versus deuterium oxide in deuterium oxide, ($K_{\text{H}}/K_{\text{O}} = 6.5$), indicative of an ionization of the water molecule in the rate-controlling step. Their results are summarized in the following mechanism.



Huttemann (17, 18) has shown that two isomeric compounds are obtained from the bicyclic phosphite VIII when it is hydrolyzed in an acidic acetone solution.



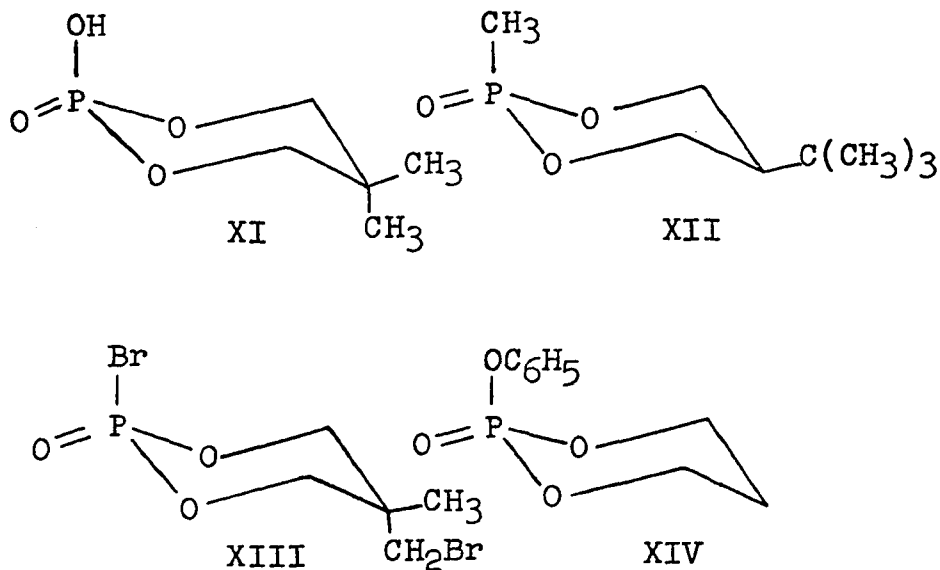
Isomerism was predicted to be at phosphorus and not at carbon based on ir and nmr data. This was substantiated by the crystal and molecular structure of IXa which verified the predictions (19). The formation of these two isomeric compounds was concluded to be in accord with the general hydrolysis mechanism of Aksnes and Aksnes (16).

The hydrolysis of I (R = Me) was investigated by Bertrand (20) who showed that in deuterium oxide the final product was $\text{CH}_3(\text{CH}_2\text{OD})_2 \text{C} \text{CH}_2\text{O}(\text{O})\text{P}(\text{OH})\text{D}$. Preliminary evidence for two cyclic intermediates of the form $\text{H}(\text{O})\text{P}(\text{OCH}_2)_2 \text{C}(\text{CH}_3)\text{CH}_2\text{OH}$, when the hydrolysis was carried out in CH_3CN , was presented. It was also postulated that the two compounds differed in stereochemistry at phosphorus but the question of two conformers vs two isomers remained unanswered. In the case where acetone was used for a solvent a solid material was isolated and shown to be $[(\text{CH}_3)_2\text{COH}] (\text{O}) \text{P}(\text{OCH}_2)_2\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$ (X). No stereochemical assignments were made.

The subject of stereochemistry of six-membered cyclic phosphorus compounds has seen a tremendous upsurge in interest in the recent literature. Investigative tools which have been used include nmr, ir, and x-ray spectroscopy and dipole moments. Earlier studies have been reviewed by Gallagher and Jenkins (21) and a complete literature search is given by White (22).

Edmundson and Mitchell (23) recently investigated a series of 5,5-disubstituted-1-oxo-1-phospha-2,6-dioxacyclohexanes. By means of variable temperature nmr studies and analysis of the ^1H nmr they concluded that these compounds are conformationally mobile systems.

X-ray diffraction studies have shown that compounds XI (24), XII (25), XIII (15), and XIV (26) all exist in one chair conformation in the solid state with an equatorial



phosphoryl oxygen in each case. The distinction between equatorial and axial is somewhat obscured in XI, XIII, and XIV due to flattening of the phosphorus end of the ring.

The related trivalent phosphorus compounds, 1-R-1-phospha-2,6-dioxacyclohexanes, have also been investigated by several groups of workers and syntheses of many of these compounds have been reported over the last 20 years (27-30). Attempts to determine the stereochemistry of these compounds on the basis of their ^1H nmr spectra have generally concluded that they exist as chair conformers in solution. Conflicting stereochemistries at phosphorus have been deduced for several of these compounds, however. An axial R, equatorial lone-pair stereochemistry is favored by Bodkin and Simpson (31), Hague et al. (25), White et al. (32), and Bogat-skii et al. (33). On the other hand, an equatorial R, axial lone-pair has been assigned by Albrand et al. (34). Details on the particular compounds investigated and the evidence presented will be given in the Results and Discussion section.

EXPERIMENTAL

Materials

All solvents and other materials not specifically mentioned were reagent grade or better and in most cases were stored over Linde 3A Molecular Sieves. Benzene used in the dipole moment measurements was purified by refluxing over sodium with a small quantity of benzophenone. When the solution became blue due to the formation of the water sensitive $\text{Na}^+[(\text{C}_6\text{H}_5)_2\text{C}-\text{O}]^-$, it was distilled through an 8" vigeroux column. Trimethylphosphite was obtained from Aldrich Chemical Corporation (97-100 percent) or from Eastman Organic Chemicals (Practical Grade). The 83 atom % ^{18}O enriched water used in the hydrolysis studies was from Yeda Research and Development Co., Ltd., at the Weizmann Institute of Science, Rehovot, Israel and was a generous gift of Dr. T. Kinstle, of this department.

Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

nmr Spectra

All spectra were obtained either on neat samples or in the solvent specified in spinning 5 mm (od) precision glass tubes. All ^1H line positions are given in ppm (δ) relative to internal tetramethylsilane, with a positive shift taken to occur at an applied magnetic field smaller

than that of the standard. All coupling constants are given in cycles per second (Hz). These spectra were obtained either on a Varian A-60 spectrometer operating at 14,100 gauss or on a Varian HA-100 spectrometer operating at 23,500 gauss at ambient temperatures of 40° and 30°, respectively. The variable temperature experiments were performed on the A-60 instrument. Temperature calibration was accomplished by measuring the chemical shift difference in CH₃OH or HOCH₂CH₂OH for low or high temperatures, respectively. The value of the temperature was obtained from a plot of chemical shift difference versus temperature supplied by Varian in the A-60 operating manual. Homonuclear decoupling experiments were performed on the Varian HA-100. The ³¹P and ¹³C spectra were obtained with a Varian HR-60 spectrometer operating at 14,100 gauss modified for field-frequency lock. The modifications are fully described by Bertrand (35). The ³¹P chemical shifts are given in parts per million (ppm) relative to the chemical shift of external 85 percent phosphoric acid. The ¹³C chemical shifts are given in ppm relative to the ¹³C isotope of the methyl group of acetic acid as an external standard. A positive shift for ³¹P and ¹³C is taken to occur at an applied magnetic field greater than that of the standard.

Infrared Spectra

Infrared spectra in the range 800-4000 cm^{-1} were obtained on a Beckman Model 12 or a Perkin-Elmer Model 12 spectrophotometer. Solids were generally run as KBr pellets or in solution in demountable cells (Barnes Engineering Co.) with sodium chloride windows and usually 0.1 mm spacers. All solution spectra were obtained in the double beam made with solvent in the reference beam.

Dipole Moments

Dielectric measurements were determined with the heterodyne beat apparatus described by Vandenbrouke et al. (36) and via the procedure outlined therein. Generally, four solutions were made up in the concentration range .0007 to .0050 mole fraction.

Conductivity Measurements

Conductivity measurements were obtained on an Industrial Instruments Inc. Model RC 16B2 Conductivity Bridge. Measurements were obtained in an acetonitrile solution. The solvent was previously dried by distillation from CaH_2 .

Preparations

1-oxo-1-methyl-4-bromomethyl-4-methyl-1-phospha-2,6-dioxacyclohexane (XV). In a thick-walled tube of approximately 100 ml volume was condensed 0.91 g (9.6 mmoles) methylbromide with 1.48 g (10 mmoles) of 1-phospha-4-

methyl-2,6,7-trioxabicyclo[2.2.2]octane. The tube and contents were then frozen with liquid nitrogen, evacuated, sealed and heated to 100° for 12 hours. The white solid obtained upon cooling was purified by recrystallization from acetone or sublimation at 85° under vacuum.

Anal. Calcd. for C₆H₁₂O₃BrP: C, 29.66%; H, 4.94%; Br, 32.89%. Found: C, 29.90%; H, 5.03%; Br, 32.33%.

1-oxo-1-methyl-4-iodomethyl-4-methyl-1-phospha-2,6-dioxocyclohexane (XVI). The procedure for preparing this compound is analogous to that of XV.

Anal. Calcd. for C₆H₁₂O₃IP: C, 24.85%; H, 4.17%; I, 43.80%. Found: C, 25.32%; H, 4.36%, I, 43.71%.

1-oxo-1-ethyl-4-bromomethyl-4-methyl-1-phospha-2,6-dioxocyclohexane (XVII). The procedure for preparing this compound is analogous to that of XV except the temperature was 150° for 24 hours.

Anal. Calcd. for C₇H₁₄O₃PBr: C, 32.70%; H, 5.45%; Br, 31.10%. Found: C, 32.90%; H, 5.55%; Br, 30.81%.

1-oxo-1-n-propyl-4-bromomethyl-4-methyl-1-phospha-2,6-dioxacyclohexane (XVIII). The procedure for preparing this compound is analogous to that of XV.

Anal. Calcd. for C₈H₁₆O₃PBr: C, 35.42%; H, 5.91%; Br, 29.47%. Found: C, 35.68%; H, 5.97%; Br, 29.40%.

1-oxo-1-n-propyl-4-iodomethyl-4-methyl-1-phospha-2,6-dioxacyclohexane (XIX). The procedure for preparing this compound is analogous to that of XV.

Anal. Calcd. for $C_8H_{16}O_3PI$: C, 30.22%; H, 5.03%; I, 39.91%. Found: C, 31.04%; H, 5.36%; I, 38.68%.

1-oxo-1-triphenylmethyl-4,4-dimethyl-1-phospha-2,6-dioxacyclohexane (XX). This compound was prepared as reported previously (37).

1-oxo-1-triphenylmethyl-4-methyl-4-chloromethyl-1-phospha-2,6-dioxacyclohexane (XXI). This compound was prepared as reported previously (38).

1-oxo-1-piperidino-4-ethyl-4-chloromethyl-1-phospha-2,6-dioxacyclohexane (XXII). This compound was prepared as reported previously (13).

Isomeric 1-oxo-1-benzyl-4-chloromethyl-4-ethyl-1-phospha-2,6-dioxacyclohexane (XXIIIa, b). This isomeric mixture was prepared according to the literature (6). The isomers were separated by fractional crystallization from carbon tetrachloride, which gave the trans isomer. Removal of the CCl_4 and fractional recrystallization from ether then gave the cis isomer.

1-oxo-1-benzyl-4-chloromethyl-4-methyl-1-phospha-2,6-dioxacyclohexane (XXIV). This compound was prepared from benzyl chloride and 1-phospha-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane via the method of Wadsworth and Emmons (6).

1-oxo-1-hydro-4-hydroxymethyl-4-methyl-1-phospha-2,6-dioxacyclohexane (XXVa, b). To 1.5 ml of CD₃CN (previously dried over Linde 3A Molecular Sieves) was added 0.20 g (1.35 x 10⁻³ moles) of 1-phospha-2,6,7-trioxabicyclo[2.2.2]-octane and 24.3 μl (1.35 x 10⁻³ moles) of H₂O (or D₂O or H₂¹⁸O, depending on the purpose of the experiment. A trace amount of concentrated H₂SO₄ was then added. Samples of the solution were then removed at various times for the nmr and ir spectra (See Results and Discussion section).

Dehydration of XXVa, b to I (R = Me). Compound I (R = Me) (2.0 g) was hydrolyzed as described above. The solvent was then removed under vacuum, a cold finger inserted in the flask and the flask evacuated and heated to 80°. A 69 percent yield of product was collected.

1-bromo-1-phospha-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane bromide. To a well-stirred, rigorously dried benzene solution of 1-phospha-4-methyl-2,6,7-trioxabicyclo[2.2.2]-octane kept in an ice water bath was slowly added an equimolar amount of bromine dissolved in benzene. The system was kept under a dry N₂ flush at all times. The

bulky yellow precipitate which forms was filtered off under N_2 , quickly washed with several portions of anhydrous ether, transferred to a stoppered flask and stored in a dry-ice chest. At room temperature the compound rearranges exothermically to give the Michaelis-Arbuzov product XIII. Nmr samples were made up by adding a small amount of the solid to an nmr tube in a dry bag, transferring the tube to a vacuum line, distilling CD_3CN in and sealing.

2-chloromethyl-2-methyl-1,3-propanediol. A mixture of 120 g of 2-methyl-2-hydroxymethyl-1,3-propanediol (1 mole), 86 g diethylketone (1 mole) and 1.0 ml of BF_3 etherate was dissolved in benzene. The solution was refluxed and the water which formed was removed by azeotropic distillation. The benzene was then distilled off at atmospheric pressure and the remaining thick oil distilled under vacuum. A 75 percent yield of product ($b_{0.5} = 100^\circ$) was realized. The integrated nmr spectrum in CCl_4 revealed the correct ratios for the ethyl (0.7-1.8 ppm), methyl (0.78 ppm), ring methylene (3.53 ppm), and hydroxymethyl methylene (3.58 ppm) absorptions.

Equimolar amounts of the above acetal and tosyl chloride were refluxed in pyridine for 24 hours. After cooling, the pyridinium tosylate was removed by filtration, excess pyridine was evaporated by atmospheric distillation and the remaining liquid was vacuum distilled to give the

chloro acetal derivative in 50 percent yield ($b_{0.5} = 80^\circ$). The integrated nmr spectrum of the neat liquid revealed the correct ratios for the ethyl (0.7-2.0 ppm), methyl (0.81 ppm), ring methylene (3.58 ppm) and chloromethyl methylene (3.67 ppm) absorptions.

Equimolar amounts of the above chloro acetal and water, with a catalytic amount of HCl, were heated at 100° for 4 hours. Diethyl ketone was removed by atmospheric distillation. The diol was recrystallized from benzene in 80 percent yield. The integrated nmr spectrum in $CDCl_3$ revealed the correct ratios for methyl (0.95 ppm), chloromethyl (3.68 ppm) and hydroxymethyl (3.61 ppm) absorptions.

1-methoxy-1-phospha-4-chloromethyl-4-methyl-2,6-dioxacyclohexane (XXXa, b). This isomeric mixture was prepared by the transesterification method of Wadsworth and Emmons (6) using 2-chloromethyl-2-methyl-1,3-propanediol rather than 2-chloromethyl-2-ethyl-1,3-propanediol. The compound was purified by vacuum distillation ($b_2 = 95^\circ$) in 50 percent yield. The ratio of a:b was 3.6:1.

1-fluoro-1-phospha-4,4-dimethyl-2,6-dioxacyclohexane (XXXI). Following a modified version of that of Schmutzler (39), 10 g of 1-chloro-1-phospha-4,4-dimethyl-2,5-dioxacyclohexane was reacted with 23 g of SbF_3 . The heterogenous mixture was magnetically stirred under nitrogen

at 50° for 4 hours. The precipitate was filtered off and the filtrate was vacuum distilled ($b_{43} = 62^\circ$) giving an 80 percent yield of product. The ^1H nmr spectrum consists of methyl groups at 0.75 and 1.23 ppm. The methylenes appear as a triplet of triplets (3.15-3.57 ppm) and a broad doublet of doublets (3.97-4.20 ppm).

1-fluoro-1-phospha-4-chloromethyl-4-methyl-2,6-dioxacyclohexane (XXXIIa, b). Preparation of this compound was analogous to that of XXXI ($b_{38} = 98-99^\circ$). The ratio of a:b was 3.9:1 and the yield of the a:b mixture was 80 percent.

1-chloro-4,4-dimethyl-1-phospha-2,6-dioxacyclohexane (XXXIII). This compound was prepared following a procedure which was briefly outlined by Edmundson (40). To a well-stirred, ice-cooled ether solution of 44 ml of phosphorus trichloride (0.50 mole) was added dropwise 49 g of 2,2-dimethyl-1,3-propanediol (0.47 mole) and 75.7 ml of pyridine (0.94 mole). The pyridine hydrochloride was removed by filtration and washed with ether. The ether was distilled from the combined filtrates at atmospheric pressure and the product was obtained by distillation ($b_{12} = 70^\circ$, lit. $b_{13} = 66^\circ$).

1-chloro-1-phospha-4-chloromethyl-4-methyl-2,6-dioxacyclohexane (XXXIVa, b). In 100 ml of ether was dissolved 6.3 ml (0.07 moles) of PCl_3 and 11.7 ml (0.14 moles) of pyridine. The 500 ml two-neck flask containing the mixture was equipped with an addition funnel and a reflux condenser. While magnetically stirring, 10.0 g (0.07 moles) of 2-chloromethyl-2-methyl-1,3-propanediol dissolved in 100 ml of ether was added over a period of 2 hours. The pyridinium hydrochloride was then filtered off under nitrogen, the ether removed by distillation at atmospheric pressure and the remaining liquid distilled under vacuum in 92 percent yield ($b_5 = 55^\circ \text{C}$). The ratio of a to b was 3.9:1.

1-bromo-1-phospha-4,4-dimethyl-2,6-dioxacyclohexane (XXXV). To 7.8 ml pyridine (0.10 mole), 4.56 ml of PBr_3 (0.05 mole) and 50 ml ether in a two-neck 250 ml flask fitted with an addition funnel and a condenser was slowly added 5.0 g (0.05 mole) 2,2-dimethyl-1,3-propanediol. After addition was complete, the pyridinium hydrobromide was filtered off and the ether removed by distillation at atmospheric pressure. The remaining liquid was vacuum distilled in 30 percent yield ($b_{18} = 72^\circ$). The appearance of the ^1H nmr spectrum is highly dependent on contaminants, such as traces of water, which apparently alter the rate of Br exchange. Basically it consists of two methyl proton

absorptions at 0.85 and 1.23 ppm. The methylene protons absorb at 3.42-3.77 and 4.03-4.32 ppm.

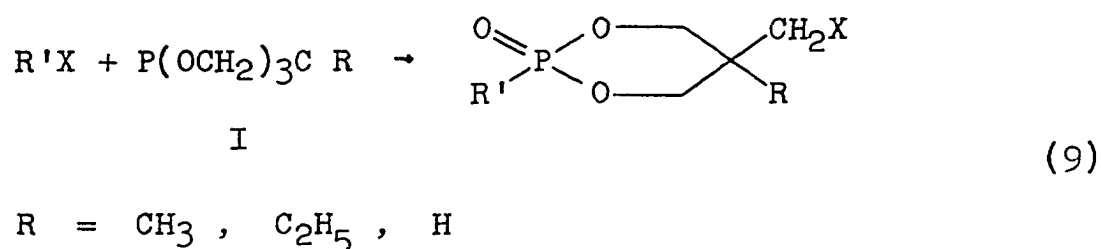
1-bromo-1-phospha-4-chloromethyl-4-methyl-2,6-dioxacyclohexane (XXXVIa, b). The preparation of this compound in 30 percent yield was analogous to that of XXXV ($b_5 = 105^\circ \text{C}$).

Bis-(bromomethyl) acetoxy phosphine oxide. To a benzene solution of 1-phospha-4-methyl-3,5,8-trioxabicyclo[2.2.2]-octane (41) kept under a flow of dry N_2 was slowly added an equimolar amount of bromine dissolved in benzene. After the addition was complete, the resultant clear solution was reduced in volume and cooled giving a white solid. The compound was recrystallized from ether.

Anal. Calcd. for $\text{C}_5\text{H}_9\text{O}_3\text{Br}_2\text{P}$: C, 19.49%; H, 2.92%; P, 10.07%; Br, 51.92%. Found: C, 19.71%; H, 2.87%; P, 9.14%; Br, 49.76%.

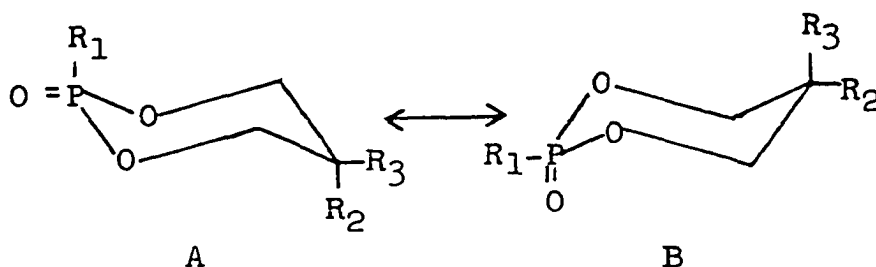
RESULTS AND DISCUSSION

From synthetic studies and a consideration of the mechanism expected for the Michaelis-Arbuzov reaction, Wadsworth and Emmons (6) concluded that the components of several organic halides as well as halogens were trans to each other in the chair form of the reaction product derived from the bicyclic phosphite I.



In an attempt to deduce the stereochemistry in solution of a series of these cyclic phosphonates their dipole moments were measured and compared with those calculated for each conformer by a vector summation of bond moments. The dipole moments were determined from the following data: dielectric constant (ϵ) and solute mole fraction (X) for three or four benzene solutions and benzene itself at 25.00 ± 0.05 °C; the equation for ϵ as a function of X as determined from a least-squares plot; and the orientation polarization (P_0) as calculated from the Cohen-Henriquez equation (42). From this data, the resultant dipole moment was calculated with the Debye equation (42). Table 1 gives the results of these experiments.

Table 1. Calculated and experimental dipole moments for conformers A and B of Michaelis-Arbuzov derivatives of bicyclic phosphites

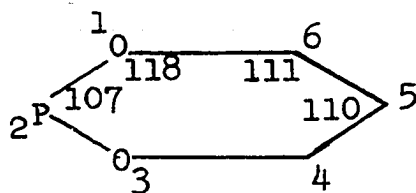


Compound	Experimental dipole moment ^a (Debye)	Structure ^b			Calculated moment	
		R ₁	R ₂	R ₃	A	B
XIII	6.59	Br	CH ₂ Br	CH ₃	4.8	3.0
XV	5.25	CH ₃	CH ₂ Br	CH ₃	5.6	3.2
XVI	4.95	CH ₃	CH ₂ I	CH ₃	5.6	3.2
XVII	4.75	C ₂ H ₅	CH ₂ Br	CH ₃	5.6	3.2
XVIII	4.78	<u>n</u> -C ₃ H ₇	CH ₂ Br	CH ₃	5.6	3.2
XIX	4.46	<u>n</u> -C ₃ H ₇	CH ₂ I	CH ₃	5.6	3.2
XXI	4.52	(C ₆ H ₅) ₃ C	CH ₂ Cl	CH ₃	5.7	3.2
XXIIIa	5.30	C ₆ H ₅ CH ₂	CH ₂ Cl	CH ₃	5.7	3.2
XXIIIb	3.42	C ₆ H ₅ CH ₂	CH ₃	CH ₂ Cl	4.8	3.0

^aBenzene was used as solvent; temperature = 25.00 ± .05 °C.

^bReasons for structural formulation as given described in text.

Moments for the two possible chair conformers of each compound were calculated by a vector summation of bond moments. Structural data are needed in order for this vectorial summation to be made and unfortunately no structural data are available for a trivalent phosphorus compound. As mentioned in the Introduction, structures of several pentavalent compounds have been investigated. As an example, the basic ring structure of 1-oxo-1-phenoxy-1-phospha-2,6-dioxacyclohexane in the solid state is a chair conformer with the bond angles and distances shown in the schematic figure below (26).



The $O_1P_2O_3$ plane makes an angle of ca. 144° with the $O_3C_4C_6O_1$ plane which in turn makes an angle of ca. 132° with the $C_4C_5C_6$ plane. The exocyclic OPR angle is 114° . These values were thus taken to be representative of cyclic phosphorus compounds and were used in calculating the dipole moment of the two conformers. Also, the exact angles were used in the calculation of XIII for which the structure has been determined by Beineke (15). It was found that this calculated value was roughly in agreement with that calculated for conformer A using the assumptions described above.

The set of bond moments used in the calculations is given in Table 2, the negative end of the bond dipole being toward the atom at the right end of the bond.

Table 2. Bond moments used in calculating dipole moments

Bond	Moment (Debye)	Bond	Moment (Debye)
C-C	0.0	C-I	1.6
C-H	0.0	C-P	1.0
C-O	1.16	P-Br	0.39
C-Cl	1.86	P-O	1.0
C-Br	1.6	P=O	2.95

Bond moments are usually empirically determined by resolving the measured moment of a molecule of known or assumed structure into component bond moments. A rather complete discussion of bond moments and the problems encountered in using bond moments derived from one molecule to predict the molecular moment of others is given by White (22). Those given in Table 2 are those concluded by White to be the best values.

All of the bond moments were then resolved into fixed and rotating components. The fixed components were resolved into x, y, and z components according to a

Cartesian coordinate system where the axial bond at phosphorus is the z axis and the xz plane is the symmetry plane bisecting phosphorus and carbon 4. These x, y, and z components were then added to give μ_x , μ_y , and μ_z . The rotating components were resolved by taking the square root of the sum of the squares of the components of the rotating moments parallel to their respective rotating axis and the rotating moment perpendicular to its rotational axis. The square root of the sum of the squares of μ_x , μ_y , and μ_z and each independently rotating component then yielded the molecular moment μ_{mol} .

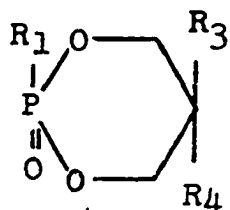
The results as shown in Table 1 suggest for the most part that these compounds exist in solution mainly as conformer A. Except for XIII and XV, the experimental moment was found to lie between the two calculated values and much closer to the higher value (i.e., conformer A) than the lower. Several reasons may account for this. First, the approximate and crude assumptions necessarily made in calculating the dipole moments render the accuracy of these values questionable. Second, an equilibrium between the two conformers may be established in solution. The experimental dipole moment would then be a weighted average of the moment for each conformer according to its relative percentage. More evidence for such a conformational equilibration will be presented later. Compound

XXIIIb has an experimental moment closer to that calculated for conformer B, however it should be noticed that the two calculated values do not differ as greatly as those for the other compounds.

Table 3 contains results of the analysis of the ^1H nmr spectra of a series of 1-R-1-oxo-1-phospha-2,6-dioxacyclohexanes. Some of these compounds were examined at various concentrations, in various solvents, and at more than one temperature. All of the 4-halomethyl-4-alkyl compounds, except XXIIIb, were derived from the Michaelis-Arbuzov reaction of an appropriate alkyl halide and $\text{P}(\text{OCH}_2)_3\text{CR}$. As a result, they all have the trans 1-R-4-halomethyl configuration as previously discussed. Compound XXIIIb was concluded to have the cis configuration (6).

The ring methylene protons constitute the AA'BB' part of an AA'BB'X spectrum where X is phosphorus. In the analyses, couplings between the methylene protons and the exocyclic R groups at position 4, or the R group on phosphorus, were ignored. In practice, the coupling between these methylenes and a 4-alkyl group is less than one Hz and couplings with the R group on phosphorus are negligible. Furthermore, if the couplings between nuclei across the ring are small relative to J_{AB} ($= J_{\text{A}'\text{B}'}$) and ν_{AB} , then the methylene resonances can be treated as the

Table 3. ^1H nmr analyses of 1-R-1-oxo-1-phospha-2,6-dioxacyclohexanes



Compound	Solvent	Concentration M	Temperature °C	R ₁	R ₃	R ₄
XV	CDCl_3	1.8	40	CH_3	CH_3	CH_2Br
	CDCl_3	0.68	40			
	CDCl_3	0.76	- 52			
	CDCl_3	0.76	1			
	$\text{C}_5\text{H}_5\text{N}$	1.0	36			
	$\text{C}_5\text{H}_5\text{N}$	1.0	84			
	$\text{C}_6\text{H}_7\text{Cl}$	0.35	75			
	$\text{C}_6\text{H}_7\text{Cl}$	0.35	164			
	C_6H_6	0.13	40			
XVI	C_6H_6	0.12	40	CH_3	CH_3	CH_2I
	CD_3CN	1.2	40			
	CDCl_3	2.3	40			
	CDCl_3	1.3	40			
	CDCl_3	0.63	40			
	CDCl_3	0.13	40			

Ring J(POCH) coupling constants		Ring methylene chemical shifts	
A	B	A	B
16.6	7.1	4.30	4.08
14.6	8.4	4.30	4.00
19.5, 23.2	4.37, 4.34	4.37, 4.34	4.18, 4.21
15.8	7.2	4.33	4.04
Sum = 24.4		Average = 4.30	
22.7, 17.5	0.9, 6.1	4.24, 4.28	4.15, 4.10
14.9	8.7	3.74	3.19
12.7	10.8	Difference = 0.57	
13.0	10.6	3.91	3.28
12	11	3.22	3.88
19.8	3.2	4.16	4.16
Sum = 23.5		Average = 4.20	
16.5	7.8	4.28	4.08
14.5	8.7	4.29	4.04
12.7	10.9	4.32	3.96

Table 3. (Continued)

Compound	Exocyclic chemical shifts			Exocyclic coupling constants
	R ₁	R ₃	R ₄	
XV	1.62	1.04	3.63	${}^2J_{\text{PH}} = 16.6-17.1$
	1.59	1.10	3.54	
	1.70	1.06	3.71	
	1.70	0.94	3.80	
	1.59	0.95	3.68	
	1.07	0.30	2.94	
	1.08	0.57	2.88	
XVI	1.05	0.56	2.53	${}^2J_{\text{PH}} = 16.9-17.2$
	1.54	0.94	3.50	
	1.61	1.03	3.46	
	1.62	1.08	3.42	
	1.60	1.09	3.37	
	1.59	1.12	3.30	

Table 3. (Continued)

Compound	Solvent	Concentration M	Temperature °C	R ₁	R ₃	R ₄
XVII	C ₆ H ₆	0.09	40	C ₂ H ₅	CH ₃	CH ₂ Br
	CDCl ₃	0.92	40			
XVIII	C ₆ H ₆	0.35	40	n-C ₃ H ₇	CH ₃	CH ₂ Br
	CDCl ₃	0.72	40			
	CDCl ₃	0.22	40			
XIX	CDCl ₃	0.89	40	n-C ₃ H ₇	CH ₃	CH ₂ I
	C ₆ H ₆	0.59	40			
XX	C ₆ H ₆	0.65	40	C ₆ H ₅	CH ₃	CH ₃
	C ₆ H ₆	0.14	40			
	CDCl ₃	1.3	40			
	CCl ₃ F	0.042	40			
	CCl ₄	0.14	40			
	CH ₃ CN	1.6	40			
	CH ₃ CN	0.26	40			
	CH ₃ CN	1.5	- 40			
	CH ₃ CN	1.5	50			
	CH ₃ CN	1.5	80			

Ring J(POCH) coupling constants		Ring methylene chemical shifts	
A	B	A	B
13	10	3.22	3.98
13.0	10.0	4.34	3.99
11.3	11.3	4.05	3.47
12.8	10.2	4.34	3.96
11.5	11.3	4.36	3.93
13.0	9.8	4.28	4.00
11.2	11.2	4.04	3.50
13.8	9.3	3.48	4.06
15.4	7.0	3.38	4.07
12.8	10.8	3.88	4.26
16.9	6.5	3.73	4.35
16.4	6.5	3.74	4.36
13.5	9.5	4.13	3.89
13.8	9.6	4.14	3.90
15.6	8.6	4.15	3.91
13.4	9.8	4.14	3.89
12.6	10.4	4.14	3.89

Table 3. (Continued)

Com- pound	Exocyclic chemical shifts			Exocyclic coupling constants
	R ₁	R ₃	R ₄	
XVII		0.64	2.66	
		1.12	3.50	
XVIII		0.73	2.99	
		1.14	3.49	
		1.16	3.45	
XIX		1.10	3.33	
		0.73	2.75	
XX		0.75	0.62	
		0.45	0.74	
		1.07	1.07	
		0.98	1.26	
		1.00	1.25	
		0.96	1.13	
		0.98	1.15	
		0.92	1.16	
		0.97	1.12	
		0.99	1.11	

Table 3. (Continued)

Compound	Solvent	Concentration M	Temperature °C	R ₁	R ₃	R ₄
XXI	C ₆ H ₆	0.17	40	C(C ₆ H ₅) ₃	CH ₃	CH ₂ Cl
	C ₅ H ₅ N	0.54	40			
	C ₅ H ₅ N	0.38	36			
	C ₅ H ₅ N	0.38	84			
	C ₆ H ₇ Cl	0.16	92			
	C ₆ H ₇ Cl	0.16	122			
	CDCl ₃	0.27	40			
XXII	CDCl ₃	1.0	40	NC ₅ H ₁₀	C ₂ H ₅	CH ₂ Cl
XXIIIa	CDCl ₃	1.5	40	CH ₂ C ₆ H ₅	C ₂ H ₅	CH ₂ Cl
	CDCl ₃	0.40	40			
	C ₆ H ₆	0.09	40			
XXIIIb	CDCl ₃	0.75	40	CH ₂ C ₆ H ₅	CH ₂ Cl	C ₂ H ₅
XXIV	CDCl ₃	0.40	35	CH ₂ C ₆ H ₅	CH ₃	CH ₂ Cl

Ring J(POCH) coupling constants		Ring methylene chemical shifts	
A	B	A	B
12.7	8.0	3.00	4.04
11.2	9.2	3.49	4.43
10.9	9.5	3.47	4.41
11.4	9.1	3.45	4.35
11.5	9.1	2.91	3.91
11.7	9.0	2.97	3.93
11.0	9.8	3.37	4.25
15.6	9.0	4.00	4.34
15.1	7.3	4.16	3.95
11.8	10.2	4.25	3.82
11.2	11.2	3.92	3.15
18.8	4.6	3.94	4.30
12.0	11.0	4.33	3.79

Table 3. (Continued)

Com- pound	Exocyclic chemical shifts			Exocyclic coupling constants
	R ₁	R ₃	R ₄	
XXI		0.38	2.96	
		0.75	3.82	
		0.75	3.82	
		0.74	3.75	
		0.23	3.17	
		0.28	3.18	
		0.76	3.63	
XXII	2.9-3.4	0.8-1.1	3.52	
XXIIIa	$\delta_{\text{CH}_2} = 3.27$	0.53-1.47	3.60	${}^2J_{\text{PH}} = 20.6-21.2$
	$\delta_{\text{CH}_2} = 3.29$	0.55-1.47	3.57	
	$\delta_{\text{CH}_2} = 2.97$	0.15-0.97	2.93	
XXIIIb	$\delta_{\text{CH}_2} = 3.25$	0.60-1.48	3.11	${}^2J_{\text{PH}} = 21.9$
XXIV	$\delta_{\text{CH}_2} = 3.33$	0.85	3.58	${}^2J_{\text{PH}} = 21.7$

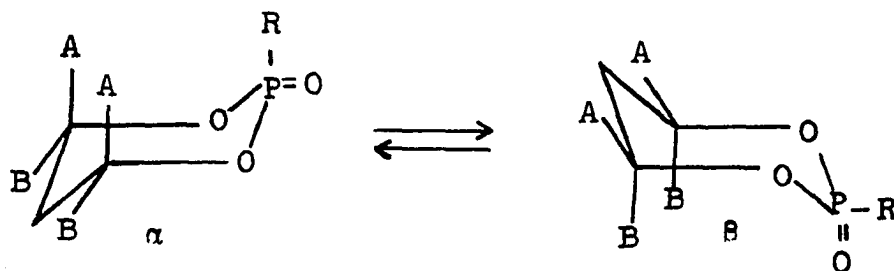
AB part of an ABX spectrum which would give a maximum of eight lines (43). This was the approximation used in determining the parameters J_{AB} , J_{AX} , J_{BX} , δ_A , and δ_B . In all cases, more lines than the theoretical eight were observed. A few of these same spectra were analyzed as AA'BB' parts of an AA'BB'X spectrum by White (22) using the LAOCN 3 iterative least-squares computer program (44). The differences in the above determined parameters between the two methods was less than 1 Hz. In the ABX analyses, there were sometimes two possibilities of assigning lines to the two AB quartets. Also, for each quartet assigned, two sets of J_{AX} , J_{BX} , ν_A , and ν_B are possible. In these cases, the correct assignment could often be made by determining the spectrum at another applied field (e.g., 100 MHz versus 60 MHz) and analyzing the spectrum so obtained. By noting which assignment gave the same values for the two spectra, the correct values were obtained. In other cases, values of J_{AX} and J_{BX} obtained from one quartet assignment were either unreasonably large or were of opposite sign (45-47).

All of the compounds described show the general features expected (48) for the assigned chemical structures. The observed dependencies of the spectral parameters for many of the compounds on solvent, concentration, or temperature yields information on the stereochemistry of the

compounds in solution. Edmundson (49, 50) earlier noted a temperature dependence for the ring methylene resonance of XIII and attributed this phenomenon to conformational equilibrium. No coupling constants or chemical shifts at the various temperatures were reported, however. More recently, Edmundson and Mitchell (23) studied a larger series of the 4,4-disubstituted-1-oxo-1-phospha-2,6-dioxacyclohexanes. As a result of variable temperature studies and ABX analyses of the ^1H nmr spectra, he concluded that these systems were conformationally mobile.

The constancy of the sum of J_{AX} and J_{BX} for the compounds examined under varying conditions is another general feature of these systems. This sum is constant even when the individual couplings change.

These spectral results are most consistent with the presence of chair conformers, with the variation of spectral parameters being a result of the changing ratio of rapidly interconverting conformers. For the conformational equilibrium shown below, the time averaged coupling



constants $J(\text{POCH}_A)$ and $J(\text{POCH}_B)$ are given by

$$J(\text{POCH}_A) = \frac{x}{x+1} J(\text{POCH}_{ax}) + \frac{1}{x+1} J(\text{POCH})_{eq} \quad (10)$$

$$J(\text{POCH}_B) = \frac{x}{x+1} J(\text{POCH}_{eq}) + \frac{1}{x+1} J(\text{POCH}_{ax}) \quad (11)$$

if the ratio of conformers is $X:1$. Therefore, the sum of $J(\text{POCH}_A)$ and $J(\text{POCH}_B)$ would always be the sum of $J(\text{POCH}_{ax})$ and $J(\text{POCH}_{eq})$, independently of X . This assumes that $J(\text{POCH}_{ax})$ and $J(\text{POCH}_{eq})$ are independent of the disposition of the exocyclic substituents at phosphorus and carbon 4; i.e., that $J(\text{POCH}_{ax})$ is the same in both conformers α and β and likewise for $J(\text{POCH}_{eq})$. If this is not the case then

$$J(\text{POCH}_A) = \frac{x}{x+1} J_{\alpha}(\text{POCH}_{ax}) + \frac{1}{x+1} J_{\beta}(\text{POCH}_{eq}) \quad (12)$$

and

$$J(\text{POCH}_B) = \frac{x}{x+1} J_{\alpha}(\text{POCH}_{eq}) + \frac{1}{x+1} J_{\beta}(\text{POCH}_{ax}) \quad (13)$$

where the subscripts α and β refer to the particular conformer. As long as $[J_{\beta}(\text{POCH}_{ax}) - J_{\alpha}(\text{POCH}_{ax})] = [J_{\alpha}(\text{POCH}_{eq}) - J_{\beta}(\text{POCH}_{eq})]$, then this would also be consistent with a constant sum of $J(\text{POCH}_A)$ and $J(\text{POCH}_B)$ with changing conformer ratio.

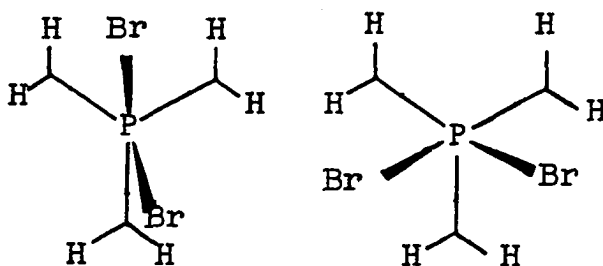
One may also use the chemical shifts of H_A and H_B to determine the conformer ratio in a similar manner providing that the conformer chemical shifts for a particular proton

are equal (i.e., that $\delta_{\alpha} H_{ax} = \delta_{\beta} H_{ax}$ and $\delta_{\alpha} H_{eq} = \delta_{\beta} H_{eq}$). This is very likely not the case due to the unknown anisotropy of the exocyclic bonds, especially those at phosphorus. The chemical shift of a substituent at C_4 would be expected to be less dependent than the methylene proton chemical shifts on the substituents at phosphorus because of the greater spatial separation from the phosphorus substituents. Thus, the chemical shift difference between two 4-methyl groups should decrease as the conformer ratio approaches unity.

In the reaction of bromine with I (R = Me) Wadsworth and Emmons (6) mentioned the formation of the phosphonium intermediate $[\text{Br} \overset{+}{\text{P}}(\text{OCH}_2)_3\text{CCH}_3] \text{Br}^-$ as a result of nucleophilic attack of the phosphite on bromine although no data were given for this intermediate product. In the present work, a benzene solution of bromine was very slowly added to an ice-cooled benzene solution of I (R = Me) in order to avoid, if possible, the very exothermic Michaelis-Arbuzov reaction. A voluminous yellow-orange precipitate formed which was found to be extraordinarily reactive to water giving $\text{O} = \text{P}(\text{OCH}_2)_3\text{CCH}_3$. The yellow solid is insoluble in all nonpolar organic solvents but is quite soluble in acetonitrile.

A pure sample of this unstable compound has never been realized. The yellow solid dissolved in CD_3CN shows in its

nmr spectrum the presence of some $O = P(OCH_2)_3CCH_3$ formed by reaction with trace amounts of water, along with small amounts of XIII which increase with time. Also present are absorptions attributable to $BrP^+(OCH_2)_3CCH_3$, $BrBrP(OCH_2)_3CCH_3$ or $Br_2P(OCH_2)_3CCH_3$, i.e., a doublet at 5.19 ppm with $J = 7.2 \text{ Hz}(\underline{CH}_2)$ and a singlet at 1.08 ppm (\underline{CH}_3) in a ratio of 2:1 respectively. The presence of the symmetrical doublet strongly suggests that the bicyclic cage present in I is retained. It also casts some doubt upon the $Br_2P(OCH_2)_3CH_3$ since the methylene protons would probably no longer be equivalent in such a structure.



By means of INDOR methods, the ^{31}P spectrum of this unstable compound was obtained. The appearance of the spectrum was a very broad absorption centered at -36.5 ppm with respect to external 85 percent H_3PO_4 . The ^{31}P chemical shift of $O = P(OCH_2)_3CCH_3$ is $+ 8.2 \text{ ppm}$ (51) while that of $[H_3C^+P(OCH_2)_3CCH_3]BF_4^-$ is $- 60.15 \text{ ppm}$ (35), $[H_3C^+P(OCH_3)_3]$ is $- 53.95 \text{ ppm}$ (35) and P^+Cl_4 is $- 86.5 \text{ ppm}$ (52).

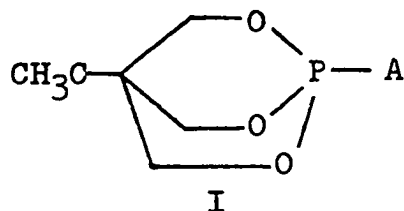
In a series of derivatives of I, Verkade et al. (38) have observed that a linear correlation exists for the POCH

coupling constant and the chemical shift of the methylene protons. As the coupling constant increases, the chemical shift moves progressively downfield. It was concluded that the rise in $J(\text{POCH})$ was due to an increase in s-character of the three P-O bonds as the phosphorus acceptor bond increases in p-character as a result of the increasing electronegativity of the acceptor groups. This increasing electronegativity is also reflected in the downfield shift of the methylene protons. The series of derivatives of I studied included the $\text{B}(\text{CH}_3)_3$ and BH_3 adducts and the CH_3CH_2^+ and $(\text{C}_6\text{H}_5)_3\text{C}^+$ ions. These four acceptor groups are given in terms of increasing electronegativity.

In this case, the postulated Br^+ acceptor is probably even more electronegative than $(\text{C}_6\text{H}_5)_3\text{C}^+$ and it would be predicted that $\text{Br}^+\text{P}^+(\text{OCH}_2)_3\text{CCH}_3$ should have the greatest downfield chemical shift for the methylene protons and also the largest $J(\text{POCH})$ value compared to the derivatives studied by Verkade et al. (38). This was found to be so as seen in Table 4. A plot of $J(\text{POCH})$ versus chemical shift for the compounds given in Table 4 (see Figure 1) was found to follow the equation $\delta = (0.25)J + 3.44$ with a correlation coefficient of 0.98 which substantiates its formulation as a phosphonium salt rather than a neutral species.

Further evidence for the ionic nature of this compound was provided by a conductometric titration of an acetonitrile

Table 4. Coupling constants and chemical shifts of I and several derivatives



Compound A =	Methylene chemical shift	J(POCH) (Hz)	Reference
lone pair	3.93	1.8	36
B(CH ₃) ₃	3.98	2.2	36
BH ₃	4.30	4.2	36
⁺ C ₂ H ₅	4.86	5.2	36
⁺ C(C ₆ H ₅) ₃	4.92	5.8	36
⁺ Br	5.19	7.2	this work

solution of I (R = Me) at 0° C with a solution of bromine (see Figure 2). At the equivalence point, i.e., when a molar amount of bromine had been added, the solution was found to exhibit an equivalent conductance of 193. A typical 1:1 electrolyte, e.g., (n-C₄H₉)₄N NO₃, has an equivalent conductance of 158 (53) in acetonitrile.

The results of the nmr and ir studies on the hydrolysis of I (R = Me) are summarized in Tables 5 and 6, respectively.

Figure 1. Plot of ${}^3J_{\text{PH}}$ versus δ_{CH_2} for $\text{P}(\text{OCH})_2\text{CCH}_3$ and several derivatives

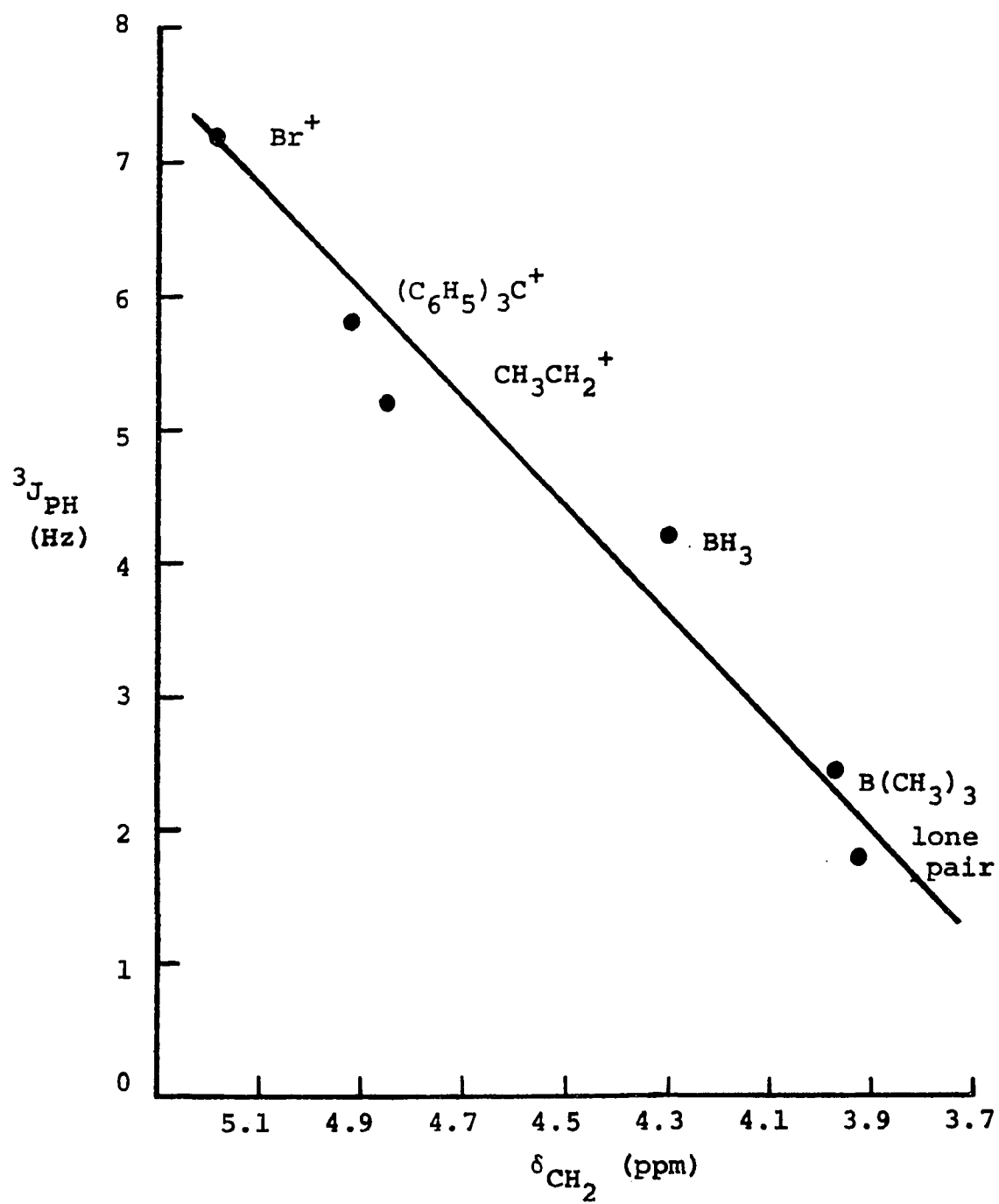


Figure 2. Plot of resistance versus ml of bromine solution added to a solution of $P(OCH_2)_3CCH_3$

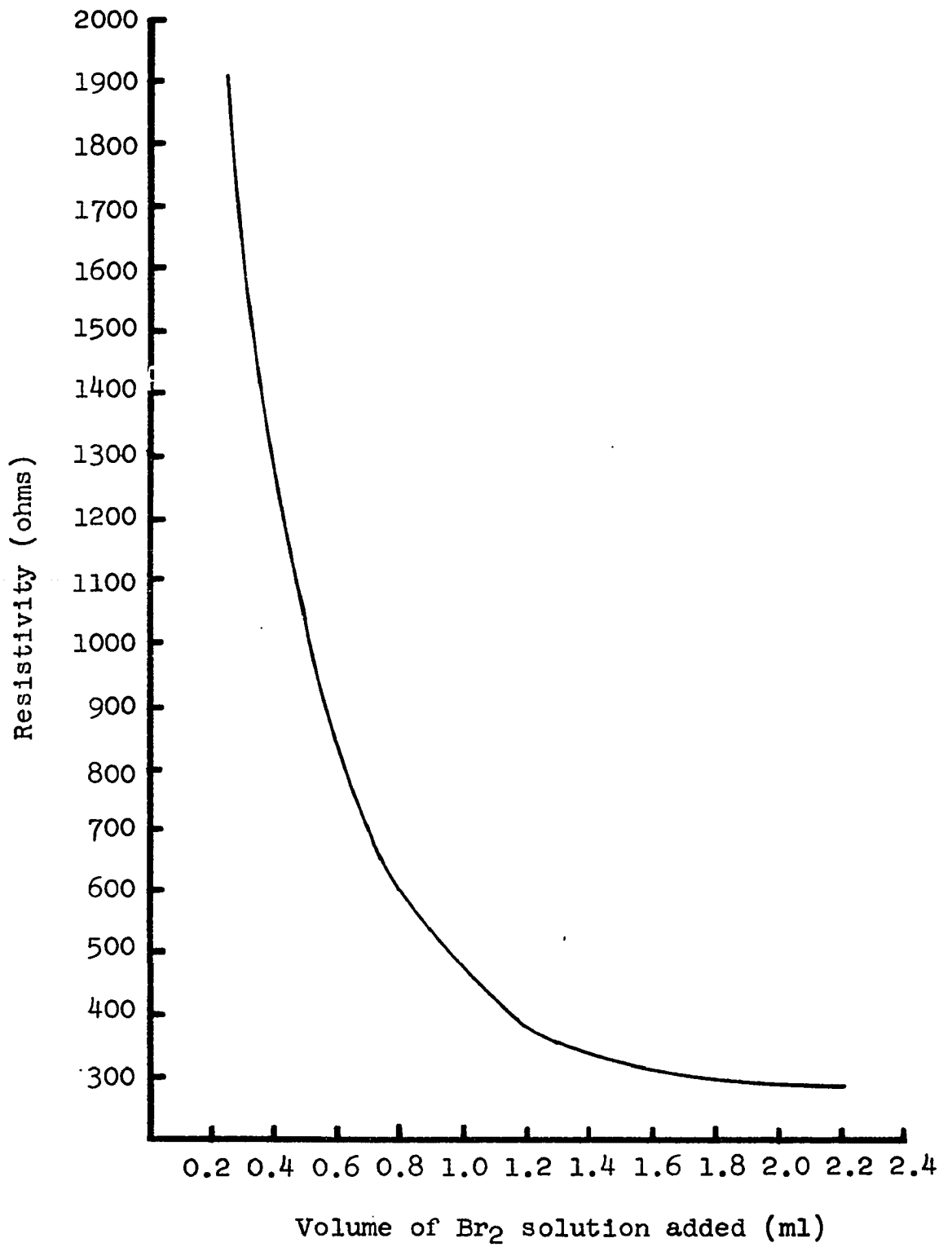
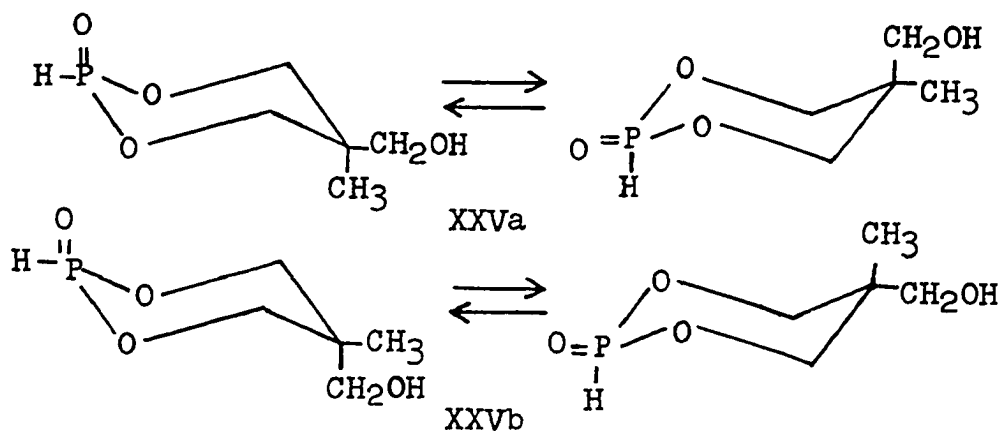


Table 5. nmr results of hydrolysis of $P(OCH_2)_3CCH_3$ 

	Chemical shifts (ppm)			
	60 MHz		100 MHz	
	H ₂ O	D ₂ O	H ₂ O	D ₂ O
axial CH ₃	1.15	1.14	1.15	1.15
equatorial CH ₃	0.81	0.79	0.80	0.79
axial <u>CH</u> ₂ OH	3.64	3.64	3.64	3.63
equatorial <u>CH</u> ₂ OH	3.36	3.33	3.34	3.33
<u>CH</u> ₂ OH	3.58	absent	3.60	absent
upfield P- <u>H</u> ^a	6.84	absent	6.86	absent
downfield P- <u>H</u>	6.86	absent	6.88	absent

$${}^a 1J_{P-H} = 677 \text{ and } 681 \text{ Hz.}$$

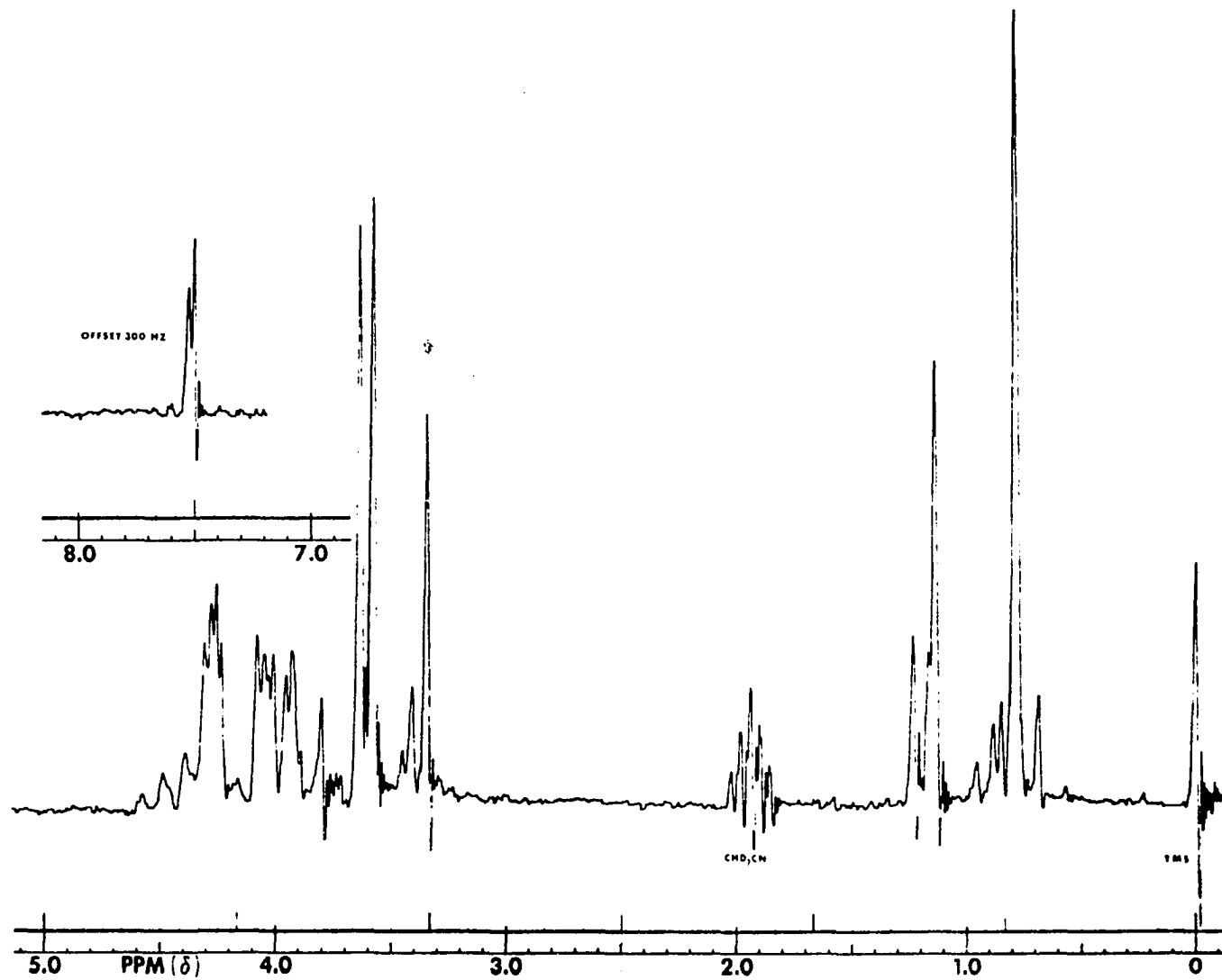
Table 6. I r results of hydrolysis of $P(OCH_2)_3CCH_3$

	H ₂ O	Frequency (cm ⁻¹) D ₂ O	H ₂ ¹⁸ O
$\nu(P=O)$	1297	1295	1253; 1294 med.
$\nu(P-H)$	2414	2410 weak	2410
$\nu(P-D)$	absent	1760	absent
$\nu(O-H)$	3510	3510 weak	3510
$\nu(O-D)$	absent	2600	absent

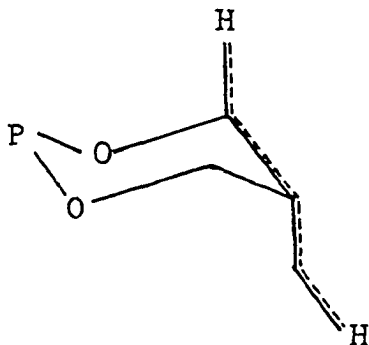
The formation of the products was followed by nmr spectroscopy in which it was found that the reaction was essentially complete after approximately two hours since no further changes in the spectrum were observed after this time. The nmr spectrum after 24 hours is shown in Figure 3.

The assignments of the nmr peaks for the stereochemically different axial and equatorial methyl groups and their respective equatorial and axial methylene chlorides are based on chemical shifts, widths at half-heights, and relative abundances. Thus, of the two methyl groups at 1.15 and 0.81 ppm, their respective widths at half-height are 1.4 and 1.0 Hz. Expansion of the 1.15 ppm peak shows that it is actually a triplet ($J = 0.6$ Hz). A planar W configuration is known to enhance four-bond

Figure 3. 60 MHz nmr spectrum of hydrolysis products of $\text{P}(\text{OCH}_2)_3\text{CCH}_3$



long-range coupling (54) and such a configuration exists between the axial ring methylene protons and one of the protons in an exocyclic axial methyl group.



No similar W type configuration exists for an exocyclic equatorial methyl group. Furthermore, irradiation at a frequency corresponding to the downfield methyl group while scanning the ring methylene protons caused a sharpening of lines in the downfield portion. No change was observed if the upfield methyl group was irradiated. Thus, the axial 4-methyl group is less shielded than the equatorial 4-methyl group.

Integration of the two methyl peaks gave a rough ratio of 1:1.75 with the 0.80 ppm (i.e., equatorial methyl) peak being the more abundant. As a result, the two methylene chloride peaks can be assigned as 3.64 ppm axial and 3.36 ppm equatorial based on their relative intensities. Again, the axial protons are less shielded than the equatorial protons.

The CH_2OH and the P-H protons were assigned as a result of their disappearance when deuterium oxide was

used for the hydrolysis. At 60 MHz, the downfield member of the P-H doublet actually appeared as two peaks with a separation of approximately 1 Hz. The upfield members definitely appear as two peaks with a separation of 5 Hz at 100 MHz and 4 Hz at 60 MHz. Thus the presence of two chemically different P-H protons is firmly established.

Phosphoryl stretching frequencies generally occur in the range 1200 to 1500 cm^{-1} (55). The large symmetrical band at 1297 cm^{-1} (H_2O) or 1295 cm^{-1} (D_2O) is assigned as the P = O stretching frequency. This was further substantiated by using 83 percent ^{18}O labelled H_2O . The band at 1294 cm^{-1} is present in medium intensity but a very intense band now appears at 1253 cm^{-1} representing a shift of 41 cm^{-1} . The ratio of the squares of these two frequencies is 1:1.07. The ratio of the reduced mass of $^{31}\text{P}-^{16}\text{O}$ to $^{31}\text{P}-^{18}\text{O}$ is 1:1.08 which is in very good agreement with the experimentally deduced ratio.

Similarly, P-H stretching frequencies are found from 2350 to 2450 cm^{-1} (56). The medium intensity band at 2414 cm^{-1} when H_2O is used is assigned to this mode. This band shifts to 1760 cm^{-1} when deuterium oxide is used and thus substantiates the assignment. The theoretical ratio of the two frequencies is calculated to be 1:1.94. The experimental value is 1:1.88. Again the absorption is very symmetrical suggesting the presence of only one

type of phosphoryl oxygen.

Bertrand's preliminary conclusions (20) concerning this reaction were that two compounds were formed which possessed different stereochemistries at phosphorus. His argument was based on the fact that the downfield doublets for the P-H proton were not of equal width at half-heights but he was unable to assign the upfield half of the doublet. In this study it was found that the two upfield peaks are separated by 5 Hz compared to the 1 Hz separation of the downfield pair. Moreover, each of the peaks are 0.35 Hz wide at half-height. The intensities are different due to the relative amounts of the two isomers present.

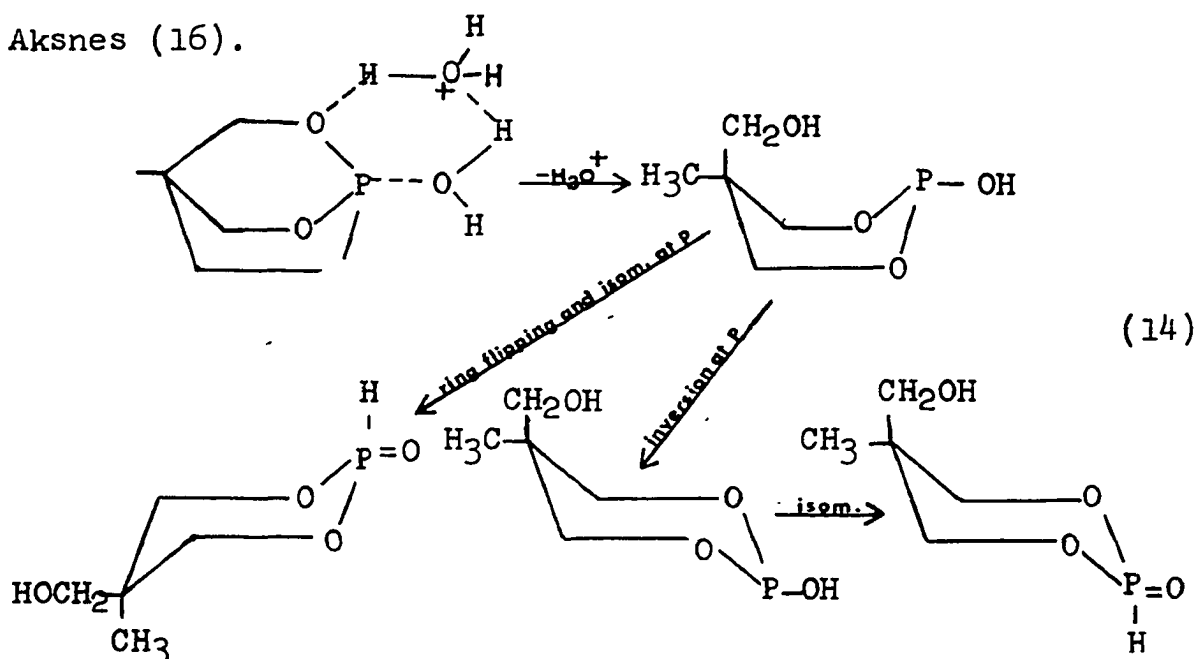
The data seem to be most readily interpreted in terms of identical stereochemistries at phosphorus in the two isomers. The actual difference in chemical shift between the two types of P-H protons is only 0.02 ppm. This is to be compared with a difference of 0.35 ppm between the protons in an axial and an equatorial methyl group. Furthermore, only one phosphoryl stretching band and only one P-H stretching frequency was observed. As a result, it seems reasonable to conclude that although two isomeric compounds are formed these isomers differ in configuration at the carbon end of the molecule rather than at phosphorus. If the proton directly bonded to phosphorus were in an equatorial position, a planar W configuration would exist

between this proton and each of the ring equatorial methylene protons. The fact that no long-range coupling between these two protons is observed mildly suggests that the P-H proton is axial in both isomers which would be in accord with the recent conclusions drawn by Lambert et al. (57) for the thermodynamically most stable position of this proton in phosphorinane ($\text{HP}(\text{CH}_2\text{CH}_2)_2\text{CH}_2$) on the basis of low-temperature nmr studies. Our tentative conclusion is also in accord with the observed tendency of the phosphoryl oxygen to adopt the equatorial position. Regardless of the actual position of the proton on the phosphorus in these isomers, it is interesting that hydrolysis leads to only one such stereochemistry in both isomers in the case of I whereas the isomerism in the hydrolysis products of VIII (IXa and IXb) is solely at phosphorus.

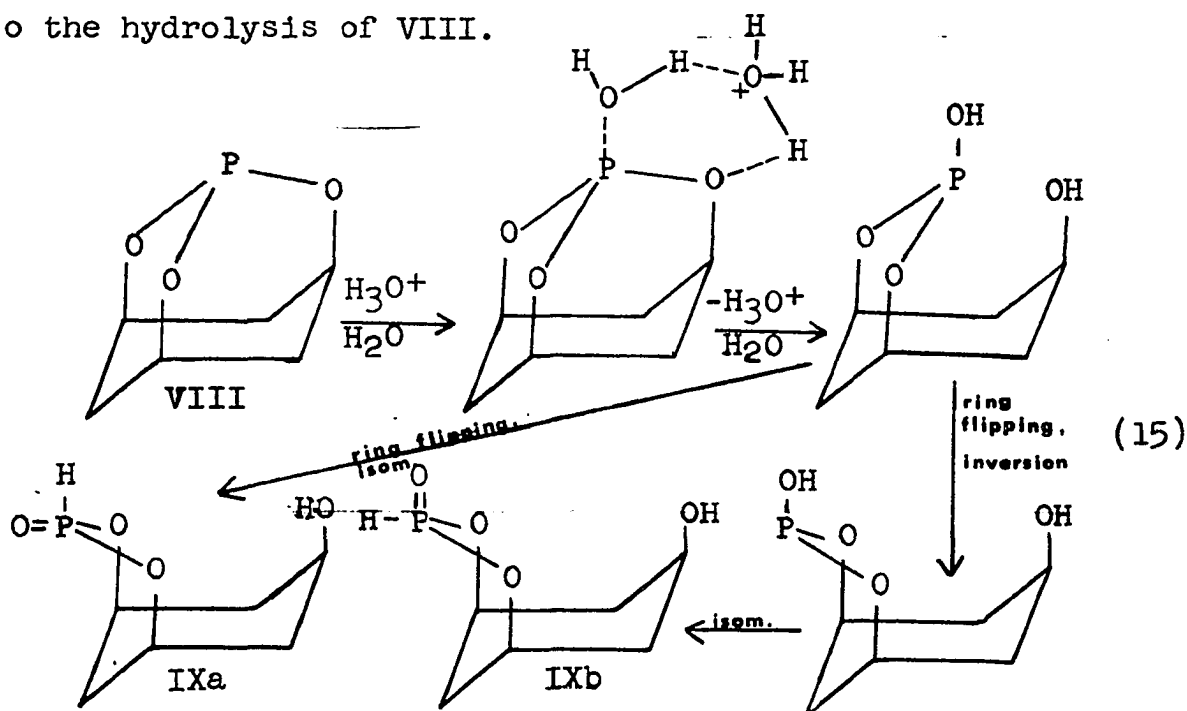
It is probable that if the other conformers of isomers XXVa and XXVb are present, their relative concentration would be negligible. If comparable quantities of the two conformers existed, the long-range coupling would be averaged out among all the ring methylene protons and methyl protons according to their relative amounts. Since this is not observed, one dominant conformer must be present in solution for each isomer.

A mechanism which accounts for the formation of the

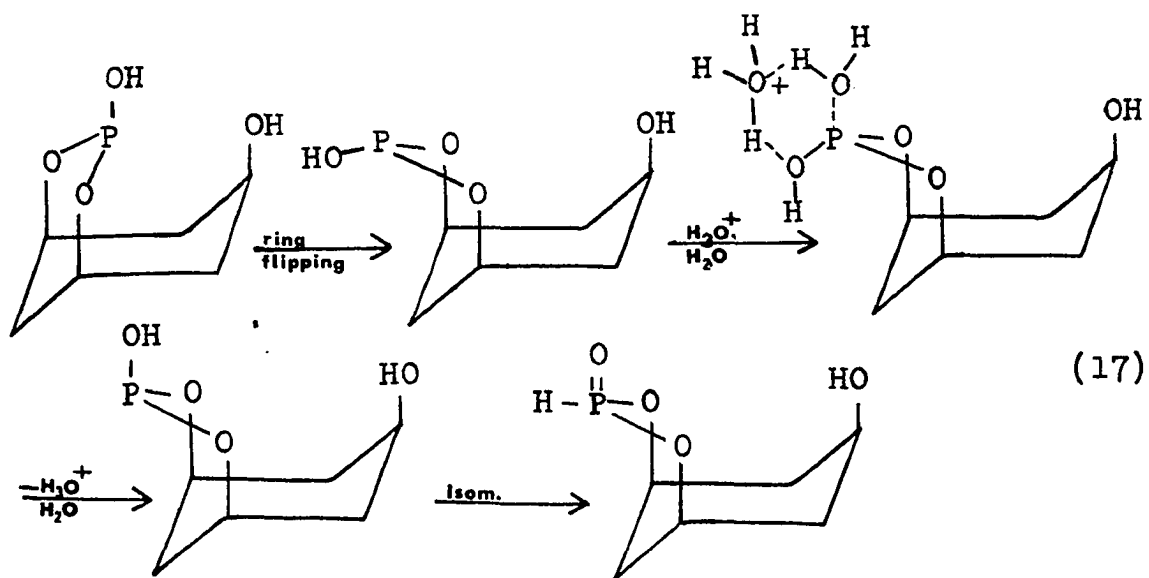
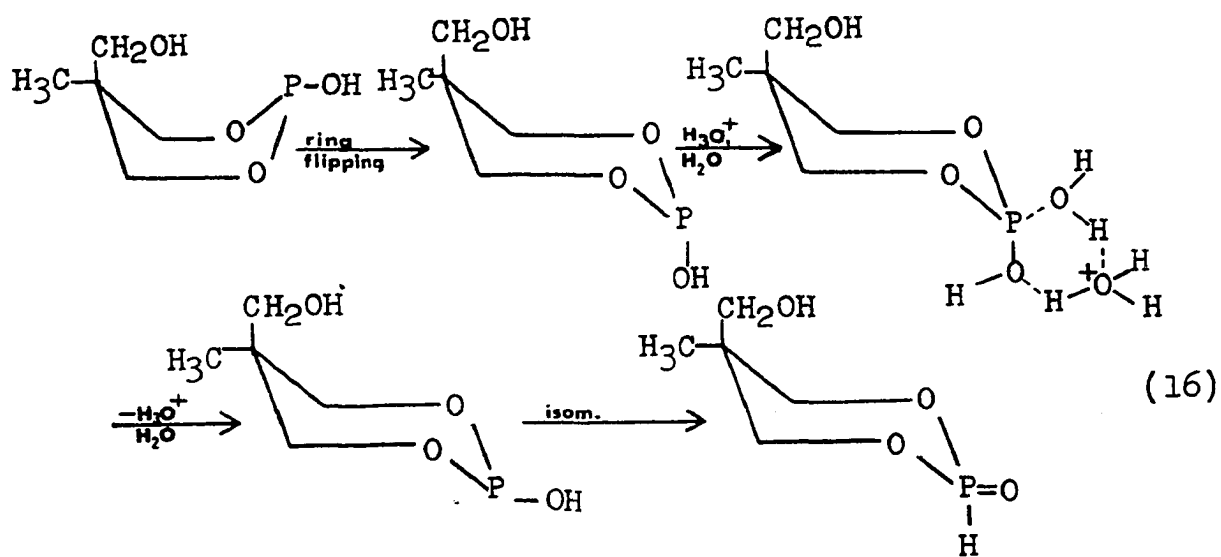
two isomers is analogous to that postulated by Aksnes and Aksnes (16).



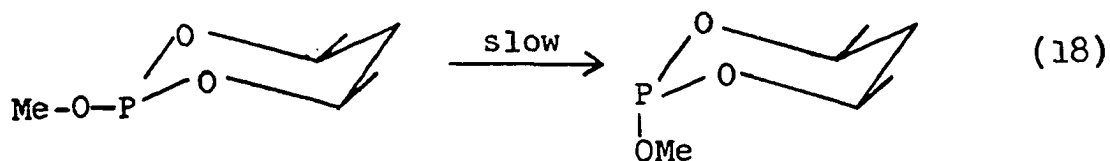
The above pathways are supported by the labelling experiments which showed that the exocyclic O and H attached to phosphorus came from the water in the hydrolysis. Thus P-O bond breaking occurs during the reaction. A similar mechanism could apply to the hydrolysis of VIII.



An alternative mechanism accounting for the experimental observations which does not necessitate inversion at phosphorus can also be proposed for both hydrolyses. The relevant steps could be as shown below. Such a



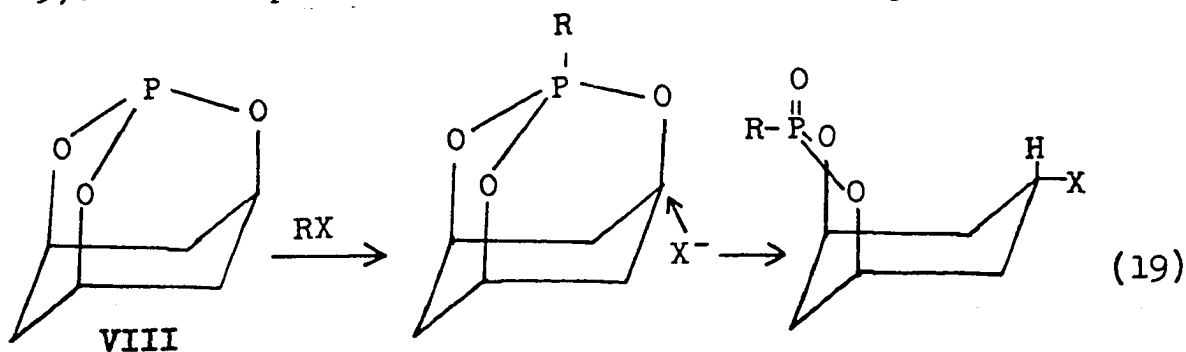
mechanism might be more preferable in that inversion at phosphorus under thermodynamic conditions is notably slow. Thus the inversion at phosphorus in the following reaction



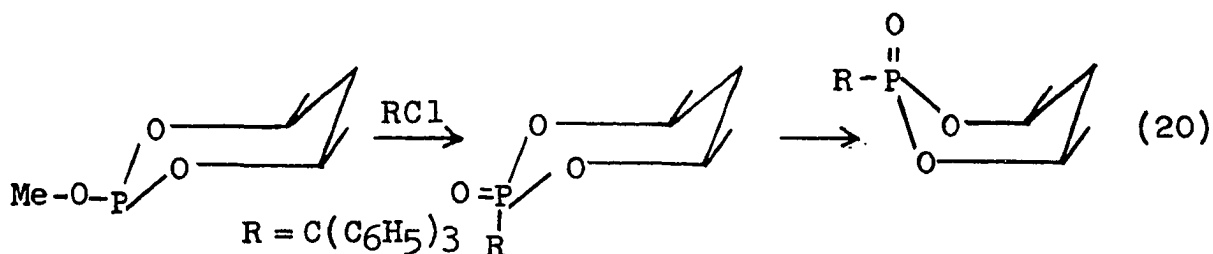
is slow when the former isomer is pure, even though the latter isomer is the more thermodynamically stable form (22). On the other hand, kinetic factors may prevail allowing facile inversion to take place in the hydrolysis process.

The temporary production of a trivalent phosphorus by P-O bond breakage permits several conclusions to be made concerning ring opening reactions of phosphites. First, the production of two isomers in the hydrolysis of VIII shows that isomerization of the phosphorous acid intermediate can take place in two stereochemically different ways. Whether IXa is a more or less thermodynamically stable configuration than IXb in the boat form of the six-membered ring remains to be investigated. Second, the preferred configuration around phosphorus in the chair-form hydrolysis products of I (i.e., equatorial oxygen and axial hydrogen) controls the isomeric stereochemistry at C₄. Third, whereas isomeric configurations at phosphorus

are at least possible in the hydrolysis of polycyclic phosphites, it is not observed in the Michaelis-Arbuzov reaction owing to the preservation of four-covalent phosphorus throughout the mechanism. Thus as shown in reaction (3) the stereochemistry at phosphorus is uniquely determined in I and the same is true of VIII (58) (reaction 19). An example of the conformational consequences of this



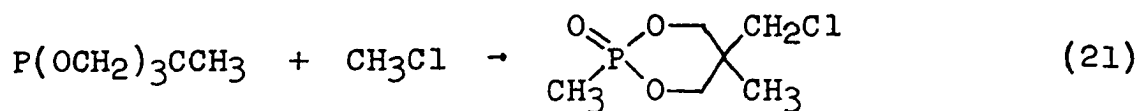
phenomenon is demonstrated by the recent crystal structure determination (59) of the Michaelis-Arbuzov product of the reaction below. Apparently the bulky $C(C_6H_5)_3$ group is responsible for the boat configuration which is adopted in the solid state structure. Isomerization at phosphorus leading to a more stable chair form cannot occur owing to the mechanism which offers the phosphorus no choice.



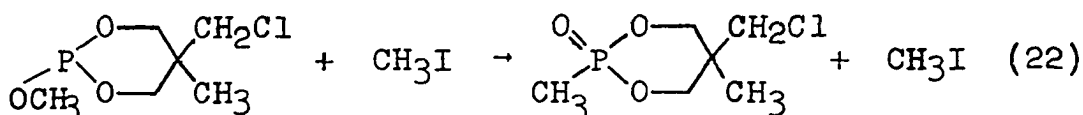
It is also interesting to note that XXVa, b can be dehydrated in 69 percent yield to I when heated under vacuum to 80°. This is similar to the behavior of IXa, b which were reported to be dehydrated at 120° under vacuum in 70 percent yield (18). It was also noted by these authors that both isomers react with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in acetone at room temperature to lose water in the formation of the copper(I) complex $(\text{CuL}_4) \text{ClO}_4$ (L = VIII).

As a result of the investigation on the 1-R-1-oxo-1-phospha-2,6-dioxacyclohexanes, it was decided that a study of the stereochemistry of the corresponding 1-R-1-phospha-2,6-dioxacyclohexanes would be of importance since these trivalent phosphorus compounds are in many cases the precursors of the corresponding pentavalent compounds. For example, the synthesis of 1-methyl-1-oxo-4-chloromethyl-4-methyl-1-phospha-2,6-dioxacyclohexane can be accomplished via the Michaelis-Arbuzov reaction of I (R = Me) and methyl chloride, or it can also be produced by the reaction of methyl iodide and 1-methoxy-4-chloromethyl-4-methyl-1-phospha-2,6-dioxacyclohexane. Reaction 22 is known to proceed stereospecifically as discussed earlier.

The syntheses of many of these compounds have been reported during the last 20 years (27-30). Besides the alkyl substitution at phosphorus, several halogen substituted compounds were also prepared. Many of these



I

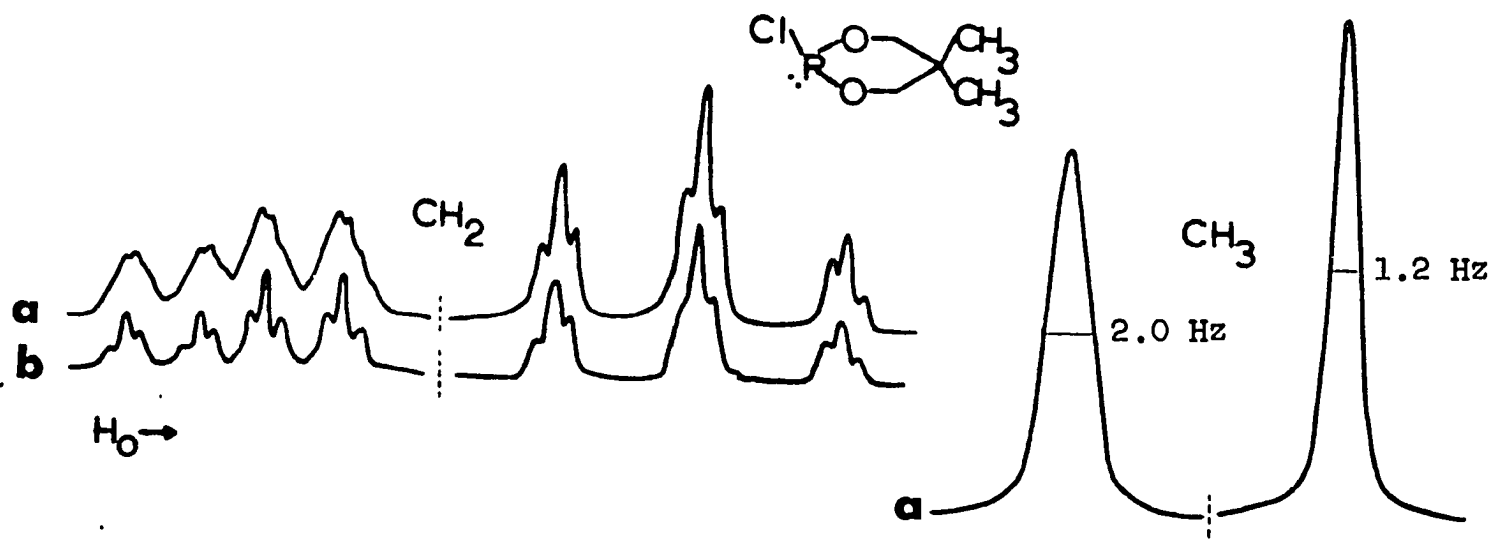


compounds were examined at several concentrations and temperatures and in various solvents in the present research.

The ^1H nmr spectra of the 4,4-dimethyl substituted compounds have many features in common. The spectrum of XXXIII is given in Figure 4a as an example. It is seen that of the two methyl resonances, which are generally separated by approximately 0.4 ppm, the downfield resonance is the broader of the two. As discussed earlier, this is a result of long-range four bond coupling with the ring axial methylene protons. Figure 4b shows the effect in the ring methylene region when the downfield methyl group is decoupled. Again, decoupling of the upper methyl absorption produces no changes. A planar W also exists between the two equatorial methylene protons giving rise to enhanced long-range coupling. As a result of these long-range couplings, unsymmetrical boats or twist-boats can be ruled out since they do not possess the appropriately positioned protons.

Figure 4a. 60 MHz nmr spectrum of XXXIII

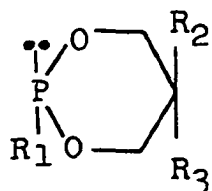
Figure 4b. 60 MHz nmr spectrum of XXXIII showing effect on methylene protons of decoupling downfield methyl peak



If these systems contained comparable quantities of rapidly-interconverting chair or boat conformers, it would be expected that the enhanced long-range coupling would be averaged out among all of the methylene and methyl protons according to the relative amounts of conformers present. That this does not occur is evidence for one dominating conformer in solution. If only the phosphorus end of the ring flipped between a chair and boat conformation, the necessary planar W's still exist for long-range coupling and therefore this possibility must be considered. The usual steric arguments against boat conformations may not be as valid in these cases since the phosphorus end of the ring may be flattened as in the chair forms of the several solid state pentavalent derivatives already discussed.

Evidence for the predominance of a chair form is available from the ring POCH coupling constants. It has been suggested (51, 60-63) that a dihedral angular dependence of $J(\text{POCH})$ exists similar to the well known $J(\text{HCCH})$ dependence on dihedral angles. In a boat form, the dihedral angles are of approximately 60° each and therefore the two values of $J(\text{POCH})$ should be approximately equal. A chair form contains dihedral angles of 180° and 60° which should give different values of $J(\text{POCH})$. This has been found to be the case as can be seen in Table 7.

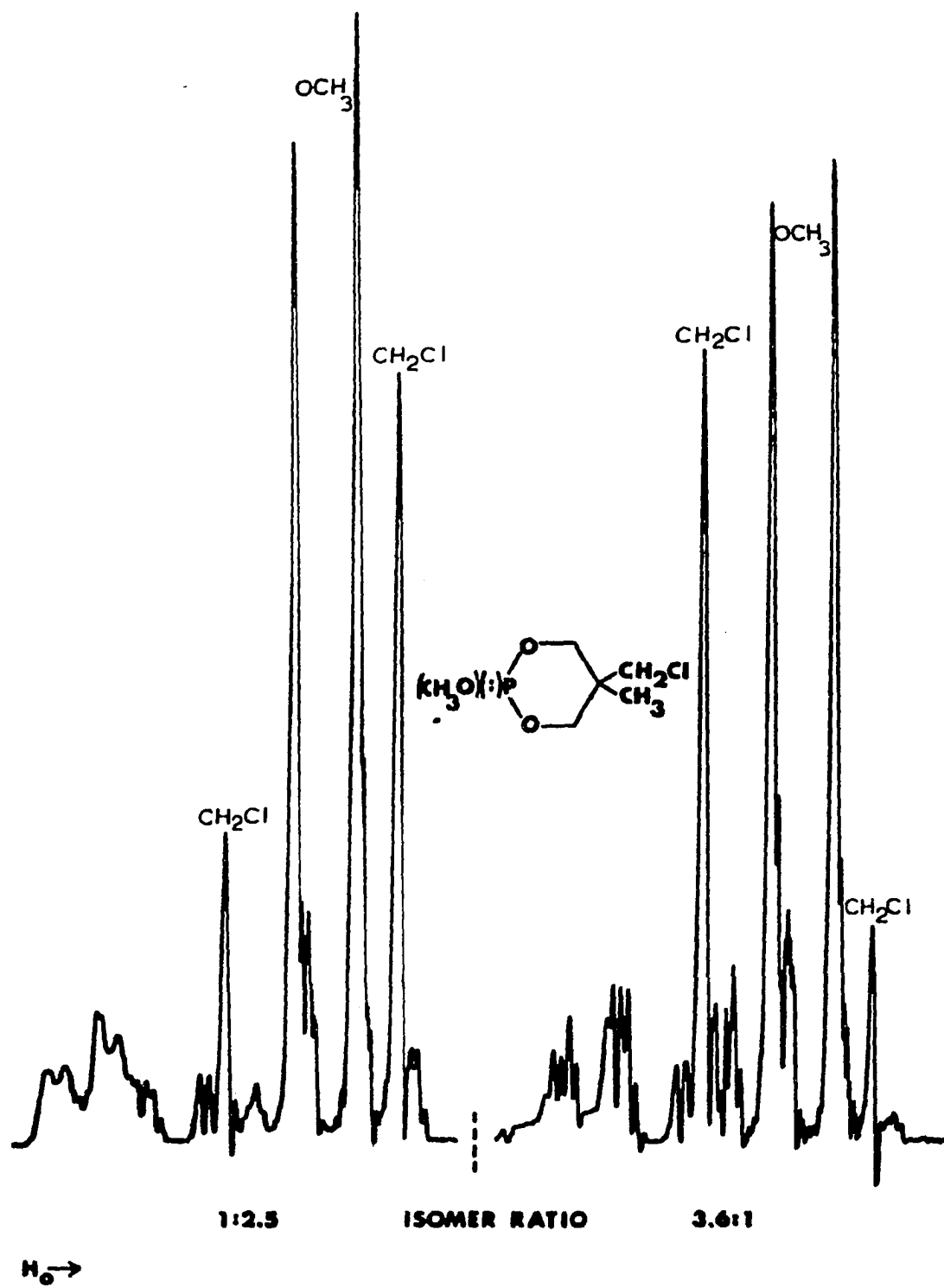
The 4-methyl-4-chloromethyl derivatives show a con-

Table 7. Coupling constants ($J(\text{POCH})$) for some 1-R-1-phospha-2,6-dioxacyclohexanes

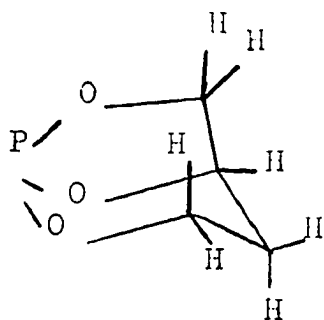
Compound	R_1	R_2	R_3	Coupling constant		Solvent
				POCH_A	POCH_B	
XXXa	OCH_3	CH_3	CH_2Cl	10.5	3.1	neat, CDCl_3
XXXb	OCH_3	CH_2Cl	CH_3	10.5	3.5	neat
XXXI	F	CH_3	CH_3	10.9	3.0	neat
XXXIIa	F	CH_3	CH_2Cl	10.5	3.5	neat
XXXIII	Cl	CH_3	CH_3	11.2	5.7	neat
XXXIVa	Cl	CH_3	CH_2Cl	10.5	5.7	neat
XXXV	Br	CH_3	CH_3	10.5	6.4	C_6H_6
XXXVI	Br	CH_3	CH_2Cl	10.5	6.5	C_6H_6

formational similarity to the corresponding 4,4-dimethyl compounds. However, the possibility of isomers now exists. That is, if one chair form is very predominant, the exocyclic 4-methyl group could be in an axial or an equatorial position. Compound XXXa has a relatively narrow 4-methyl resonance with respect to compound XXXb (see Figure 5). This indicates that the a isomer possesses an equatorial methyl group while the b isomer possesses an

Figure 5. 60 MHz nmr spectra of two isomeric mixtures of
XXXa, b. Methyl resonances are not shown

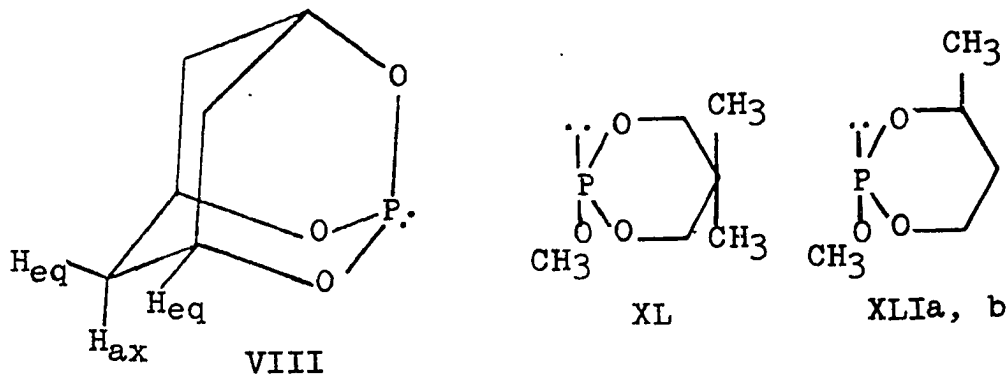


axial methyl group. In fact, the 4-methyl resonance of XXXb, upon expansion appears as a triplet with $J = 0.7$ Hz which was also observed by Gagnaire et al. (64). This is attributed to coupling with the axial methylene protons as previously discussed. In accordance with this, the low-field half of the ring methylene resonance of XXXb is broadened with respect to that of XXXa. When the chloromethyl group is present in an axial position, it apparently does not have its protons appropriately positioned for W coupling to the axial ring methylenes. If the chlorine is positioned as far away from the ring as possible this would be the case. In the transesterification preparation of the isomeric mixture XXXa and b, it was found by integration that the ratio of a:b was 3.6:1; that is, the isomer with equatorial CH_3 and axial CH_2Cl (see Figure 5) predominates. This may be a result of the longer C-Cl bond versus the C-H bond giving less steric interaction for an axial chloromethyl than an axial methyl group. In the six-membered chair shown below Kainosho and Nakamura (65) analyzed $J(\text{POCH}_{\text{ax}})$ as 2.5 Hz and $J(\text{POCH}_{\text{eq}})$ as 9 Hz.

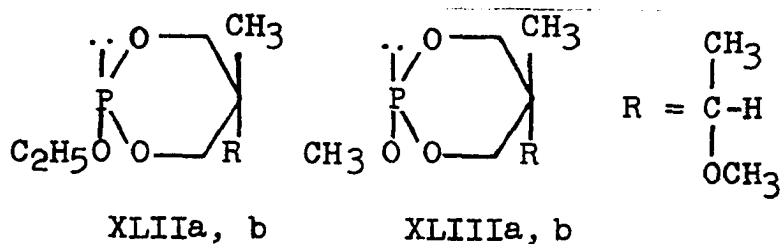


This tends to confirm the coupling assignments given in Table 7.

The question of the stereochemistry at phosphorus has been investigated by several workers. Gagnaire et al. (64) have concluded that the preferred stereochemistry is equatorial R, axial phosphorus lone pair in XXXI, XXXIII and several other related compounds. Their argument is based on steric factors and the dependence of the magnitude of $J(\text{POCH})$ on the POCH dihedral angle and the disposition of the phosphorus lone pair relative to the coupled nuclei. The same conclusion was reached by Albrand et al. (34) for related compounds. They used similar arguments and introduced the POCCH coupling constants as supporting evidence. In these arguments the values of the cyclic $J(\text{POCCH})$ and $J(\text{POCH})$ in XL and XLI were compared with those determined by Verkade and King (51) for the bicyclic adamantane phosphite (VIII) shown below. A $J(\text{POCH}_{\text{eq}})$ of 10.8 Hz in XL versus 6 Hz in VIII; a $J(\text{POCCH}_{\text{eq}})$ of 3.6 Hz in XLIa versus 0.5 Hz in VIII; and a $J(\text{POCCH}_{\text{ax}})$ of 0.5 Hz in XLIa



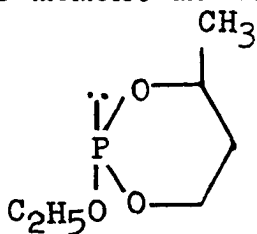
versus 0.0 Hz in VIII suggested that the methoxyl group in XL and XLIa is not axial and is therefore equatorial. They concluded that the stereochemical disposition of the phosphorus lone-pair has a large influence on the phosphorus ring hydrogen coupling constants. These arguments do not carry as much weight when it is realized that $J(\text{POCH}_{\text{ax}})$ in the two isomers of XLI differ by only 1 Hz. This suggests that lone pair disposition is not very important. Furthermore, one of the values of $J(\text{POCCH})$ is about 2.5 Hz in XLIa which supposedly has a different stereochemistry at phosphorus than XLIIb. Thus, neither XLIa nor XLIIb have four-bond couplings similar to those of VIII. Also, the bonding and structure of XL and XLIa, are not accurately known and comparison of these coupling constants may not be justified. Bogat-ski et al. (33) stated that XLIIa, b and XLIIIa, b possess an equatorial alkoxy group from the form



of the ring methylene proton resonance but no reasoning was given.

On the other hand, White et al. (32), Hague et al. (25), and Bodkin and Simpson (31) have concluded that the alkoxy group occupies the axial position in at

least the more stable isomer of three different pairs of geometrically isomeric phosphites. These conclusions were arrived at by investigation on reaction products of the phosphites which are believed to form in a stereospecific manner. Thus, x-ray diffraction results on one compound obtained from the reaction of XLIVa, b and methyl iodide and on another compound of XLIVa, b and t-butylhydroperoxide suggest that the methoxyl group of XLIVa is axially disposed in a chair conformer. The BH_3 adduct of XXXa, b is assumed to form with retention of configuration while sulfur does so in XLVa, b. Dipole moment measurements agreed with calcu-



XLVa, b

lated values based on vectorial summation of bond moments for the BH_3 adducts of XXXa, b. Thus the a isomer, which is the thermodynamically stable form is expected to possess an axial alkoxy group, while the b isomer has an equatorial alkoxy group. In the cases where no isomers exist, the predominance of an axial alkoxy group seems most likely.

Other heterocyclic systems also seem to adopt the sterically unfavorable axial position. For example, an axial oxygen, equatorial sulfur lone pair geometry has been found for the 1-oxo-1-thia-2,6-dioxacyclohexanes (66).

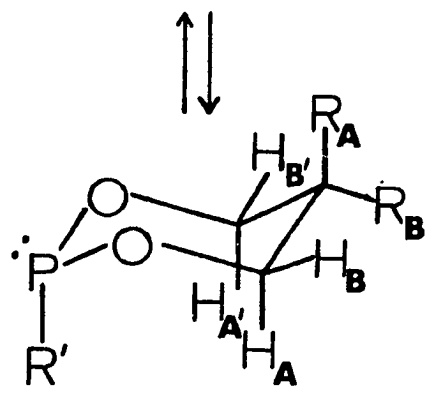
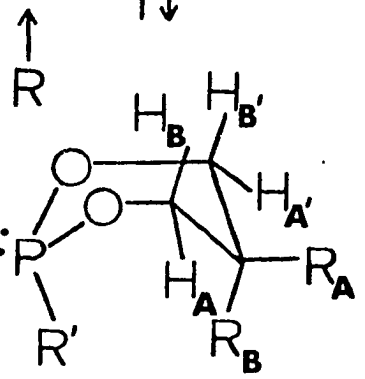
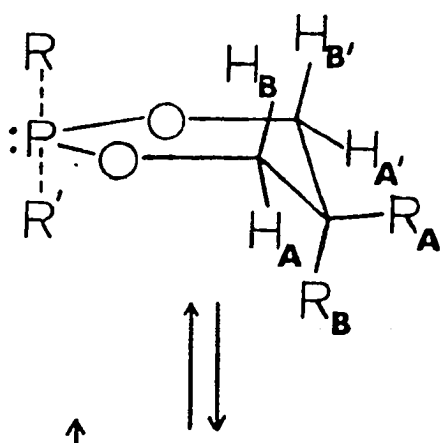
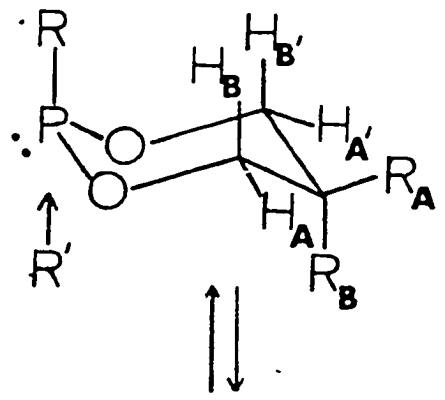
Also, an axial alkoxy, equatorial hydrogen stereochemistry is observed in 2-alkoxy-1,3-dioxacyclohexanes (67).

The equatorial alkoxy stereochemistry favored for the b isomers and axial for the a isomers seems also likely to hold for the halogen isomers. Thus the chlorine in XXXIVa is very probably axial since its reaction with methanol in base gives mainly XXXb as would be expected for an SN_2 mechanism.

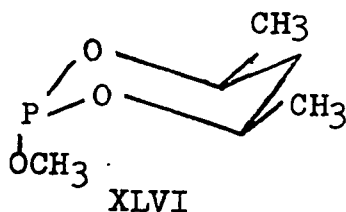
The temperature and concentration dependencies for many of the 1-R-1-phospha-2,6-dioxacyclohexanes ($R = OCH_3, F, Cl, Br$) can be accounted for on the basis of an intermolecular exchange of the exocyclic R group at phosphorus involving an inversion of the bonds to phosphorus. A possible mechanism for this process is shown in Figure 6. This mechanism is assumed to be the same for all the molecules investigated. In the initial structure, $H_A, H_A',$ and R_A are cis to R while $H_B, H_B',$ and R_B are trans to R. This cis, trans relationship is inverted in the final product.

The process is deduced to be an intermolecular exchange rather than an intramolecular inversion at phosphorus followed by ring flipping for two reasons. Dilution with chloroform causes sharpening and separation of resonances that exhibit partial coalescence. This was also observed by Goldwhite and Fontal (68) in 1-chloro-3,3,4,4-tetramethyl-1-phospha-2,5-dioxacyclopentane. They

Figure 6. Proposed intermolecular exchange mechanism for
1-R-1-phospha-2,6-dioxacyclohexanes



found that the process causing the two methyl resonances to coalesce could be slowed by dilution with benzene, toluene, chloroform and dioxane. The aromatic solvents used could cause $\Delta \delta \text{CH}_3$ to change via a concentration dependence in the absence of exchange. However, the results obtained with chloroform and dioxane suggest an intermolecular exchange. Also, White (22) showed that tetraphenylarsonium chloride causes the 3,5 dimethyl resonances of XLVI to broaden suggesting that the rate-

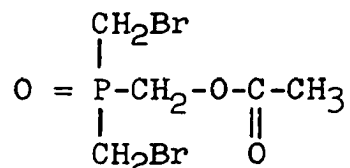


controlling step of the process involves attack of chlorine on the cyclic molecule.

The rate of exchange for the isomeric pairs XXXa, b, XXXIIa, b, XXXIVa, b, and XXXVIa, b depends on the exocyclic R in the order: $\text{CH}_3\text{O} < \text{F} < \text{Cl} < \text{Br}$. The order $\text{CH}_3\text{O} < \text{F}$ is based on the fact that the ratio of the fluoro isomers changed appreciably from 40° to 161° whereas the ratio of methoxyl isomers did not during approximately the same length of time. The extent of spectral broadening for a series of compounds can be used as an indication of relative exchange at a given temperature if the uncoalesced lines are equally separated in all the compounds. For

Table 8 gives the results of various nmr experiments including ^1H , ^{13}C , and ^{31}P which were performed on this compound. The ^{13}C and ^{31}P spectra, and the signs of all the coupling constants, were obtained by means of inter-nuclear double resonance (INDOR) experiments which allow the determination of the relationship between the ordering of the transition energies of a second nucleus which is coupled to the first nucleus as long as both nuclei are coupled to a third nucleus. This relationship gives the relative signs of the couplings of the first two nuclei with respect to the third. Friedman and Gutowsky (70) describe and prove a mnemonic method for establishing the relative signs of the coupling constants in an AMX system by means of double resonance experiments. Whiffen (71) extended the discussion to the case in which the magnetogyric ratios of the coupling nuclei have different signs. Since all the nuclei mentioned in this dissertation have nuclear spin $I = 1/2$ and the same sign for their magnetogyric ratios, the determination of the relative signs of coupling constants from the double resonance experiments is rather straightforward.

Absolute signs of coupling constants can also be determined, although the experiments involved are usually much more complex. Several sources of such information include: 1) high resolution nmr spectrum in those cases

Table 8. Results of NMR experiments on bis (bromomethyl) acetoxy phosphine oxide^a

Bromomethyl group

$\delta_{\text{H}} = 3.12 \text{ ppm}$	${}^2\text{J}(\text{PH}) = - 6.5 \text{ Hz}$
$\delta_{\text{C}} = - 0.398 \text{ ppm}^{\text{b}}$	${}^1\text{J}(\text{PC}) = + 67 \text{ Hz}$
$\delta_{\text{P}} = - 33.55 \text{ ppm}^{\text{c}}$	

Acetoxy group

$\delta_{\text{CH}_2} = 4.37 \text{ ppm}$	${}^2\text{J}(\text{PH}) = - 4.2 \text{ Hz}$
$\delta_{\text{C}} = - 37.51 \text{ ppm}$	${}^1\text{J}(\text{PC}) = + 88 \text{ Hz}$
$\delta_{\text{CH}_3} = 2.22 \text{ ppm}$	

^aCD₃CN used for solvent.

^bChemical shift given with respect to external ¹³CH₃COOH: naturally abundant ¹³C.

^cChemical shift given with respect to external 85 percent H₃PO₄.

wherein cross terms between different relaxation mechanisms are important (72-74); 2) nmr spectra of partially oriented molecules obtained by application of a strong electric field to a sample of polar molecules (75, 76) or by dissolving the molecules of interest in a liquid-crystal

matrix (77, 78); 3) molecular beam techniques (79); or
4) broad-line spectral analysis of solid-state samples (80).

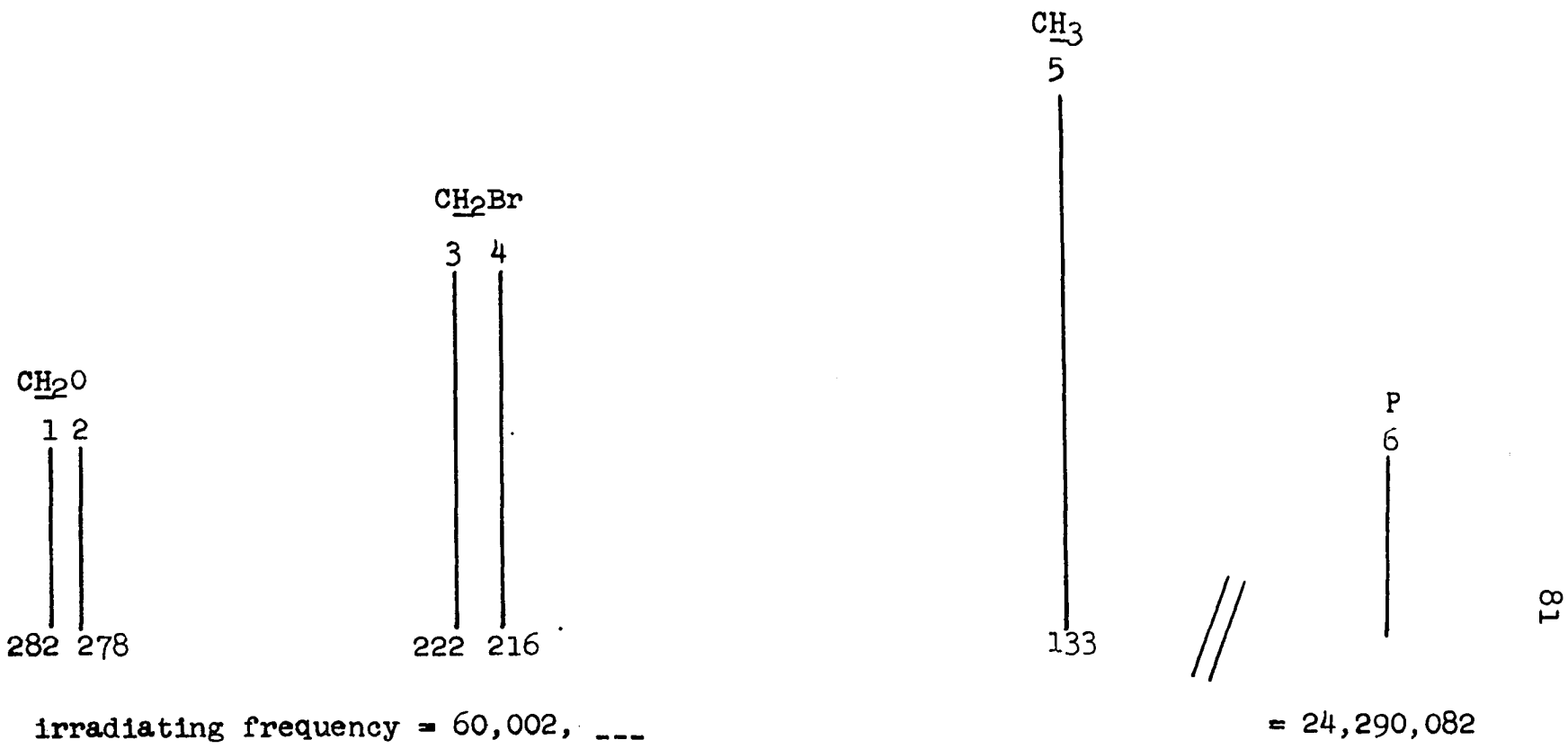
From such measured absolute signs, the signs of most other coupling constants in the same and related molecules have been determined via measurements of relative signs. To date, all data available appear to be consistent with the sign of the directly bonded ^{13}C - ^1H coupling constant to be absolutely positive (81). Relating signs of other couplings in a given molecule to this positive coupling constant then affords their absolute sign.

The procedure for obtaining INDOR spectra by means of the instrumentation available at Iowa State University has been given by Bertrand (35) and therefore will not be discussed here.

Figure 7a gives a representation of the ^1H and ^{31}P nmr spectra and shows the connectedness of the transitions. Similarly, Figure 7b shows how the lower half of the ^{13}C sidebands for each of the ^1H doublets is connected to the ^{13}C and ^{31}P transitions.

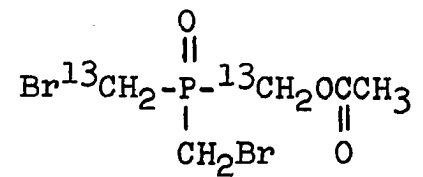
To calculate the ^{31}P chemical shifts obtained by means of the INDOR method, it is necessary to determine the frequency of a compound with a known ^{31}P chemical shift, such as $\text{P}(\text{OCH}_3)_3$, when the magnetic field is such that the protons in the internal standard used for the field-frequency lock resonate at 60,002,000 Hz. The known ^{31}P

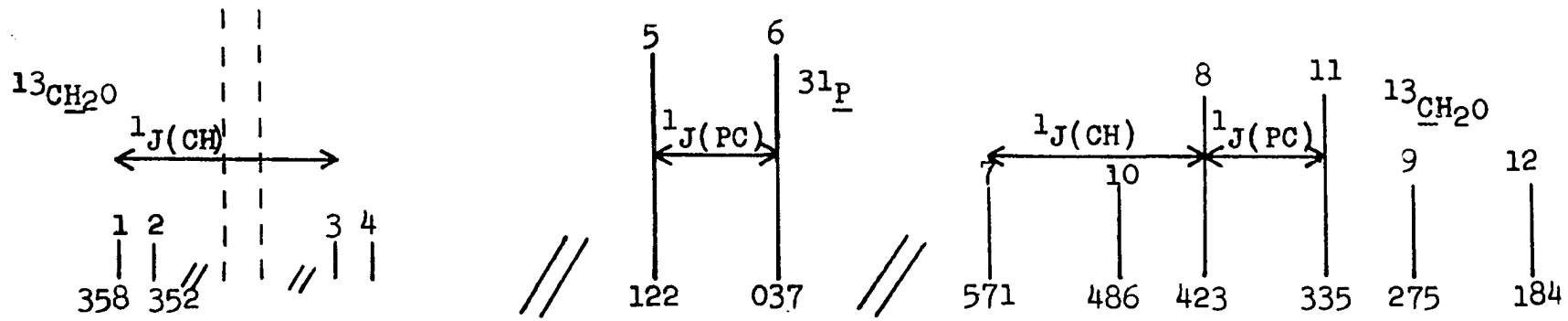
Figure 7a. Schematic representation of ^1H and ^{31}P nmr spectra of bis(bromomethyl) acetoxy phosphine oxide



lines 1, 2, 3, 4 \longleftrightarrow line 6

Figure 7b. Schematic representation of ^1H , ^{13}C , and ^{31}P nmr spectra of

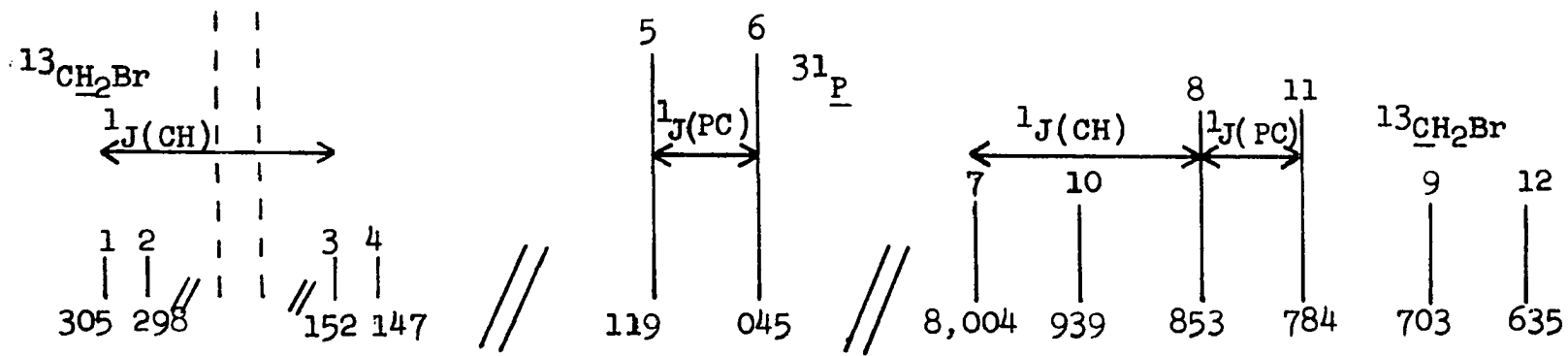




irradiating
frequency = 60,002, --- = 24,290, --- = 15,088, ---

lines 2, 4 \longleftrightarrow lines 7, 8, 9 lines 1, 2 \longleftrightarrow line 5

lines 1, 3 \longleftrightarrow lines 10, 11, 12 lines 3, 4 \longleftrightarrow line 6



irradiating
frequency = 60,002, --- = 24,290, --- = 15,087, ---

lines 2, 4 \longleftrightarrow lines 7, 8, 9 lines 1, 2 \longleftrightarrow line 5

lines 1, 3 \longleftrightarrow lines 10, 11, 12 lines 3, 4 \longleftrightarrow line 6

chemical shift and the frequency at which it now appears can be used to calculate the frequency at which 85 percent H_3PO_4 would appear when the spectrometer is locked as described above. The difference between the frequency of an unknown ^{31}P compound and the calculated frequency for 85 percent H_3PO_4 , divided by the frequency of 85 percent H_3PO_4 and multiplied by 10^6 then gives the chemical shift in ppm with respect to 85 percent H_3PO_4 . For example, when the internal locking standard used is tetramethylsilane, i.e., when the field is such that these methyl protons resonate at 60,002,000 Hz, then the 85 percent H_3PO_4 frequency is 24,289,267 Hz. Values for unknown phosphorus compounds which occur at higher frequency than this would thus be resonating at lower field, and those at a lower frequency would be at higher field.

The ^{13}C chemical shifts are given with respect to the ^{13}C isotope of the methyl group in acetic acid and were determined in the same manner as the ^{31}P chemical shifts.

In a study of the systematic trends of coupling constants between directly bonded nuclei, Jameson and Gutowsky (81) formulated a model which predicted both positive and negative coupling constants for ^{31}P - ^{13}C coupling. Jameson (82) later showed that the transition in the sign of the coupling constant in compounds of phosphorus is in agreement with intuitive arguments based

on hybridization and the effect of ligand electronegativity on hybridization. Thus, for P(III) compounds, the P-C coupling constant is small negative, becoming positive in P⁺(IV) compounds and P(V) compounds, and increasingly positive as more electronegative atoms are bonded to phosphorus. At the same time, the geminal PCH coupling constant is positive for P(III) compounds, becoming negative in P⁺(IV) and P(V) compounds.

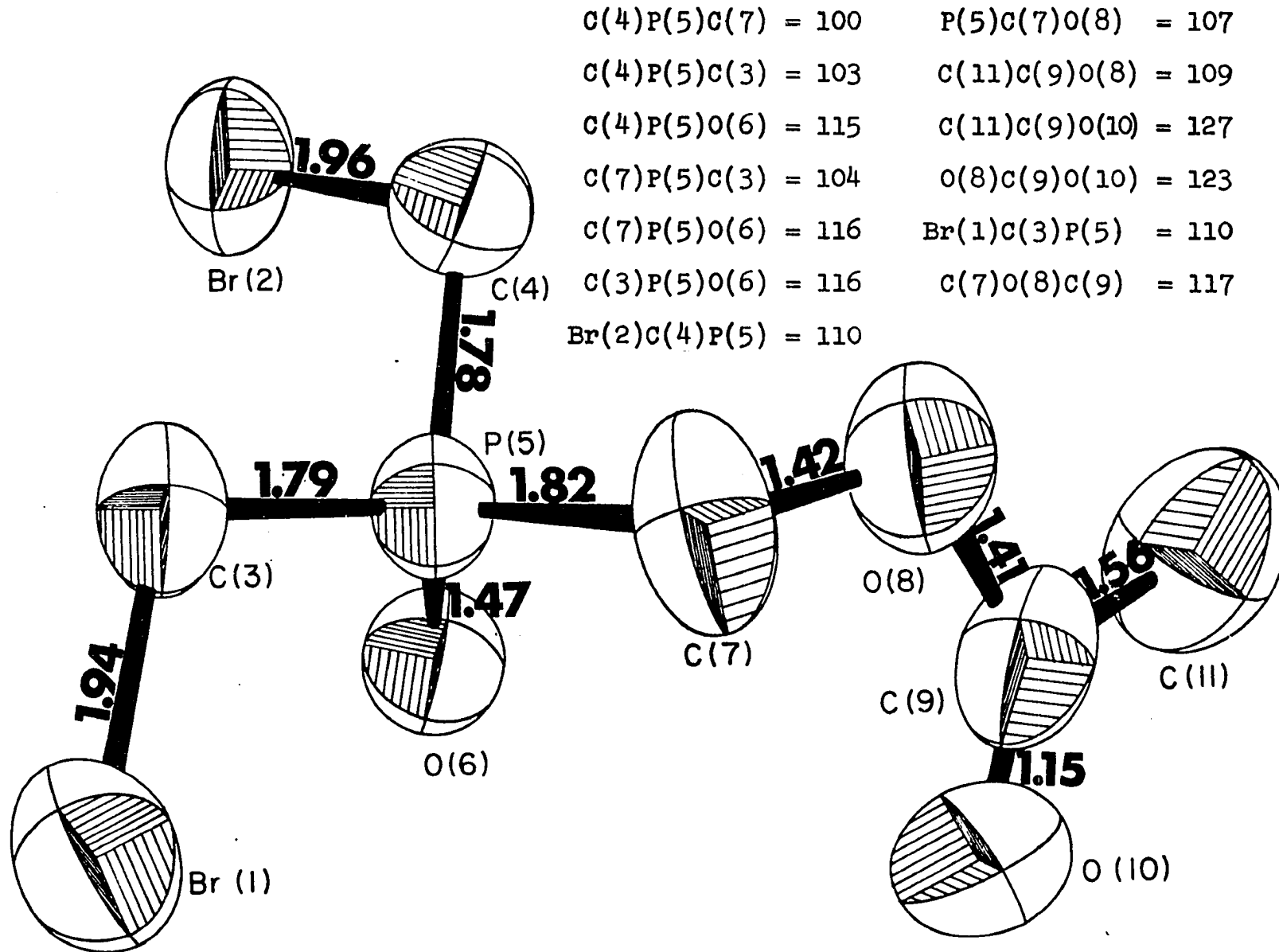
In the compound studied here, the ¹³C chemical shift in P-¹³C-O is further downfield than that in P-¹³C-Br reflecting the more electronegative oxygen being attached. Furthermore, both P-C couplings are positive with $^1J(^{31}\text{P}-^{13}\text{C}-\text{O})$ being larger than $^1J(^{31}\text{P}-^{13}\text{C}-\text{Br})$. This is in accord with the electronegativity arguments given by Jameson (82).

The compound is further characterized by its ir spectrum. The large band at 1220 cm⁻¹ attributable to phosphoryl stretching and the band at 1752 cm⁻¹ due to the carbonyl group along with the 1252 cm⁻¹ C=O stretch all attest to the formulation as given.

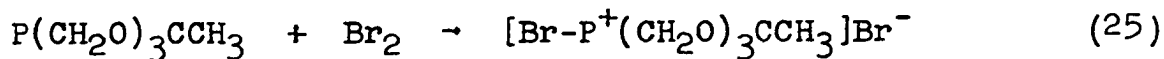
Furthermore an x-ray crystal structure determination has now been completed (83). Figure 8 is a representation of the molecular structure and also gives the bond lengths and angles which were determined.

The formation of this compound probably proceeds by

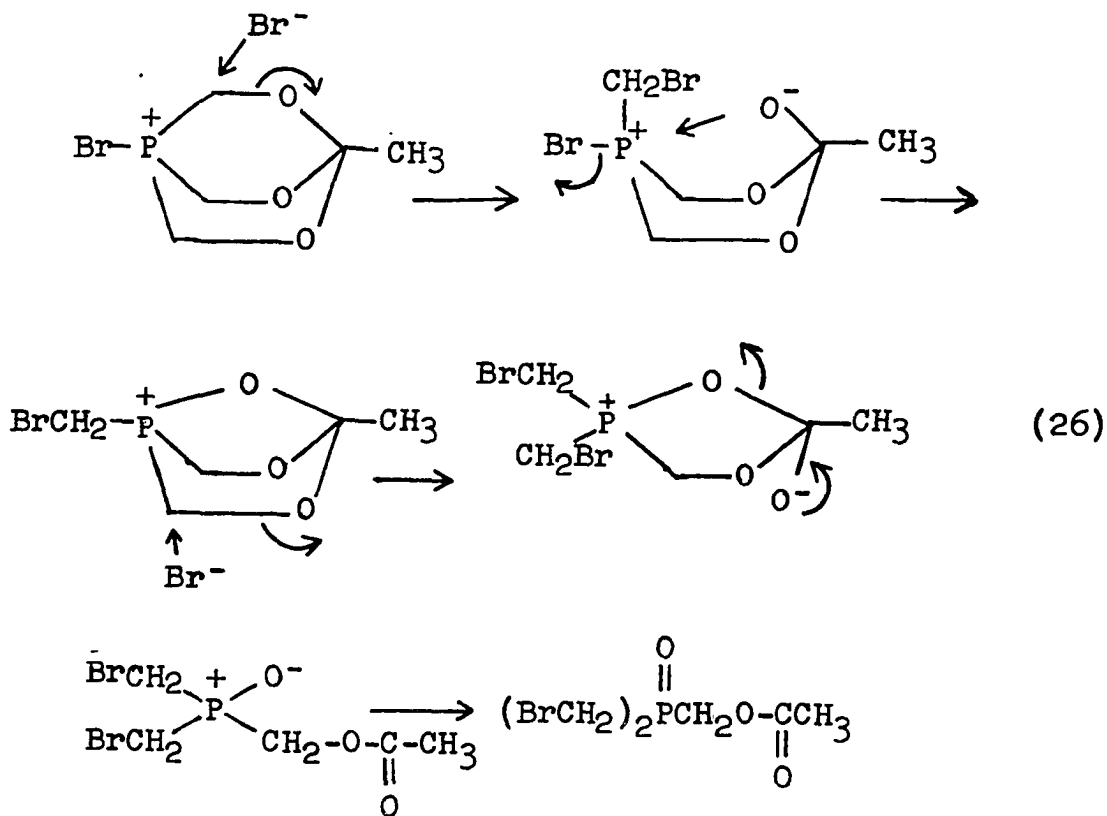
Figure 8. Molecular structure of bis(bromomethyl) acetoxy phosphine oxide



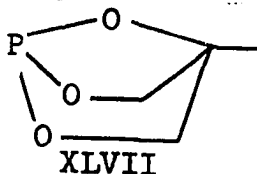
nucleophilic attack of phosphorus on bromine forming an intermediate phosphonium compound.



A possible mechanism for its conversion to the final phosphine oxide product is given below.



The intermediate [2.2.1] bicyclic compound is not unlikely since the [2.2.1] phosphite compound (XLVII) has been well characterized by Denney and Varga (84).



SUGGESTIONS FOR FURTHER RESEARCH

In the reaction of bromine with the bicyclic phosphite $P(OCH_2)_3CCH_3$, it has been shown by conductivity and nmr studies that an intermediate of the form $[BrP^+(OCH_2)_3CCH_3]Br^-$ is formed. Also, in the analogous reaction with the bicyclic phosphine $P(CH_2O)_3CCH_3$, the initial formation of $[BrP^+(CH_2O)_3CCH_3]Br^-$ is postulated. Further attempts at isolating these two intermediates by using nonreactive anions, e.g., ClO_4^- , BF_4^- , $B(C_6H_5)_4^-$, or PF_6^- , should be made. Furthermore, although the compound $[BrP^+(OCH_2)_3CCH_3]Br^-$ was shown to be an electrolyte in acetonitrile, it might exist as a penta-covalent compound in nonpolar solvents. The stereochemistry about the phosphorus would be interesting if this were so, since the formation of a trigonal bipyramidal configuration would be strongly hindered by the cage nature of the phosphite. The same may also be true for the bicyclic phosphine and analogous experiments with this compound may also prove to be useful in this regard.

PART II. LOW-VALENT TRANSITION METAL
COMPLEXES OF PHOSPHORUS LIGANDS

INTRODUCTION

Complexes with metal atoms formally in the d^8 configuration are involved in many important reactions in homogenous catalysis (85). The stereochemistry of these d^8 complexes varies from normally five-co-ordinate compounds of Mn(-I) and Fe(0) to four-co-ordinate Ni(II) and Pt(II). Within this range lies the Co(I), Rh(I) and Ir(I) group of metals for which both four- and five-co-ordination are known.

Hydride complexes of the transition metals have been quite extensively investigated in the last ten years. Recent interest has been focused on hydride complexes of the second- and third-row transition metals and their role in homogenous catalytic reactions (86). Although the chemistry of these low-valent hydrides has come to be much better understood, very little is known about the stereochemistry of these complexes.

Keim (87) first reported the synthesis of $\text{HRh}[\text{P}(\text{C}_6\text{H}_5)_3]_4$ which was later more extensively investigated by Dewhirst et al. (88). The hydride resonance of this compound was a broadened singlet at room temperature and there was no detectable change in the appearance of the lines on cooling to -60° . It was concluded that even at this low temperature, the phosphine ligands were still exchanging rapidly enough to cause line broadening. A trigonal bipyramidal structure was suggested on the basis of the low (< 1 Hz) Rh-H coupling

and the analogous coupling (0.8 Hz) in $\text{HRh}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_3$ which is known from x-ray studies to be trigonal bipyramidal (89). The crystal structure of $\text{HRh}[\text{P}(\text{C}_6\text{H}_5)_3]_4$ was reported by Baker and Pauling (90). The hydride ligand was not located, but the four phosphorus atoms were found to be arranged tetrahedrally about the Rh atom. It was concluded that the hydride must be located on a C_3 axis in order to be consistent with crystal symmetry. The crystal structure of the similar mixed ligand complex $\text{HRh}[\text{As}(\text{C}_6\text{H}_5)_3][\text{P}(\text{C}_6\text{H}_5)_3]_3$ was also investigated by Baker et al. (91). It was found to be isomorphous with $\text{HRh}[\text{P}(\text{C}_6\text{H}_5)_3]_4$ with the As and P atoms randomly occupying the four tetrahedral heavy-atom ligand positions with the hydride atom trans to both As and P. The ir spectrum contained two absorptions attributable to Rh-H stretching vibrations also suggesting its trans relationship to two different ligands. In complexes of this type, apparently the H atom does not affect the regular tetrahedral arrangements of the heavy atom ligands.

Also investigated by Dewhurst (88) was the complex $\text{HRh}[(\text{C}_6\text{H}_5)_2\text{PCH}_3]_4$. At -60° , the hydride nmr spectrum appears as a doublet of quintets ($J(\text{RhH}) = 7.0 \text{ Hz}$, $^2J(\text{PH}) = 18.0 \text{ Hz}$). It was thus concluded that this structure must be square pyramidal with the four equivalent P nuclei forming the base and the hydride the apex.

Reported recently was the crystal structure of

$\text{HCo}(\text{PF}_3)_4$ (92). This complex was found to have P-Co-P angles of 101.8° , 108.2° , 109.7° , and 118.0° . Various positions for the hydrogen atom were considered and a model was favored in which the hydrogen occupies an apical position of a distorted trigonal bipyramid.

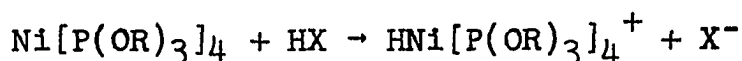
The first phosphite-stabilized hydride complexes reported were $\text{HCo}[\text{P}(\text{OEt})_3]_4$ and trans- $\text{FeH}_2[\text{P}(\text{OEt})_3]_4$ by Kruse and Atalla (93). It was later noted by Tebbe et al. (94) that the Fe complex was actually a mixture of cis and trans forms undergoing rapid intramolecular rearrangement at room temperature. The Co complex exhibited a quintet in the hydride nmr region and no temperature dependence was observed. As a result, a square pyramidal structure was also suggested for this complex (93).

Levison and Robinson (95, 96) prepared a series of hydrido (triarylphosphite) complexes of Co and Rh of formula $\text{HRh}[\text{P}(\text{OAr})_3]_4$. The cobalt complex gave a quintet in the hydride nmr region. However, x-ray powder photographs indicated that $\text{HCo}[\text{P}(\text{OAr})_3]_4$ and $\text{Ni}[\text{P}(\text{OAr})_3]_4$ were isomorphous. This suggested a tetrahedral configuration for the four phosphite ligands in the Co complex, with the hydride ligand situated along the trigonal axis. The nmr equivalence of the four P atoms would then be due to a rapid intramolecular rearrangement at room temperature. A variable temperature experiment was not reported. The corresponding Rh complex

also gave a high-field quintet with each member split into a doublet by ^{103}Rh . Whereas $\text{HRh}[\text{P}(\text{C}_6\text{H}_5)_3]_4$ shows line broadening and loss of fine structure attributable to rapid ligand exchange, $\text{HRh}[\text{P}(\text{OC}_6\text{H}_5)_3]_4$ does not. The spectrum is sharp and well resolved indicating slow exchange at room temperature or the absence of exchange. This would be in accord with the higher π -acidity of $\text{P}(\text{OAr})_3$ with respect to $\text{P}(\text{C}_6\text{H}_5)_3$. Compounds of the type $\text{IrH}(\text{CO})[\text{P}(\text{OAr})_3]_3$ were also reported. These complexes were not isolated however and only evidence for their existence in solution was described.

The complex $\text{HIr}[\text{P}(\text{OC}_6\text{H}_5)_3]_4$ was reported by Giusto (97) and it also exhibited a quintet in the high-field nmr region. Both the square-pyramidal arrangement and the tetrahedral arrangement of the P atoms with rapid intramolecular rearrangement were considered as possible stereochemistries.

Very recently, Drinkard et al. (98) have shown that addition of strong acids to solutions of NiL_4 ($\text{L} = \text{P}(\text{OEt})_3$, $\text{P}(\text{OMe})_3$, $\text{P}(\text{OC}_6\text{H}_5)_3$) lead to the appearance of a high-field nmr signal which is characteristic of a hydride directly bound to the nickel. These resonances were observed with such acids as HCl , H_2SO_4 , and CF_3COOH . The high-field resonance has a quintet structure and was attributed to the following reaction:

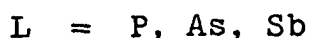
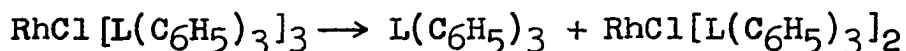


The nmr spectra were independent of the anions used. The ^{31}P spectrum provided confirmatory evidence in that a doublet with the same coupling as observed for the quintet hydride appeared at a different chemical shift than the starting complex. Schunn (99) carried out this reaction with $\text{Ni}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2$ and was able to obtain stable, isolable complexes of the formula $\text{HNi}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]^+ \text{X}^-$ ($\text{X} = \text{BF}_4^-, \text{AlCl}_4^-, \text{HCl}_2^-$). The hydride nmr resonance was observed, but no fine structure was resolved. An extensive study of the preparation and characterization, kinetics and thermodynamics of formation, and decomposition of $\text{HNi}[\text{P}(\text{OEt})_3]_4\text{X}$ was carried out by Tolman (100). The rate constant for hydride formation from HClO_4 in CH_3OH at 25° was found to be $1550 \text{ M}^{-1}\text{sec}^{-1}$. A $\Delta H^\ddagger = 13 \pm 1 \text{ kcal/mole}$ and $\Delta S^\ddagger = -2 \pm 3 \text{ eu}$ were also determined.

Rhodium(I) complexes of the form $\text{Rh}(\text{CO})\text{XL}_2$ ($\text{X} = \text{Cl}, \text{Br}; \text{L} = \text{P}, \text{As}$ or Sb containing ligands) have been made by the reaction of L on rhodium carbonyl chloride solutions, or in some cases from the ligand and alcoholic solutions of rhodium trichloride. In the case of the triphenyl phosphine chloro complex, dipole moment measurements indicate that the phosphine groups are trans to one another (101). This particular complex is one of the most effective hydroformylation catalysts yet discovered amongst this group of metals.

A rhodium(III) dihydride species has been proposed as the intermediate in the catalysis process (102).

The reaction of triaryl phosphites with $(\text{Rh}(\text{CO})_2\text{Cl})_2$ was investigated by Vallarino (103). Two series of compounds could be prepared by using stoichiometric amounts of phosphite. For example, $\text{Rh}(\text{CO})\text{Cl}[\text{P}(\text{OC}_6\text{H}_5)_3]_2$ was prepared by adding a four molar amount of ligand to a benzene solution of $(\text{Rh}(\text{CO})_2\text{Cl})_2$. Using an excess of ligand yielded the complex $\text{RhCl}[\text{P}(\text{OC}_6\text{H}_5)_3]_3$. With phosphines, complexes of the form RhClL_3 can be prepared from an ethanolic solution of rhodium trichloride and ligand (104-106), or from the reaction of $(\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl})_2$ and excess ligand (107). These complexes have been found to undergo the following dissociation reaction in solution (106).



The resulting species in solution is likely to have a weakly bound solvent molecule in the fourth co-ordination site. The particular compound $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ has been found to undergo a number of electrophilic addition reactions. Also, because of the vacant co-ordination site available in the solvated species, attack by nucleophiles may also occur on the rhodium. The reaction with carbon monoxide to form $\text{Rh}(\text{CO})\text{Cl}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ was found to be irreversible. This is

in contrast to the analogous phosphite complexes since RhClL_3 can be prepared from $\text{Rh}(\text{CO})\text{ClL}_2$ when L is a phosphite ligand as mentioned previously. The catalytic activity of $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ has been extensively studied by Wilkinson and co-workers (106). It has been shown to be an efficient catalyst for the homogenous hydrogenation by molecular hydrogen of nonconjugated olefins and acetylenes under ambient conditions. From these studies it has been shown that for the catalytic reactions to occur effectively, a delicate balance of equilibria must be maintained and that lability of the intermediates is critical. These requirements are only partially fulfilled by complexes such as $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_2\text{H}]_3$, $\text{Rh}(\text{SnCl}_3)[\text{P}(\text{C}_6\text{H}_5)_3]_3$, and $\text{RhCl}[\text{P}(\text{OC}_6\text{H}_5)_3]_3$ (106).

The formation of complexes of formula $\text{Ru}(\text{CO})_2\text{X}_2\text{L}_2$ where X is a halide ion and L is a phosphorus containing ligand has been reported in the recent literature by several different methods. For example, boiling the complex salt $[\text{Ru}_2\text{Cl}_3[\text{P}(\text{Et}_2\text{C}_6\text{H}_5)]_6]\text{Cl}$ with potassium hydroxide in alkyl alcohol yielded both cis and trans forms of $\text{RuCl}_2(\text{CO})_2(\text{PR}_3)_2$ (108). Oxidation of trans- $\text{Ru}(\text{CO})_3\text{L}_2$ with iodine can also give both cis and trans isomers depending on the particular L used (109). The addition of ligand to the blood-red solution of $\text{Ru}(\text{CO})_n(\text{Cl})_m$, obtained by bubbling carbon monoxide through a refluxing ethanol solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$,

has also been found to yield $\text{RuCl}_2(\text{CO})_2\text{L}_2$ isomers (110).

The stereochemistry of these complexes is usually determined by infra-red and nuclear magnetic spectroscopy. Thus the appearance of only one carbonyl band in the vicinity of 1900 to 2100 cm^{-1} is indicative of trans carbonyl groups, while the appearance of two bands in the same region suggests cis carbonyl ligands. If the phosphorus ligand contains one or more protons strongly coupled to the phosphorus atom, the appearance of these protons as a doublet has been taken to be indicative of cis geometry while their appearance as a "triplet" is suggestive of trans geometry. Thus in the series of complexes of $\text{RuX}_2(\text{CO})_2[\text{PMe}_2(\text{C}_6\text{H}_5)]_2$ (111), both nmr and ir techniques were used in ascertaining the stereochemistry of these complexes.

EXPERIMENTAL

Materials

Ruthenium trichloride, rhodium trichloride, and iridium trichloride were purchased from Engelhard Industries.

Instrumentation

Instruments used for obtaining nmr and ir spectra are the same as described in Part I. Infra-red spectra in the range 50-700 cm^{-1} were obtained with a Beckman Model 11 grating spectrophotometer.

Preparations

μ -dichlorotetracarbonyldirrhodium(I). This was prepared by the reaction of carbon monoxide at atmospheric pressure with rhodium(III)chloride (112).

Chlorocarbonyl bis(L)rhodium(I). Complexes of this type were prepared by direct reaction of the appropriate molar amount of ligand with a benzene solution of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$. All preparations were carried out under pre-purified nitrogen.

L = 1-phospha-4-methyl-2,6,7 trioxabicyclo[2.2.2]-octane. A light yellow precipitate forms which is recrystallizable in slight amounts from acetonitrile. The compound was found to be too insoluble for an nmr spectrum.

Anal. Calcd. for $\text{C}_{11}\text{H}_{18}\text{O}_7\text{P}_2\text{RhCl}$: 28.57% C, 3.90% H, 7.68% Cl. Found 27.90% C, 3.69% H, 8.05% Cl.

L = 1-phospha-4-n-propyl-2,6,7-trioxabicyclo[2.2.2]-octane. A light yellow precipitate forms which is recrystallizable in slight amounts from acetonitrile. The compound was found to be too insoluble for an nmr spectrum.

L = 1-phospha-4-n-pentyl-2,6,7-trioxabicyclo[2.2.2]-octane. Recrystallization of this light yellow compound from benzene incorporates one mole of benzene per mole of complex as shown by its nuclear magnetic resonance spectrum. Recrystallization from chloroform yielded the desired complex free of solvent.

Anal. Calcd. for $C_{19}H_{34}O_7P_2RhCl$: 41.64% C, 5.92% H, 6.18% Cl. Found 39.78% C, 6.10% H, 7.61% Cl.

L = 1-phospha-4-methyl-3,5,8-trioxabicyclo[2.2.2]-octane. This bright yellow precipitate is recrystallizable from hot benzene in 76% yield.

Anal. Calcd. for $C_{11}H_{18}O_7P_2RhCl$: 28.54% C, 3.89% H, 7.68% Cl. Found 28.59% C, 3.98% H, 7.85% Cl.

L = 1-phospha-4-n-butyl-3,5,8-trioxabicyclo[2.2.2]-octane. This yellow precipitate is recrystallizable from hot benzene forming platelets.

Hydridotetrakis[1-phospha-4-n-propyl-2,6,7-trioxabicyclo[2.2.2]octane]cobalt(I). To a solution containing 2.04 g (8.7 mmoles) of $Co(NO_3)_2 \cdot 6H_2O$, 6.2 g (35 mmoles) of $P(OCH_2)_3CC_3H_7$, 5.0 ml of 2,2-dimethoxypropane and approximately 50 ml of absolute ethanol was slowly added a solution

of 1.50 g of NaBH_4 dissolved in 30 ml of absolute ethanol. The system was kept under a nitrogen flush. The violet solution was rapidly decolorized and a pale yellow precipitate formed. The precipitate was recrystallized from a chloroform-ethanol mixture giving white needles. The compound slowly oxidizes in solution.

Anal. Calcd. for $\text{C}_{28}\text{H}_{53}\text{O}_{12}\text{P}_4\text{Co}$: 43.98% C, 6.94% H, 16.23% P. Found 43.03% C, 6.61% H, 18.71% P.

Hydridotetrakis[1-phospha-4-n-propyl-2,6,7-trioxabicyclo[2.2.2]octane]rhodium(I). In an inert atmosphere, approximately 25 ml of absolute ethanol was added to 0.92 g (1 mmole) of $\text{HRh}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_3$ (113) and 0.88 g (5 mmole) of $\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7$. The yellow suspension was magnetically stirred for several hours during which time the yellow color slowly disappeared giving a white suspension. The white powder was filtered off under nitrogen and washed several times with small portions of anhydrous ether or pentane. The complex is quite soluble in polar organic solvents but is quite sensitive to air and/or moisture when in solution.

Hydridocarbonylbistriphenylphosphine(1-phospha-4-n-propyl-2,6,7-trioxabicyclo[2.2.2]octane)iridium(I). In an inert atmosphere 25 ml of absolute ethanol was added to 1.01 g (1 mmole) of $\text{HIr}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_3$ (113) and 0.176 g (1 mmole) of $\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7$. The yellow suspension was magnetically

stirred for four hours yielding a white suspension. The off-white powder was filtered off under nitrogen and washed with several portions of anhydrous ether. The complex was characterized from its ir and nmr spectra.

Hydridocarbonyltriphenylphosphinebis[1-phospha-4-n-propyl-2,6,7-trioxabicyclo[2.2.2]octane]iridium(I). This white complex was prepared analogously to the above complex except a 5:1 ratio of $P(OCH_2)_3CC_3H_7$ to $HIr(CO)[P(C_6H_5)_3]_3$ was used. Characterization was accomplished from its ir and nmr spectra.

Hydridotetrakis[1-phospha-4-methyl-2,6,7-trioxabicyclo[2.2.2]-octane]nickel(II)tetrafluoroborate. The preparation of this complex was carried out in a vacuum line system. To 0.973 g (5 mmoles) $AgBF_4$ dissolved in a minimum amount of degassed 1,2-dimethoxyethane was condensed an equimolar amount of HCl. The AgCl formed was filtered off and condensed into a reaction vessel containing 1.23 g (1.6 mmoles) of $Ni[P(OCH_2)_3CCH_3]_4$ (114). Approximately 20 ml of degassed methylene chloride was then condensed into this reaction vessel. The vessel was then allowed to come to room temperature and magnetically stirred for three hours. The suspension which formed was filtered in a glove-bag filled with dry nitrogen. The off-white powder obtained was washed with several portions of anhydrous ether and dried under vacuum. The solid was found to be too insoluble

for recrystallization.

Dicarbonyldichlorobis(L)ruthenium(II). Complexes of this type were prepared by the addition of the stoichiometric amount of ligand to a solution prepared by bubbling carbon monoxide through a refluxing ethanolic solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$. A stoichiometric amount of 2,2-dimethoxypropane was also added to remove the water of hydration.

L = 1-phospha-4-methyl-2,6,7-trioxabicyclo[2.2.2]-octane. The yellow precipitate which formed was recrystallized from ether.

Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{O}_8\text{Cl}_2\text{P}_2\text{Ru}$: 27.48% C, 3.44% H, 13.55% Cl. Found 26.16% C, 3.37% H, 12.65% Cl.

L = 1-phospha-4-n-propyl-2,6,7-trioxabicyclo[2.2.2]-octane. The yellow precipitate was recrystallized from methanol.

Anal. Calcd. for $\text{C}_{16}\text{H}_{26}\text{O}_8\text{Cl}_2\text{P}_2\text{Ru}$: 33.10% C, 4.48% H, 12.24% Cl. Found: 32.36% C, 4.79% H, 11.98% Cl.

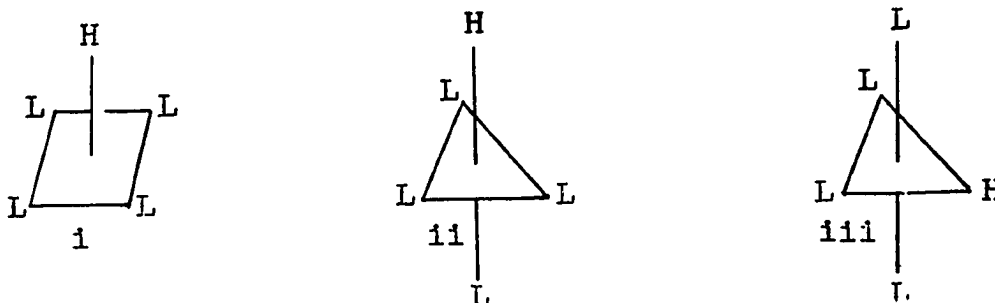
L = 1-phospha-4-n-pentyl-2,6,7-trioxabicyclo[2.2.2]-octane. This yellow precipitate was also recrystallized from methanol.

Anal. Calcd. for $\text{C}_{20}\text{H}_{34}\text{O}_8\text{Cl}_2\text{P}_2\text{Ru}$: 37.74% C, 5.35% H, 11.16% Cl. Found: 37.19% C, 5.82% H, 11.22% Cl.

RESULTS AND DISCUSSION

Table 9 lists the known phosphite complexes of formula HML_4^{+n} along with the nmr parameters reported for the hydride ligand. Also given are the new complexes $\text{HCo}[\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7]_4$ and $\text{HRh}[\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7]_4$ which were prepared as part of this dissertation.

The solution stereochemistry of these complexes has been briefly commented upon by most of the investigators. For a five-co-ordinate complex of formula HML_4 there are three idealized stereochemistries possible: (i) square pyramidal (C_{4v}); (ii) trigonal bipyramidal with the hydride in the apical position (C_{3v}); and (iii) trigonal bipyramidal with the hydride in an equatorial position (C_{2h}).



If these three structures are considered as static configurations, only i would be consistent with four equivalent L ligands and thus the nmr spectrum of the hydride should appear as a 1:4:6:4:1 quintet if L is a phosphorus ligand. Structure ii would be expected to show a doublet of quartets with the doublet trans coupling constant being much larger than the triplet cis coupling constant.

Table 9. Hydride-phosphite complexes of type HML_4^{+n}

Compound	δ	$^2J(\text{PH})(\text{Hz})$	Multiplicity	Reference
$\text{HCo}[\text{P}(\text{OCH}_2\text{CH}_3)_3]_4$	-15.8	20.00	quintet	93
$\text{HCo}[\text{P}(\text{OC}_6\text{H}_5)_3]_4$	-13.58	17	quintet	95
$\text{HCo}[\text{C}_6\text{H}_5\text{P}(\text{OCH}_2\text{CH}_3)_2]_4$	-14.3	21	quintet	115
$\text{HCo}[\text{C}_6\text{H}_5\text{P}(\text{OC}_6\text{H}_5)_2]_4$		no data reported		116
$\text{HCo}[\text{P}(\text{O}-m\text{MeC}_6\text{H}_4)_3]_4$	-13.40	16	quintet	96
$\text{HCo}[\text{P}(\text{O}-p\text{MeC}_6\text{H}_4)_3]_4$	-13.44	17	quintet	96
$\text{HCo}[\text{P}(\text{O}-p\text{ClC}_6\text{H}_4)_3]_4$	-14.25	16	quintet	96
$\text{HCo}[\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7]_4$	-13.61	11.4	quintet	this work
$\text{HRh}[\text{P}(\text{OC}_6\text{H}_5)_3]_4^{\text{a}}$	-10.36	44.5	doublet of quintets	95
$\text{HRh}[\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7]_4^{\text{b}}$	-10.74	44.5	doublet of quintets	this work
$\text{HIr}[\text{P}(\text{OC}_6\text{H}_5)_3]_4$	-13.0	25	quintet	97

^a $^1J(\text{RhH}) = 7.0 \text{ Hz.}$

^b $^1J(\text{RhH}) = 9.0 \text{ Hz.}$

Table 9. (Continued)

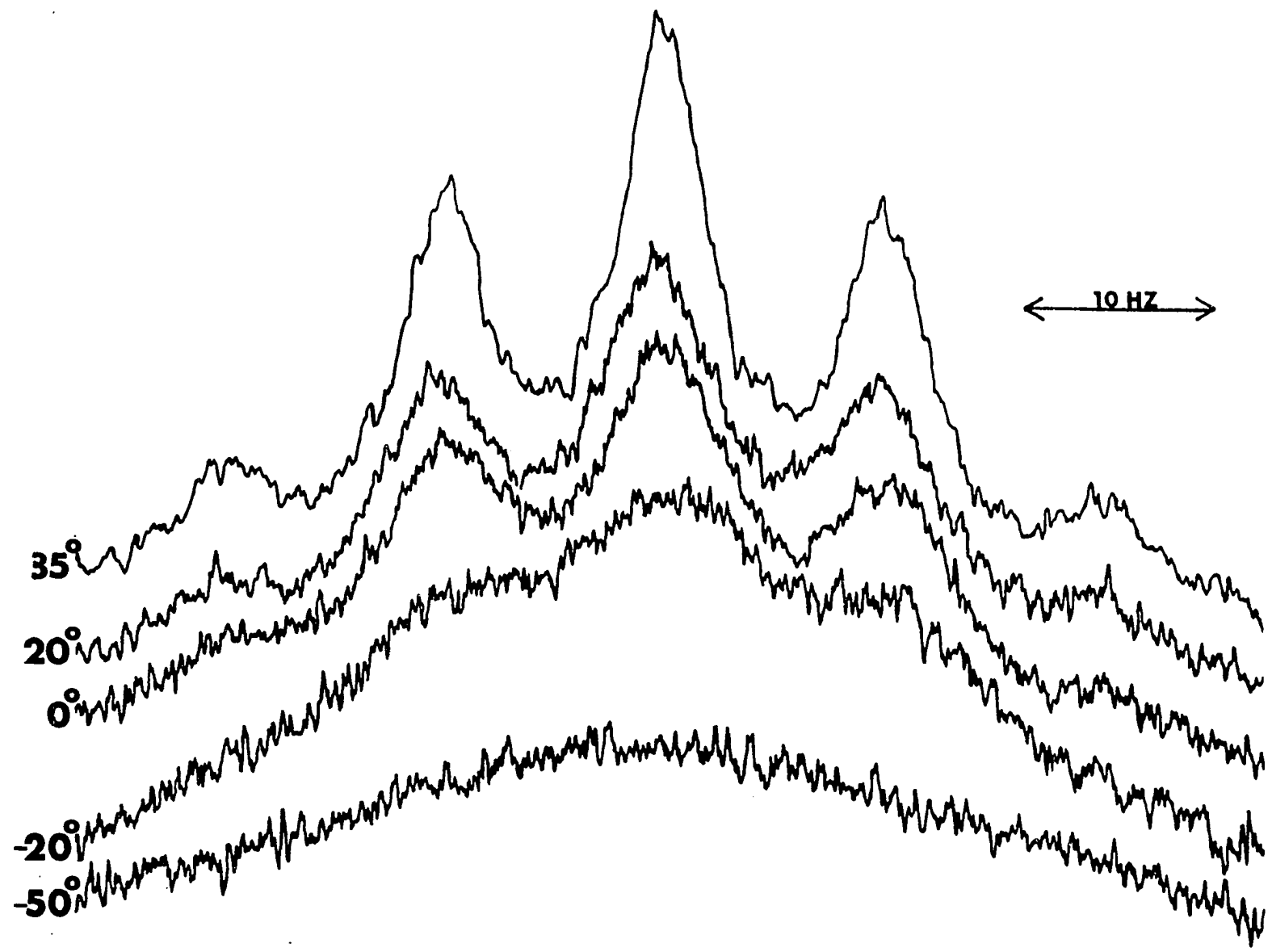
Compound	δ	${}^2J(\text{PH})(\text{Hz})$	Multiplicity	Reference
$\text{HNi}[\text{P}(\text{OCH}_2\text{CH}_3)_3]_4^+$	-14.3	26.0	quintet	98
$\text{HNi}[\text{P}(\text{OCH}_2)_3\text{CCH}_3]_4^+$	-13.1	42.0	quintet	this work

Structure iii should appear as a triplet of triplets. Thus the appearance of the hydride nmr spectrum would be expected to enable the determination of the structures of these complexes without ambiguity.

As seen in Table 9, whenever fine structure is observed for these hydride resonances, it appears as a 1:4:6:4:1 quintet. Rhodium complexes yield a doublet of quintets due to the additional coupling with the ^{103}Rh nucleus, $I = 1/2$. This is strongly suggestive of the square pyramidal structure 1.

The complex $\text{HCo}[\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7]_4$ shows line broadening at room temperature. Similar broadening was reported for $\text{HCo}[\text{P}(\text{OC}_6\text{H}_5)_3]_4$ (95), $\text{HCo}[\text{P}(\text{OCH}_2\text{CH}_3)]_4$ (93), and $\text{HCo}(\text{PF}_3)_4$ (117), and was attributed to the quadrupole moment of ^{59}Co . A variable temperature nmr study was carried out on $\text{HCo}[\text{P}(\text{OCH}_2\text{CH}_3)_3]_4$ and no temperature dependence of the spectrum was found (93). As a result this complex was concluded to be square pyramidal in solution. Figure 9 shows the nmr spectrum in the hydride region for $\text{HCo}[\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7]_4$ at various temperatures. As can be seen, this complex does show a temperature dependence in that as lower temperatures are attained, broadening of the spectral lines is observed. This suggests that rapid intramolecular exchange of the phosphorus ligands is occurring and that as the temperature is lowered, the

Figure 9. Hydride nmr spectrum of $\text{HCo}[\text{P}(\text{OCH}_2)_3\text{C}_3\text{H}_7]_4$ at various temperatures



exchange is slowed down. Unfortunately, at the lowest temperature attainable with the instrumentation available, intramolecular exchange was still occurring at a rate fast enough to broaden the spectrum. Tolman (118) has recently investigated a series of zero-valent nickel complexes of phosphorus ligands and has proposed a dominant role for steric effects on the stability of these complexes. These steric effects were semi-quantitatively determined by measuring the ligand cone angle, which is the angle the ligand sweeps out if free rotation about the metal-phosphorus bond is assumed. In a series of complexes of type H_2ML_4 ($M = Fe, Ru$), Muetterties (119) found that intramolecular rearrangement barriers were somewhat dependent on the ligand cone angle. The complex which has the ligand with the smallest cone angle was found to have the highest barrier while the one with the largest ligand cone angle was found to have the smallest barrier. In this respect it seems surprising that no temperature dependence was observed for $HCo[P(OCH_2CH_3)_3]_4$ (93) while $HCo[P(OCH_2)_3CC_3H_7]_4$ did show a temperature dependence since the ligand cone angles are 109 ± 2 and $101 \pm 2^\circ$, respectively (118). The temperature range over which $HCo[P(OCH_2CH_3)_3]_4$ was investigated was not reported and thus it may be possible that this complex was undergoing rapid intramolecular exchange and a low enough temperature to slow down this exchange was not reached.

In a comparison of $\text{HRh}[\text{P}(\text{C}_6\text{H}_5)_3]_4$ and $\text{HRh}[\text{P}(\text{OC}_6\text{H}_5)_3]_4$, Levison and Robinson (95) noticed that the phosphine complex showed line broadening and loss of fine structure which they attributed to rapid intramolecular ligand exchange. In contrast, $\text{HRh}[\text{P}(\text{OC}_6\text{H}_5)_3]_4$ appeared as a sharp, well resolved doublet of quintets. They concluded that exchange was either absent or slow in this complex which would be in accord with the higher π -acidity of $\text{P}(\text{OC}_6\text{H}_5)_3$ ligands relative to $\text{P}(\text{C}_6\text{H}_5)_3$ ligands. The hydride spectrum of $\text{HRh}[\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7]_4$ also appears as a sharp, well-resolved doublet of quintets. The high π -acidity of the bicyclic ligand has been well established (120), and thus it may well be that this complex is also undergoing slow or no intramolecular exchange at room temperature.

The addition of CF_3COOH to a CH_2Cl_2 solution of $\text{Ni}[\text{P}(\text{OCH}_2)_3\text{CCH}_3]_4$ immediately produces a color change to a light purple. An nmr spectrum of this solution showed an absorption at -13.1δ which is attributable to a hydride ligand. Because of the low solubility, and relatively high molecular weight of the starting complex, the observation of the hydride nmr was made quite difficult. Its appearance as a quintet (the two outer peaks were barely distinguishable above the noise level) again suggests a square pyramidal structure in the absence of rapid intramolecular exchange. The value of the coupling constant $^2J(\text{PH}) = 42 \text{ Hz}$

is appreciably higher than that in $\text{HNi}[\text{P}(\text{OCH}_2\text{CH}_3)_3]_4^+$ (26.0 ± 0.5 Hz) (98) and also higher than that in the isoelectronic complex $\text{HCo}[\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7]_4$ (11.4 Hz). (The stereochemical nonrigidity of this complex was discussed earlier. Therefore, this may not be a true limiting value of J.) The fact that the J values for the Ni(II) hydrides are larger than in the Co(I) hydrides may be due to the more highly charged and smaller Ni(II) nucleus and therefore a larger concentration of s character. The large difference in J between $\text{HNi}[\text{P}(\text{OCH}_2\text{CH}_3)_3]_4^+$ and $\text{HNi}[\text{P}(\text{OCH}_2)_3\text{CCH}_3]_4^+$ is unexplainable at this time.

Under anaerobic conditions, a solution of HBF_4 (prepared by addition of HCl to a AgBF_4 solution) was added to a solution of $\text{Ni}[\text{P}(\text{OCH}_2)_3\text{CCH}_3]_4$. A dirty white solid formed which was filtered and washed. Elemental analyses of this solid supported its formulation as $\text{HNi}[\text{P}(\text{OCH}_2)_3\text{CCH}_3]_4\text{BF}_4$. Due to the insolubility of the complex, a recrystallizable sample could not be obtained. As a result, the analyses are not very satisfactory (see Experimental). An infrared spectrum of this solid as a Nujol mull was essentially identical to that of $\text{Ni}[\text{P}(\text{OCH}_2)_3\text{CCH}_3]_4$ except for the appearance of two new bands at 2020 cm^{-1} and 800 cm^{-1} . These two absorptions can be attributed to the Ni-H stretching and bending modes, respectively (121).

Because of the insolubility of the above compound,

several attempts were made at protonating NiL_4 complexes where $\text{L} = \text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7$ and $\text{P}(\text{OCH}_2)_3\text{CC}_5\text{H}_{11}$. It was hoped that the longer alkyl chain would increase the solubility of the complexes in organic solvents. However, both nmr experiments and vacuum line experiments failed to produce any of the desired complexes. Perhaps there is a secondary steric interference of the alkyl chains on the ligands preventing the approach of a proton.

The reaction of $\text{HIr}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_3$ with varying amounts of ligand to yield the complexes $\text{HIr}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2[\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7]$ and $\text{HIr}(\text{CO})\text{P}(\text{C}_6\text{H}_5)_3[\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7]_2$, hereafter referred to as A and B respectively, was surprising in that complete substitution of the $\text{P}(\text{C}_6\text{H}_5)_3$ ligand could not be achieved. Also, unlike the analogous rhodium complex, the carbonyl ligand remains intact.

The question of the stereochemistry of complexes A and B was investigated by means of nmr and ir studies. These results are summarized in Table 10. Figures 10 and 11 are schematic representations of the ^1H and the ^{31}P spectra as obtained by INDOR methods. Also given is the connectedness of the ^1H transitions to their respective ^{31}P transitions which enabled the relative signs of the coupling constants to be obtained using the mnemonic method of Friedman and Gutowsky (70).

The stereochemical nonrigidity of d^8 penta-co-ordinate

Table 10. nmr and ir parameters for compounds

Compound	A H ₂ Ir(CO)[P(C ₆ H ₅) ₃] ₂ P(OCH ₂) ₃ CC ₃ H ₇			B H ₂ Ir(CO)P(C ₆ H ₅) ₃ [P(OCH ₂) ₃ CC ₃ H ₇] ₂			Stretching frequencies (cm ⁻¹) ^a	
	P ₁ ^b	P ₂	Hydride	² J _{P₁P₂ (Hz)}	² J _{P₁H}	² J _{P₂H}	ν _{C=O}	ν _{Ir-H}
A	-12.3 ^c	-92.2	-11.5 ^d	+ 175	+ 18.4	+ 12.8	1960	2080
B	- 8.68	-87.3	-12.3	+ 57	+ 25.0	+ 3.2	1937	2043

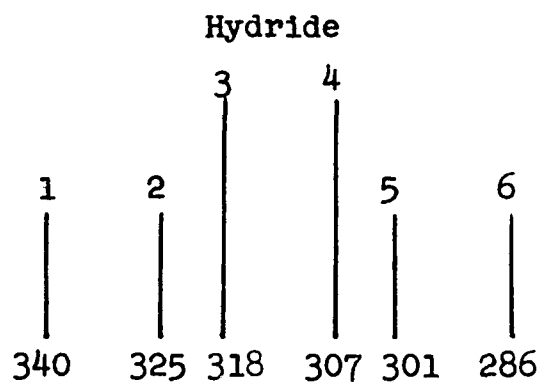
^aNujol mull.

^bP₁ refers to the P(C₆H₅)₃ ligand while P₂ refers to P(OCH₂)₃CC₃H₇ ligand.

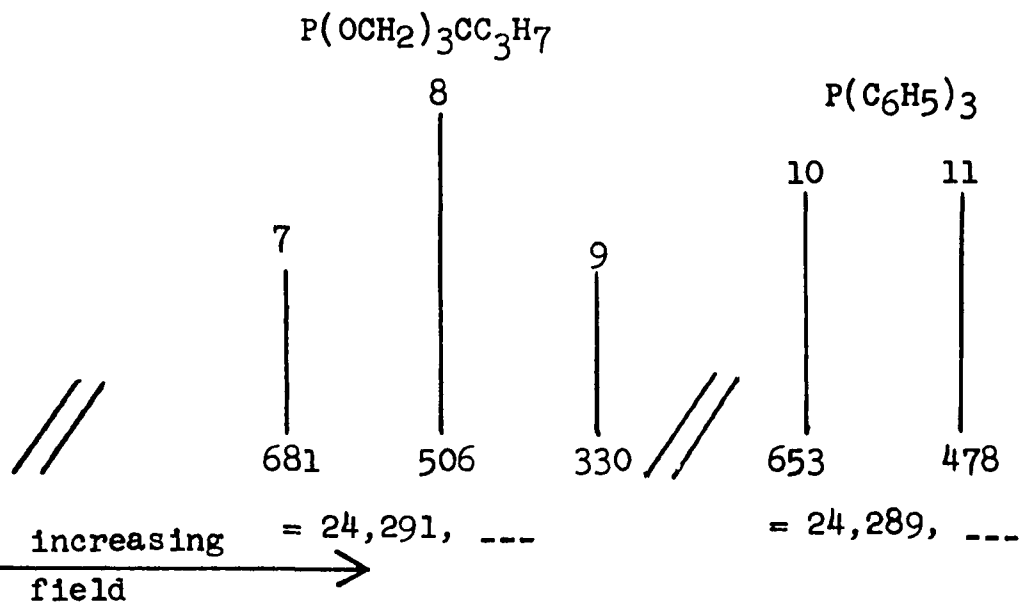
^cPhosphorus chemical shifts given in ppm with respect to external 85% H₃PO₄.

^dHydride chemical shifts are reported in δ units relative to internal Si(CH₃)₄.

Figure 10. Schematic representation of ^1H and ^{31}P nmr spectra of $\text{HIr}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2[\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7]$. Only P-P' coupling shown in ^{31}P spectra



irradiating
frequency = 60,001, ---



line 1 ← → lines 9, 11

line 3 ← → lines 8, 11

line 5 ← → lines 7, 11

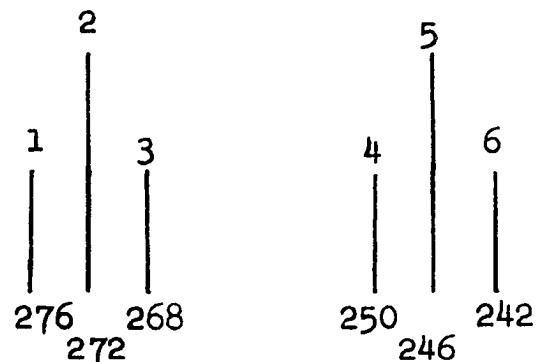
line 2 ← → lines 9, 10

line 4 ← → lines 8, 10

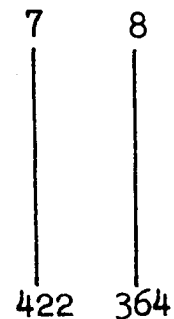
line 6 ← → lines 7, 10

Figure 11. Schematic representation of ^1H and ^{31}P nmr spectra of $\text{HIr}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3][\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7]_2$. Only P-P' coupling shown in ^{31}P spectra

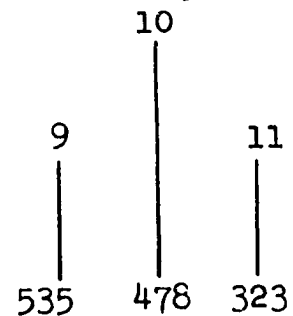
Hydride



$\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7$



$\text{P}(\text{C}_6\text{H}_5)_3$



irradiating
frequency = 60,001, ---

increasing
field →
= 24,291, ---

= 24,289, ---

line 1 ↔ lines 7, 9
line 2 ↔ lines 7, 10
line 3 ↔ lines 7, 11

line 4 ↔ lines 8, 11
line 5 ↔ lines 8, 10
line 6 ↔ lines 8, 9

complexes has already been discussed with respect to complexes of type HML_4 . Yagupsky and Wilkinson (122) have shown that the complex $HIr(CO)_2[P(C_6H_5)_3]_2$ exists in solution as two isomers. Thus, the ir spectrum as a Nujol mull consists of an Ir-H stretch at 2029 cm^{-1} and two $C \equiv O$ stretches at 1970 and 1915 cm^{-1} (cis $C \equiv O$ groups). However, in solution each of these three bands splits into two. The relative intensities of the two bands are solvent, concentration, and temperature dependent. Furthermore, the 1H nmr in the hydride region exists as a triplet but is also dependent on solvent, concentration and temperature; e.g., the magnitude of the observed coupling constant varies with changing solvents between 1.5 Hz and 8.5 Hz at 35° C . This observed triplet is thus an average of two separate triplets and since typical cis ^{31}P -M-H coupling constants are in the range 15 - 50 Hz , they concluded the two coupling constants are opposite in sign. At -70° in CS_2 , two triplets were obtained in a ratio of $2:1$ with couplings of 19 and 35 Hz respectively. The existence of two species can be rationalized in terms of a five-co-ordinate species together with a six-co-ordinate solvated species, or two five-co-ordinate species. It was found that substantial amounts of both species were present in solvents with very low co-ordinating ability, such as cyclohexane. Also, adding even a 10-mole excess of a strongly co-ordinating solvent to a solution of

$\text{IrH}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$ in a poorly co-ordinating solvent caused only a trivial change in the ir and nmr spectra. As a result, it was concluded that two five-co-ordinate species were present. Three structures, each of symmetry C_s , and three structures with symmetry C_{2v} were considered as possibilities for the two isomers. The observation of considerable coupling between the Ir-H and the two $\text{C} \equiv \text{O}$ stretching vibrations suggested a trans H-Ir-CO fragment present in the isomer of trigonal bipyramidal C_s symmetry. The C_{2v} structures were all consistent with the ir data for the other isomeric species and no unequivocal establishment of an individual structure within the C_{2v} group was made.

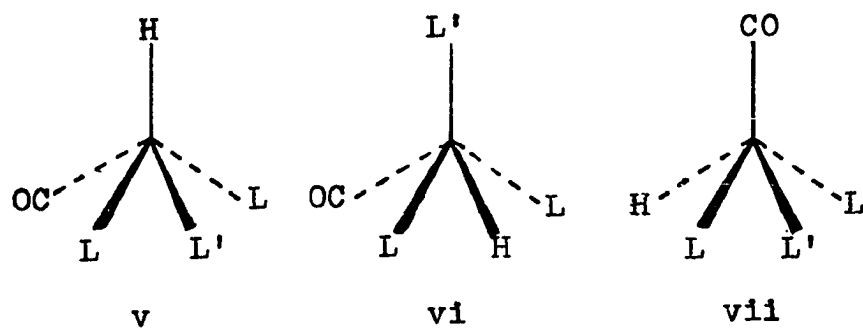
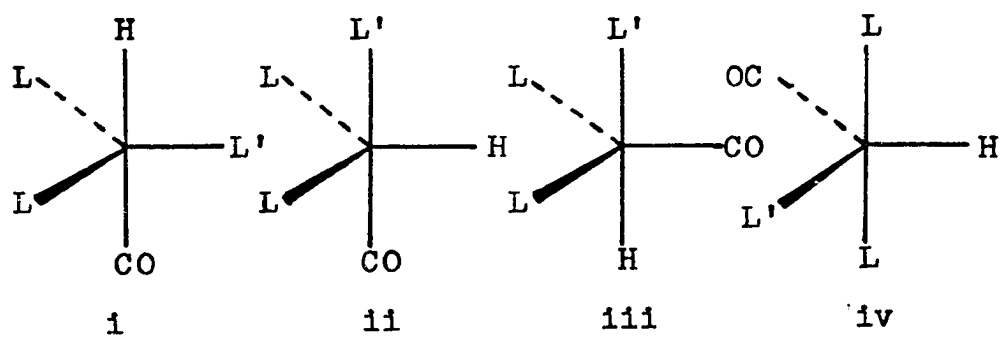
The appearance of the hydridic proton nmr spectrum in both compounds A and B as a doublet of triplets means that the two identical phosphorus ligands in each of the complexes must be equivalent with respect to the hydride; hence the 1:2:1 triplet. Each member of this triplet is then split into a doublet by the other phosphorus-containing ligand present in the complex.

Also, the appearance of the ^{31}P spectrum of $\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7$ as a triplet in A and of the ^{31}P of $\text{P}(\text{C}_6\text{H}_5)_3$ as a triplet in B allows one to conclude that the two identical phosphorus ligands in each of the complexes are also equivalent with respect to the other single phosphorus ligand.

For a complex of type $\text{HIr}(\text{CO})\text{L}_2\text{L}'$, structures i - vii (Figure 12) all have equivalent L ligands as required. As drawn, these are idealized extremes of trigonal bipyramidal (TBP) and square pyramidal (SP) structures and in the real molecule, considerable distortions would be expected. These structures are all of C_s symmetry and the close relationship between TBP and SP, as discussed by Muetterties and Schunn (123) is easily seen within their distorted forms. Thus, distortion of vi by means of an increase in the H-Ir-C angle converts structure vi into i. Similarly, concerted vibrations may well be sufficient to carry each of these idealized structures into one another.

A series of six-co-ordinate Ir(III) hydride complexes containing phosphine ligands was studied by Chatt et al. (124) in which they found that coupling constants between a hydrogen nucleus and a phosphorus in mutually cis positions is 11-21 Hz, while for a phosphorus in a trans position to a hydride, it is 130-163 Hz. This large difference in cis and trans H-M-P coupling constants has been extensively used in determining the stereochemistry of hydride complexes. One exception to this trend seems to be the complex cis $\text{H}_2\text{Fe}[\text{C}_6\text{H}_5\text{P}(\text{OC}_2\text{H}_5)_2]_4$ which was studied by Tebbe et al. (94). Although it was not pointed out as an exception, it was found that the cis $^2\text{J}_{\text{HP}}$ coupling constant was 66.5 Hz while the trans $^2\text{J}_{\text{HP}}$ coupling was either 24 Hz or unresolvably

Figure 12. Possible isomeric structures for complex of type $\text{HM}(\text{CO})\text{L}_2\text{L}'$ where L is equivalent with respect to H and L'



small. The relatively small values for $^2J_{PH}$ in compounds A and B appears to mitigate against a trans H-M-P fragment, if it too is not an exception in this respect.

The complex $\text{HIr}(\text{CO}[\text{P}(\text{C}_6\text{H}_5)_3]_3)$, which is the reactant in the preparation of compounds A and B, has been shown to be trigonal bipyramidal with the three phosphorus ligands in the equatorial plane (89). Replacement of one of the three $\text{P}(\text{C}_6\text{H}_5)_3$ groups with $\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7$ would not be expected to appreciably distort the stereochemistry and thus structure 1 could be postulated for complex A. The carbonyl stretching frequency is found to increase by 39 cm^{-1} as compared to the starting compound. This would be a result of the better π back-bonding ability of $\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7$ as compared to $\text{P}(\text{C}_6\text{H}_5)_3$. Also, one would expect the two $^2J_{PH}$ coupling constants to be of the same sign (as is observed) since the H-M-L and H-M-L¹ geometries would be approximately the same.

The ring methylene protons of $\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7$ in B register as a sharp 1:2:1 "triplet" suggesting that these two ligands are in mutually trans positions. This triplet appearance is a result of strong phosphorus-phosphorus coupling between two chemically equivalent but magnetically nonequivalent phosphorus nuclei when they are in mutually trans positions (125). It has seen extensive use in the literature as a simple method for determining stereo-

chemistry. However, certain exceptions have been noted (126, 127). In this particular case, the sharpness of the peaks and the intensity of the central envelope lend credence to the fact that these two ligands are probably in mutually trans positions.

As a result of the arguments cited above, structures iv, v, vi, and vii could be postulated for compound B. In order to possess the proper symmetry, all of the SP structures must contain a trans L-M-L; that is, the two identical phosphorus ligands must be at opposite corners of the square plane in the SP structure. The arguments cited for a trans L-M-L as a result of the appearance of the methylene protons in $P(OCH_2)_3CC_3H_7$ apply when the L-M-L angle is approximately 180° , i.e., an octahedral, square planar, or diaxial TBP arrangement. In the SP case, the central metal atom would probably not be within the square plane, thus giving a trans L-M-L angle of less than 180° . Structure iv thus seems to be a more likely choice for compound B. Again, the close relationship of the idealized SP and TBP structures must be emphasized.

The reason for the two different signs for the two $^2J(PMH)$ coupling constants in B is not obvious. As mentioned earlier, this was also observed for the two isomers of $HIr(CO)_2[P(C_6H_5)_3]_2$. Possibly the different angular relationships between the H and the two different

P nuclei and the different orbitals involved in the Ir-H and Ir-P bonds are responsible.

Rhodium(I) complexes of the formula $\text{Rh}(\text{CO})\text{ClL}_2$, where $\text{L} = \text{P}(\text{OCH}_2)_3\text{CR}$ ($\text{R} = \text{Me}$, n-propyl, n-pentoyl) or $\text{L} = \text{P}(\text{CH}_2\text{O})_3\text{CR}$ ($\text{R} = \text{Me}$, n-butyl) were obtained by reacting the appropriate molar amount of ligand with a benzene solution of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$. These complexes are given in Table 11 along with the appropriate nmr and ir data where they were obtainable. The methyl and n-propyl phosphite complexes were found to be extremely insoluble in most organic solvents.

The stereochemistry of these square-planar systems is most likely trans, since only one type of methylene proton appears in the nmr spectrum. This would be analogous to $\text{Rh}(\text{CO})\text{Cl}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ which was shown to be trans by a dipole moment study (101).

By using excess amounts of ligand in the reaction with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, the compound of formula $\text{Rh}(\text{CO})\text{ClL}_2$ which is initially formed reacts further with the ligand displacing the carbonyl as shown by the disappearance of the 2000 cm^{-1} band in the ir. With the phosphite ligands, this reaction is quite slow due to the insolubility of the initially formed product. Attempts at obtaining analytically pure compounds of RhClL_3 were not met with success.

With the phosphine ligand $\text{P}(\text{CH}_2\text{O})_3\text{CCH}_3$, again formation

Table 11. Complexes of formula $\text{Rh}(\text{CO})\text{ClL}_2$

L =	$\delta_{\text{CH}_2}^{\text{a}}$	$\nu(\text{C}=\text{O})^{\text{b}}$ (cm^{-1})
$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	- ^c	2000
$\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7$	- ^c	2000
$\text{P}(\text{OCH}_2)_3\text{CC}_5\text{H}_{11}$	4.3 ^d	2000
$\text{P}(\text{CH}_2\text{O})_3\text{CCH}_3$	4.63 ^e	2000
$\text{P}(\text{CH}_2\text{O})_3\text{CC}_4\text{H}_9$	4.63 ^e	2000

^aChemical shift of the methylene protons in the cage relative to internal TMS.

^bIn KBr.

^cToo insoluble for nmr.

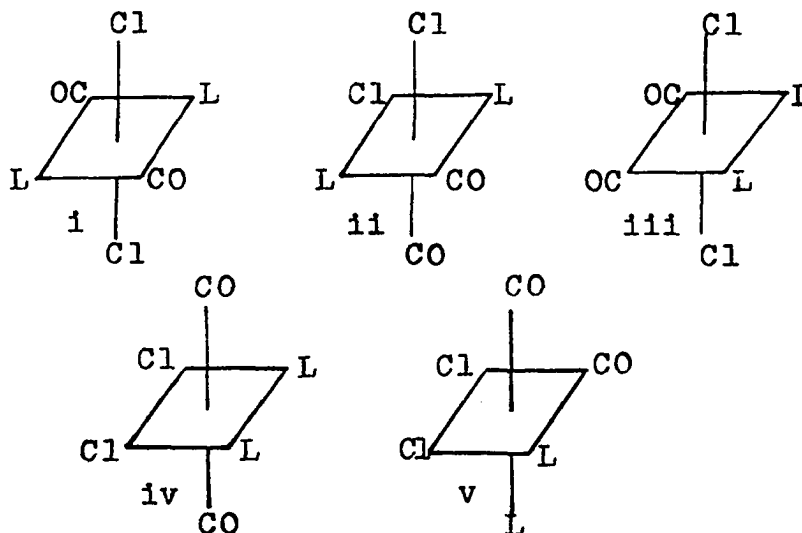
^dBroad singlet. Width at half-height = 3.2 Hz.

^eSharp singlet. $^2J(\text{PH}) = 0$.

of $\text{Rh}(\text{CO})\text{ClL}_2$ initially occurs as evidenced by its precipitation. Excess ligand then converts this yellow benzene suspension into a bright red solution. The formation of black intractable oils rapidly occurs from this solution. Attempts at isolating $\text{RhCl}[\text{P}(\text{CH}_2\text{O})_3\text{CCH}_3]_3$ again were unsuccessful.

The formation of complexes of the formula $\text{RuCl}_2(\text{CO})_2\text{L}_2$ where L is a phosphine ligand has been investigated by various workers as mentioned in the

introduction. The work reported herein is concerned with the ligand $P(OCH_2)_3CR$ where $R = \underline{n}$ -propyl or \underline{n} -pentyl. The results which were obtained are summarized in Table 12. These complexes can exist in several isomeric forms as shown below.



Addition of a two-molar amount of ligand to the blood-red solution obtained by bubbling carbon monoxide through a refluxing ethanol solution of $RuCl_3 \cdot 3H_2O$, slowly produces a yellow precipitate. Using the \underline{n} -pentyl phosphite ligand, it was found that only one carbonyl band was present, at 1980 cm^{-1} , suggesting the presence of trans carbonyl groups. The 1H nmr in the methylene region appeared as a sharp 1:2:1 "triplet" at 4.39 ppm. This triplet pattern has been used extensively in assigning the stereochemistry of two phosphorus ligands as being trans to one another as mentioned previously. For example, Burt et al. (109)

Table 12. nmr and ir results obtained on complexes of formula $\text{RuCl}_2(\text{CO})_2\text{L}_2$

L =	Structure ^a	δ_{CH_2} ^b	$\nu(\text{C}=\text{O})$ ^c	$\nu(\text{Ru}-\text{Cl})$ ^c
$\text{P}(\text{OCH}_2)_3\text{CC}_5\text{H}_{11}$	i	4.39, "triplet"	1980	345
$\text{P}(\text{OCH}_2)_3\text{CC}_5\text{H}_{11}$	iv	4.41, broad	2030	345
$\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7$	i	4.47, "triplet"	2040	
$\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7$	ii	4.38, "triplet"	1985, 2030	

^aSee text, p. 128, for each of these structures.

^bChemical shift of methylene protons with respect to internal $\text{Si}(\text{CH}_3)_4$. CDCl_3 solution.

^cIn cm^{-1} , Nujol mull.

reported two "triplets" for the reaction mixture obtained by addition of iodine to trans-Ru(CO)₃[P(OCH₂)₃CC₂H₅]₂. The ir spectrum of this isomeric mixture showed the presence of three carbonyl bands, two for a cis isomer and one for a trans. Thus both structures i and ii were postulated for this isomeric mixture which was reported as inseparable. It thus seems probable that the ligand P(OCH₂)₃CC₅H₁₁ yields initially the complex trans Ru(CO)₂Cl₂[P(OCH₂)₃CC₅H₁₁]₂ of stereochemistry i.

Recrystallization of this complex from acetonitrile yields a yellow-orange compound with one carbonyl absorption at 2030 cm⁻¹. The ¹H nmr spectrum of the methylene protons now appears as a broad, featureless absorption at 4.41 ppm. These results again suggest that the two carbonyl ligands are trans to one another which occurs in both structures i and iv. Since i contains the trans phosphorus ligands, which have been shown to appear as a "triplet", this complex must now have isomerized to structure iv.

Investigation in the far ir region of these two isomeric complexes shows the presence of a strong absorption at 345 cm⁻¹ which can be attributed to the Ru-Cl stretching mode (121). Within experimental error, the two isomers yielded the same frequency for this absorption and only one band was observed in the case of isomer iv whereas two would have been expected owing to the cis relationship of the

chlorines.

An anomalous behavior of the yellow complex on heating was also found. At approximately 60° under vacuum it becomes a dark red while refluxing in alcoholic solvents returns the yellow color. The ir spectra of the yellow and red forms are identical from 50 cm⁻¹ to 4000 cm⁻¹. Experimental observations qualitatively show the red form to be more soluble in organic solvents than is the yellow form. Apparently, these are two crystalline forms of the same isomer. Chatt et al. (128) have shown that yellow trans-RuCl₂(CO)₂[P(CH₂CH₃)₃]₂ isomerizes to the white cis form at 160° in the solid state, or in solution above 80°. The trans isomer gives a carbonyl absorption at 1988 cm⁻¹ while the cis form shows two bands at 2042 and 1977 cm⁻¹. The cis form was shown as structure iii, i.e., with trans Cl and cis phosphorus ligands although the reasons for this particular stereochemistry were not given. It was rationalized that the cis isomer, in spite of its much larger dipole moment, should be more stable than the trans isomer since the carbonyl ligand, being a strongly double bonding ligand, prefers not to be in a trans position to another carbonyl.

Use of the n-propyl phosphite ligand, P(OCH₂)₃CC₃H₇, again gives a yellow precipitate which shows two triplets for the methylene protons in its nmr spectrum suggesting

two isomers, each with trans phosphorus ligands. Fractional recrystallization from methanol separates these two isomers into a cis carbonyl and a trans carbonyl form. The isomer of stereochemistry **i** gives $\nu(\text{CO})$ at 2040 cm^{-1} and $\delta(\text{POCH}_2)$ at 4.47 ppm while the isomer of stereochemistry **ii** registers $\nu(\text{CO})$ at 1985 cm^{-1} and 2030 cm^{-1} with $\delta(\text{POCH}_2)$ at 4.38 ppm.

SUGGESTIONS FOR FURTHER RESEARCH

The nmr parameters of the two iridium hydride complexes $\text{HIr}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2[\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7]$ and $\text{HIr}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3][\text{P}(\text{OCH}_2)_3\text{CC}_3\text{H}_7]_2$ were investigated and possible stereochemistries of these two compounds were postulated. The former compound was concluded to have a trans H-Ir-CO configuration. It has been noted by several workers (129, 130) that in complexes containing a trans H-M-CO, there is strong coupling between $\nu(\text{M-H})$ and $\nu(\text{C=O})$, both vibrations being of A_{1g} symmetry. By analyzing the corresponding deuterium compound, a large shift in $\nu(\text{C=O})$ was seen to occur, thus being indicative of the trans H-Ir-CO fragment. $\text{IrH}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_3$, which is the starting compound for the above mentioned mixed phosphine-phosphite complexes, is known to exchange with deuterium to form $\text{IrD}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_3$ (131). Thus the preparation of the deuterium analogues may be helpful in ascertaining whether or not either compound contains a trans H-Ir-CO fragment.

Also, an x-ray structure determination of one or both of these complexes could be used to unambiguously support or contradict the proposed structures.

The cobalt and rhodium hydride complexes prepared should lend themselves suitable to ^{59}Co and ^{103}Rh nmr spectroscopy by means of the INDOR method. Besides

obtaining the metal atom chemical shifts of these compounds, the metal-phosphorus coupling constants could also be determined. These studies may prove useful in better understanding of the chemical bonding in the complexes and the nature of heavy-atom chemical shifts.

An x-ray crystal structure determination of a complex of type HML_4 would also be useful. Those structures which have been done on complexes of this type, e.g., $HRh[P(C_6H_5)_3]_4$ and $HCo(PF_3)_4$, have been examples in which the hydride nmr spectrum was a very broad quintet structure indicative of possible intramolecular rearrangement. A structure should be performed on a complex which shows sharp, well resolved lines at room temperature, since it seems that these complexes may exist in solution as a square pyramidal structure with the hydride in the apex. Such a compound would possibly be $HRh[P(OCH_2)_3CC_3H_7]_4$.

More studies should be carried out on rhodium and iridium complexes of $P(CH_2O)_3CCH_3$. This particular ligand would seem to be better suited for dissociation in solution, thus producing the necessary co-ordinatively unsaturated complex which would be required for homogenous catalysis.

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