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Stereochemistry and bonding in organophosphorus compounds

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STEREOCHEMISTRY AND BONDING IN ORGANOPHOSPHORUS COMPOUNDS

by

Dennis William White

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.

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Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1970

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I. INTRODUCTION

The importance of organophosphorus compounds in biochemistry (1-2) and toxicology (3-5) is well known. Knowledge of their electronic and stereochemical structures is essential to the understanding of the roles they play in these fields. Since these compounds are often quite complex, initial structural studies are best made on model compounds. Many (I-CVII) of the models to be considered herein are listed in Tables 1-5. Included are open-chain and five- and six-membered mono- and bi-cyclic compounds containing either tricoordinate, trivalent phosphorus or tetracoordinate, pentavalent phosphorus. Also, all of them contain at least two alkoxyl groups bonded to phosphorus and the rings always have a $\underbrace{\mathrm{PO(C)}_n\mathrm{O}}$ skeleton (n=2,3).

The purpose of the ^{1}H and ^{31}P nmr, infrared, and dipole moment studies to be described in this Thesis is to increase our knowledge of the following areas:

- Solution stereochemistry of the six-membered monocyclic compounds
    - Number and percentages of conformational isomers (conformers)
    - Form (chair, boat, etc.) of these conformers
    - Stereochemical preferences of the exocyclic groups
    - Rate of conformer interconversion
    - Dependencies of conformer percentages on the solvent, concentration and temperature
    - Rate of phosphorus atomic inversion

Nature of the exocyclic bond to phosphorus in 1-substituted-1-phospha-2,6-dioxacyclohexanes

Solution stereochemistry of the open-chain compounds $X:P(OR)_3$

Rotation of the OR groups about the PO bonds

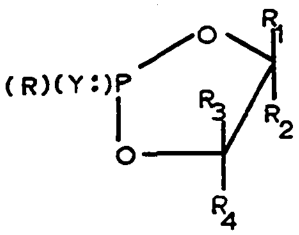
Dependence of the stereochemistry on X

Variation of the σ- and π-bonding characters of the phosphoryl linkage from open-chain to monocyclic to bicyclic trialkyl phosphates

Relative stabilities of the BH_3 adducts of open-chain, monocyclic, and bicyclic trialkyl phosphites

Cause of the doublet phosphoryl stretching band in the infrared spectra of the bicyclic phosphates.

Table 1. 1-Phospha-2,5-dioxacyclopentanes



Compound[a]	R	Y	R_1	R_2	R_3	R_4
I	OCH_3	0	H	H	H	H
II	OCH_3	0	CH_3	CH_3	CH_3	CH_3
III	OCH_3	-	H	H	H	H
IV	OC_2H_5	-	H	H	H	H
V	$N(C_2H_5)_2$	-	H	H	H	H
VI	OCH_3	-	CH_3	CH_3	CH_3	CH_3
VII	OC_6H_5	-	CH_3	CH_3	CH_3	CH_3
VIII	C_6H_5	-	CH_3	CH_3	CH_3	CH_3
IX	$N(CH_3)_2$	-	CH_3	CH_3	CH_3	CH_3
X	Cl	-	CH_3	CH_3	CH_3	CH_3
XI A,B	Cl	-	CH_3	H	H	H
XII A,B	OCH_3	-	CH_3	H	H	H
XIII A,B	OC_2H_5	-	CH_3	H	H	H
XIV	Cl	-	H	H	H	H
XV	F	-	H	H	H	H
XVI	OC_6H_5	-	H	H	H	H
XVII	$OCOCH_3$	-	H	H	H	H
XVIII	$OCOC_6H_5$	-	H	H	H	H
XIX A,B	Cl	-	CH_3	H	CH_3	H

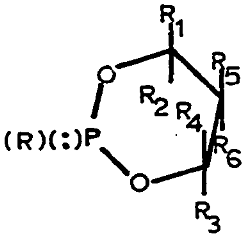
---

[a] A and B are geometrical isomers. Isomer A is thermodynamically more stable at room temperature.

Table 1 (continued)

Compound[a]	R	Y	R_1	R_2	R_3	R_4
XX	Cl	-	CH_3	H	H	CH_3
XXI A,B	OCH_3	O	CH_3	$COCH_3$	CH_3	$COCH_3$
XXII	OCH_3	O	CH_3	$COCH_3$	$COCH_3$	CH_3
XXIII A,B	OCH_3	O	H	C_2H_5	CH_3	$COCH_3$

Table 2. Trivalent 1-phospha-2,6-dioxacyclohexanes



Compound[a]	R	R_1	R_2	R_3	R_4	R_5	R_6
XXIV	OC_6H_5	H	H	H	H	CH_3	CH_3
XXV	$OC(CH_3)_3$	H	H	H	H	CH_3	CH_3
XXVI A,B	OC_2H_5	H	CH_3	H	H	H	H
XXVII A,B	OCH_3	H	CH_3	H	H	H	H
XXVIII A,B	OCH_3	H	H	H	H	CH_3	H
XXIX	OCH_3	H	H	H	H	CH_3	CH_3

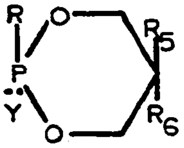
---

[a] A and B are geometrical isomers. Isomer A is thermodynamically more stable at room temperature.

Table 2 (continued)

Compound[a]	R	R_1	R_2	R_3	R_4	R_5	R_6
XXX A,B	OCH_3	H	H	H	H	$C(CH_3)_3$	H
XXXI A,B	OCH_3	H	H	H	H	CH_2Cl	CH_3
XXXII A,B	OCH_3	H	CH_3	CH_3	H	H	H
XXXIII	OCH_3	CH_3	H	CH_3	H	H	H
XXXIV	OCH_3	H	H	H	H	H	H
XXXV	$N(CH_3)_2$	H	H	H	H	CH_3	CH_3
XXXVI	F	H	H	H	H	CH_3	CH_3
XXXVII A,B	F	H	H	H	H	CH_2Cl	CH_3
XXXVIII	Cl	H	H	H	H	CH_3	CH_3
XXXIX A,B	Cl	H	H	H	H	CH_2Cl	CH_3
XL A	Cl	H	H	H	H	$C(CH_3)_3$	H
XLI A	Cl	H	CH_3	CH_3	H	H	H
XLII	Cl	CH_3	H	CH_3	H	H	H
XLIII A	Cl	H	CH_3	H	H	H	H
XLIV	Br	H	H	H	H	CH_3	CH_3
XLV A,B	Br	H	H	H	H	CH_2Cl	CH_3
XLVI	C_6H_5	H	H	H	H	CH_3	CH_3
XLVII	SC_6H_5	H	H	H	H	CH_3	CH_3

Table 3. Pentavalent 1-phospha-2,6-dioxacyclohexanes

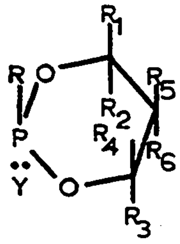


Compound	R	Y	R_5	R_6
XLVIII	CH_3	0	$\underline{t}\text{-}C_4H_9$	H
XLIX	Br	0	CH_3	CH_2Br
L	OC_6H_5	0	H	H
LI	OH	0	CH_3	CH_3
LII	$N(CH_3)_2$	S	CH_3	CH_3
LIII	$NH(\underline{n}\text{-}C_3H_7)$	0	CH_3	CH_3
LIV	$NH(\underline{n}\text{-}C_5H_{11})$	0	CH_3	CH_3
LV	$NH(\underline{t}\text{-}C_4H_9)$	0	CH_3	CH_3
LVI	$N(C_2H_5)_2$	0	CH_3	CH_3
LVII	$O\underline{n}\text{-}C_3H_7$	0	CH_3	CH_3
LVIII	$O\underline{n}\text{-}C_4H_9$	0	CH_3	CH_3
LIX	OC_6H_5	0	CH_3	CH_3
LX	OCH_3	0	CH_3	CH_3
LXI	OC_2H_5	0	CH_3	CH_3
LXII	$O\underline{i}\text{-}C_3H_7$	0	CH_3	CH_3
LXIII	$O\underline{p}\text{-}C_6H_4CH_3$	0	CH_3	CH_3
LXIV	$0\text{-}3,5\text{-}(CH_3)_2C_6H_3$	0	CH_3	CH_3
LXV	$0\text{-}2,6\text{-}(CH_3)_2C_6H_3$	0	CH_3	CH_3
LXVI	$0\text{-}2,6\text{-}(\underline{t}\text{-}C_4H_9)_2\text{-}4\text{-}(CH_3)C_6H_2$	0	CH_3	CH_3
LXVII	$C_6H_5CH_2$	0	C_2H_5	CH_2Cl
LXVIII	$C_6H_5CH_2$	0	CH_2Cl	C_2H_5

Table 3 (continued)

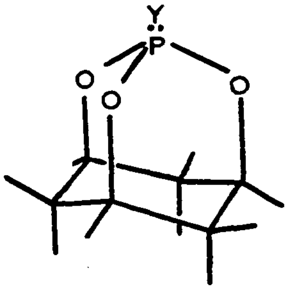
Compound	R	Y	R_5	R_6
LXIX	$C_6H_5CH_2$	O	CH_2Cl	CH_2Cl
LXX	Cl	O	C_2H_5	CH_2Cl
LXXI	Cl	O	CH_2Cl	C_2H_5
LXXII	NC_5H_{10}	O	C_2H_5	CH_2Cl
LXXIII	NC_5H_{10}	O	CH_2Cl	C_2H_5
LXXIV	NC_5H_{10}	O	CH_3	CH_2Cl
LXXV	NC_5H_{10}	O	CH_2Cl	CH_3
LXXVI	Cl	O	CH_3	CH_2Cl
LXXVII a,b	NC_5H_{10}	O	CH_3	CH_3
LXXVIII	OCH_3	O	H	H
LXXIX	OCH_3	BH_3	CH_3	CH_3
LXXX	OCH_3	BH_3	CH_2Cl	CH_3
LXXXI	OCH_3	BH_3	CH_3	CH_2Cl

Table 4. Additional pentavalent 1-phospha-2,6-dioxacyclohexanes

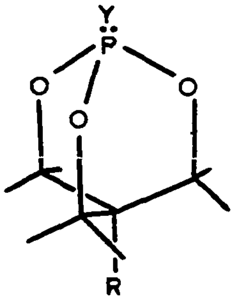


Compound	R	Y	R_1	R_2	R_3	R_4	R_5	R_6
LXXXII	OC_6H_5	0	H	CH_3	H	H	H	H
LXXXIII	OC_6H_5	0	CH_3	H	H	H	H	H
LXXXIV	OC_6H_5	0	CH_3	CH_3	H	CH_3	H	H
LXXXV	OC_6H_5	0	CH_3	CH_3	CH_3	H	H	H
LXXXVI	OC_6H_5	0	H	H	H	$CH(CH_3)_2$	CH_3	CH_3
LXXXVII	OC_6H_5	0	H	H	$CH(CH_3)_2$	H	CH_3	CH_3
LXXXVIII	$CH_2C_6H_5$	0	H	H	CH_2Cl	H	H	H
LXXXIX	Br	0	H	H	CH_2Br	H	H	H
XC	OCH_3	BH_3	CH_3	H	H	CH_3	H	H
XCI	OCH_3	BH_3	H	CH_3	CH_3	H	H	H

Table 5. Bicyclic and open-chain derivatives

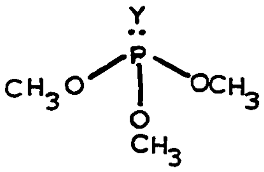


Compound	Y
XCII	-
XCIII	BH_3
XCIV	0
XCV	S
XCVI	$[-Ni(PO_3C_6H_9)_4](ClO_4)_2$

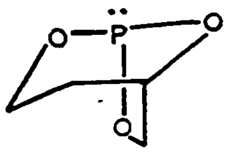


Compound	Y
XCVII(R)	-
XCVIII(R)	BH_3
XCIX(R)	0
C(R)	$\{-Ag[P(OCH_2)_3CR]_3\}(ClO_4)$

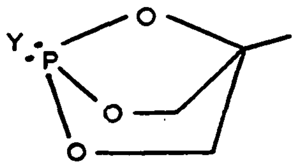
Table 5 (continued)



CI - CIII



CIV



CV - CVII

Compound	Y
CI	-
CII	BH_3
CIII	0
CIV	
CV	-
CVI	BH_3
CVII	0

II. REVIEW OF LITERATURE

The goal of this chapter is to present the more important results and conclusions of other investigators pertinent to the study of the areas mentioned in the Introduction. The methods used to synthesize most of the compounds studied have been described in recent reviews (2,6) and books (7a,7b,8). The two volumes by Sasse (7a,7b) provide a complete coverage of the synthetic literature of organophosphorus compounds through 1961 and 1962, respectively. The book by Gefter contains useful tables of structural formulas, physical data and literature references of monocyclic compounds (8, pp. 112-122). The hydrolysis of phosphate esters, especially monocyclic esters, has received considerable attention because of its biological importance and this area has been reviewed by Westheimer (9). Some of the stereochemical aspects to be discussed below have been reviewed very recently (10, pp. 22, 44-6, 51-5, 70, 71, 79, 80, 83, 84).

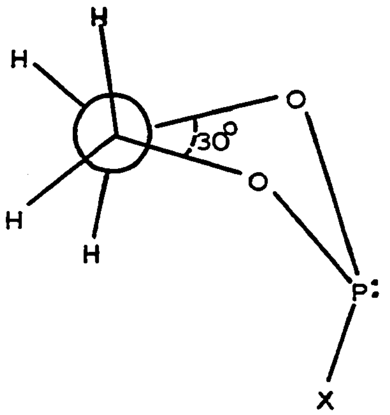
The stereochemistry of the five-membered monocyclic derivatives has been studied primarily by x-ray diffraction and nmr methods. The solid state molecular structures of the phosphates I (11) and II (12) are puckered and have equivalent bond distances except for the ring C-C and C-O distances which are longer in the tetramethyl derivative. The puckering is greater in II, presumably due to steric crowding of the four methyl groups bonded to the ring carbon atoms. More significantly, the methoxyl methyl group is centered between the ring oxygen atoms in I but is over the phosphoryl oxygen in II, representing a methoxyl rotation of approximately 180°. Newton, _et_ _al_. (12) expected the methyl groups to cause some shifting of the position of this group but were surprised at its magnitude. They explained the presence of just these two extreme positions in terms of favorable p-d π-bonding of the methoxyl oxygen to phosphorus rather than in terms of hydrogen bonding of the methoxyl methyl to one or more of the other three oxygen atoms. Also, the fact that the symmetry of the oxygen π-orbitals in these cyclic molecules permits one less π-bond (giving a more positive phosphorus) than in open-chain esters was used to partially account for the relatively-great rate of hydrolysis of the former.

The influence of intermolecular interactions on stereochemistry is difficult to determine and the assumption of similar stereochemistry in the solid and in solution is thus not necessarily justified. ^{1}H nmr spectroscopy has recently begun to yield some useful information on solution stereochemistries. Foster and Fyfe (13) concluded from such studies that the trivalent phosphorus atoms in III-V have a tetragonal arrangement of groups about them and do not invert rapidly on the nmr time scale. The methylene ^{1}H nmr resonances of the pure compounds, shown at high resolution but not analyzed, are complex multiplets rather than the doublets expected if the groups about phosphorus were planar or averaged to a planar configuration due to rapid phosphorus atomic inversion. Goldwhite and Fontal (14,15) arrived at the same conclusion for VI-X. Additional evidence for slow phosphorus inversion was the constancy of the chemical shifts (14) of the two peaks, rather than one, observed for the four methyl groups for VI-VIII over at least a 100°C temperature range. Although the chemical shift of the low-field peak for the dimethylamino derivative (IX) was solvent dependent and coincided with that of the other peak in dilute benzene or toluene, a variable temperature study confirmed slow phosphorus inversion for this compound also up to at least 151°C. The chloro compound (X) is unique because the spectrum is a singlet for the neat liquid at room temperature but broadens and finally splits into two peaks if the temperature is lowered or if the liquid is diluted with an inert solvent. The latter observation and the dependence of the coalescence temperature and the chemical shift difference on concentration in aromatic solvents indicated that thermal inversion of phosphorus, a concentration independent process, was not the only cause of the single peak at higher temperatures. A likely process was thought to be a bimolecular chloro exchange involving an inversion at phosphorus. Goldwhite also obtained the spectra of XI A,B and XII A,B (14). The two methyl resonances that were found for each were attributed to two geometrical isomers in ratios of 1.65:1 and 1.55:1, respectively. Aksnes, Ericksen and Mellingen (16) added XI A,B and XIII A,B to a solution of sulfur in carbon disulfide and found approximately equal amounts of thiophosphate isomers in the latter case by partial gas chromatographic separation. These workers assumed that the ratio of isomeric phosphites was the same as that of the thiophosphates.

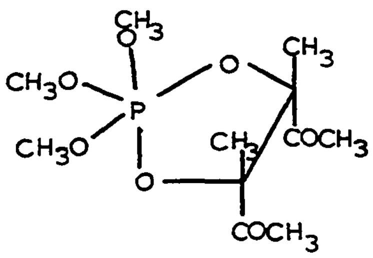
Gagnaire and coworkers (17) analyzed the ^{1}H nmr spectra of six 1-R-1-phospha-2,5-dioxacyclopentanes (III, XIV-XVIII) and the three isomers of 1-chloro-1-phospha-3,4-dimethyl-2,5-dioxacyclopentane (XIX A,B and XX). The two POCH coupling constants for the first six derivatives were found to be about $\pm$1.5 and $\pm$9.5 Hz, i.e., essentially independent of the exocyclic group R. Two cyclic isomers (XIX A and B) were spectrally detected in the product of the action of meso-2,3-butanediol on phosphorus trichloride. The symmetry of the spectrum indicated a plane of symmetry for each isomer, but J(POCH) was 2Hz for the major isomer and 9Hz for the minor isomer. Also, a reversible isomer ratio change took place with changing temperature, it being 12:1 at 30° and 7:1 at 120°C. The isomerization, attributed to either intra- or inter-molecular phosphorus inversion, was slow relative to the nmr time scale but too fast for isolation of either of the isomers. The chlorine atom was tentatively concluded to be anti to the methyl groups in the major isomer and syn in the minor one on the basis of the greater size of the chlorine atom compared to the phosphorus lone electron pair and the deshielding effect of the chlorine on protons in its vicinity. The chloro compound (XX) derived from racemic 2,3-butanediol is unique among those studied because it lacks a plane of symmetry. A cyclic deformation resulting from this lack of symmetry was postulated to account for the rather different set of POCH coupling constants of 4.2 and 0 Hz. In order to account for the coupling constants of the other compounds, these authors proposed that the spatial disposition of the phosphorus lone pair of electrons plays a role in the coupling, possibly through an overlap of the nonbonding lobe of the orbital of the CH fragment and the lone-pair orbital.

More recently, Haake and coworkers (18) analyzed the spectra of III (benzene), XIV (benzene) and XVI (cyclohexane) and in each case postulated two equivalent twist-envelope forms, one of which is approximately shown below. The coupling constants agree with those found by

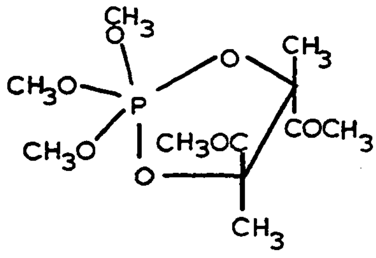
Gagnaire, et al. (17) for the neat compounds within 0.6 Hz. The twist was determined by finding one set of constants k_1 and k_2 that would permit the vicinal ^1H-^1H coupling constants for these compounds and ethylene sulfite from the equations $J_{cis} = k_1 \cos^2 \phi$ and $J_{trans} = \frac{1}{2} [k_2 \cos^2 (120 + \phi) + k_1 \cos^2 (120 - \phi)]$, wherein ϕ is the dihedral angle between the two ring CCO planes; the best correlation involved the omission of the data for XIV. The angle ϕ was thus found to be 32° for III and 27° for XVI. The envelope nature of the rings, rather than the orientation of the phosphorus lone pair (17), was postulated to account for the large difference between the POCH coupling constants for each compound. The chloro compound XIV is superficially like X (15) because the spectrum of neat XIV was a singlet at room temperature which broadened and split into two peaks as the temperature was lowered. Dilution with an inert solvent produced a complex spectrum corresponding to the doublet for X. In contrast, Gagnaire, et al. (17) observed a complex spectrum for the neat XIV. Moreover, the observance of a singlet is puzzling because analysis of the complex spectrum (17) revealed POCH coupling constants of ±1.6 and ±9.8 Hz.



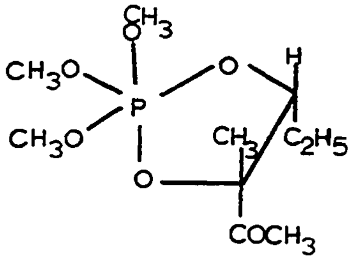
Less is known about the solution stereochemistry of tetracoordinate phosphorus five-membered monocycles. Ramirez and coworkers showed (19, 20) that the compound obtained by slow crystallization from ether of the cyclic product(s) of reaction of CVIII with one mole equivalent of water was one of the two possible <u>meso</u>-phosphates (XXI A,B). Moreover, it underwent a slow stereomutation at phosphorus in solution, probably catalyzed by traces of methanol. The ratio of <u>meso</u> isomers became nearly equal upon aging of the solution as shown by the relative intensities of the separate ^{1}H nmr resonances for the two. The racemic oxyphosphorane CIX hydrolyzed to give the one possible racemic phosphate XXII. These workers have also examined the ^{1}H and ^{31}P nmr and infrared spectra of other cyclic phosphate hydrolysis products of oxyphosphoranes (20). As an example, CX gave a mixture of the two isomeric XXIII A,B. The infrared spectra were very similar but among the differences in the nmr spectra were the ^{31}P chemical shifts and ^{31}P coupling constants to the ring protons which were -13.95 ppm and 4.4 Hz for one and -15.21 ppm and 14 Hz for the other. The isomer with the smaller coupling constant was tentatively assigned a puckered



CVIII



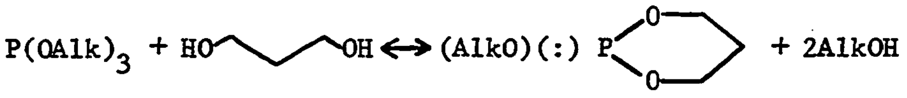
CIX



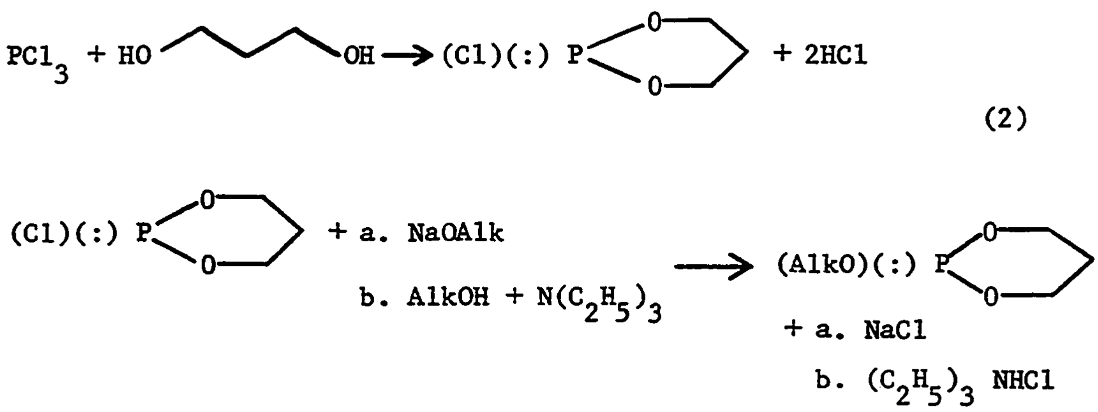
CX

ring structure with the acetyl group cis to the phosphoryl oxygen. The POCH dihedral angle would be closer to 90° in this cis isomer than in the other, giving a smaller coupling constant, and the assumed deshielding effect of the phosphoryl bond would give rise to the observed relative chemical shifts of each of the H, CH_3, C_2H_5 and $COCH_3$ types of protons in the two isomers.

No solid state structure has been reported for a trivalent phosphorus 1-R-1-phospha-2,6-dioxacyclohexane, probably because most are liquids at room temperature. Knowledge of the solution stereochemistry of these compounds has lagged behind that of the superficially similar 1,3-dioxacyclohexanes (21, 22) and 1-oxo-1-thia-2,6-dioxacyclohexanes (23). Denney and Denney reported chemical and ^1H nmr data suggesting the existence of several pairs of geometrical isomers for six-membered ring phosphites early in 1966 (24). The two methods used to prepare these methoxyl derivatives are outlined in Equations 1 and 2. The phosphite XXVIII, prepared as in Equation 1, showed two doublet resonances for the



(1)



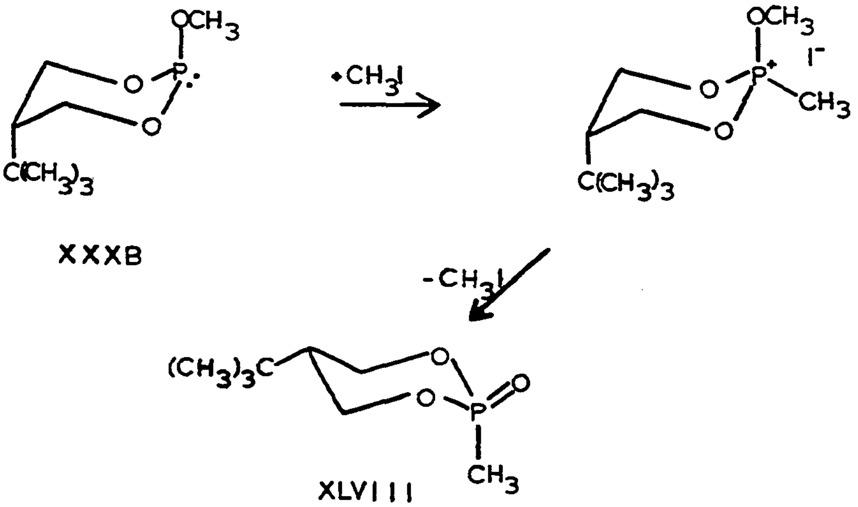
(2)

methyl group (R_5) that had chemical shifts very similar to those of the methyl (R_5, R_6) resonances for XXIX; the ratio of the areas of the peaks for XXVIII A and B was 4:1 in carbon tetrachloride. The phosphite XXVII, prepared similarly, showed just one methyl (R_2) resonance. However, preparation as in Equation 2a yielded various ratios of two cyclic products (XXVII A,B) as indicated by the various ratios of the previously-found methyl (R_2) resonance to a new one. Treatment of one of these mixtures with a trace of methanol caused the new resonance to disappear. In an analogous manner, one methyl (R_2, R_3) resonance was found for XXXII and two for XXXIII when prepared as in Equation 1. However, preparation of a mixture of XXXII and XXXIII as in Equation 2a resulted in a spectrum with just one additional methyl resonance. Treatment of this mixture with a trace of methanol resulted in the loss of the new resonance and a compensating gain in the relative area of that due to XXXII A. Efforts to separate XXVIII A and B, XXVII A and B, or XXXII A and B by gas-liquid-partition chromatography were unsuccessful. However, oxidation yielded mixtures of the corresponding phosphates that could thus be separated. These pairs were thought to be geometrical isomers rather than non-interconverting conformers. On the one hand, transesterification (Equation 1) was considered to have given an equilibrium mixture of isomers. On the other hand, the action of sodium methoxide on the chloro derivatives (Equation 2a), apparently having the same preferred configuration as the phosphites, involved an inversion of configuration at phosphorus. The fact that the isomer ratios via Equation 2a were always less than the inverse of those via Equation 1 was attributed to isomerization of the less-thermodynamically stable isomer

(B) under the reaction conditions of Equation 1.

Aksnes, Eriksen and Mellingen carried out a similar investigation of XXVI A,B and arrived at analogous conclusions (16). Nearly pure unstable isomer XXVI B was obtained via Equation 2b because the weaker nucleophile ethanol was used in place of sodium ethoxide. Also, XXVI B isomerized rapidly in the presence of traces of acid. The ratios of chloro (XLIII) and ethoxy (XXVI) isomers were determined by gas chromatographic analysis of the corresponding thiophosphates as discussed previously for the five-membered analogs. In this manner the chloro compound (XLIII) was deduced to be configurationally pure. The assumption that it has the same configuration as the stable phosphite XXVI A then led to the hypothesis that the second step of Equation 2b proceeds with inversion at phosphorus.

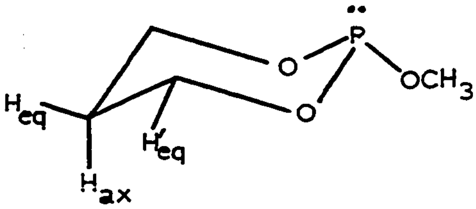
Characterization of the conformation(s) of the 1-phospha-2,6-dioxacyclohexanes XXX A,B and XL A has recently been accomplished by Hargis and Bentrude (25). One isomer of XL and a 1:9 ratio of XXX A:B were prepared by Equation 2b in contrast to the 9:1 ratio of XXX A:B prepared by Equation 1. Comparison of the vicinal HCCH coupling constants for XXX A and XL A with those for the corresponding 1,3-dioxacyclohexanes (21) indicated that the t-butyl group is equatorial in both. Furthermore, the differences in magnitudes of the POCH coupling constants, 11.28 and 5.24 Hz for XL A and 10.98 and 2.89 Hz for XXX A, are more indicative of the quite different 180° and 60° POCH dihedral angles of a chair conformer than the approximately-equal angles of a boat. The analogous coupling constants for XXX B differ considerably from those for XXX A and varied with the solvent and temperature. The preferred interpretation of the data involves an equilibrium of rapidly interconverting chair conformers in which the major conformer possesses an axial *t*-butyl group. Even more recently, Bentrude and Hargis have presented evidence for the axial disposition of the methoxyl group at phosphorus in XXX A and B (26). Reaction of methyl iodide with mixtures of various ratios of the phosphites XXX A and B was found to be highly stereoselective. An x-ray crystal structure study (27) of the product (XLVIII) formed from XXX B showed the six-membered rings to be in the chair conformation with the *t*-butyl and methyl groups *cis* to each other and equatorially and axially oriented, respectively. If the reaction proceeded as shown in Equation 3 (28, pp. 37-45), the methoxyl group must be *trans* to the *t*-butyl group in XXX B and therefore predominantly axial because the *t*-butyl group was shown (25) to be predominantly axial. Consequently, the methoxyl group in XXX A must be axial also because XXX A and B are geometrical isomers and the *t*-butyl group in XXX A was found to be equatorial (25).

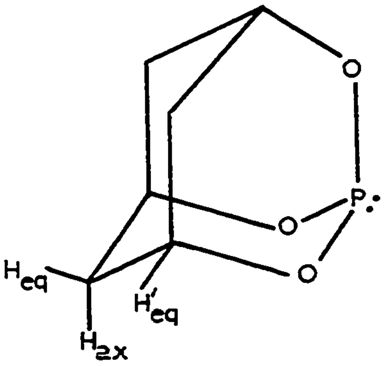


(3)

Gagnaire, Robert and Verrier (29, 30) determined the ^1H nmr spectral temperature variation and parameters for a series of 4,4-dimethyl derivatives (XXIV, XXIX, XXXVI, XXXVIII, XXXV, and XLVI). The temperature independence of the coupling constants and chemical shifts for the first four between -40°C and +155°C plus the existence of different resonances for axial and equatorial methyl groups (R_5, R_6) and ring methylene protons (R_1-R_4) led them to conclude that one conformer is present for each compound and that it is rigid at the frequencies of observation of the nmr. Comparison of the results of the spectral analysis with those for other cyclic compounds indicated a chair form for the single conformer with an equatorial exocyclic group R (vide infra) at phosphorus.

Albrand, Gagnaire, Robert and Haemers have arrived at the same stereochemical conclusions for XXXII A and XLI A from ^1H nmr spectral analysis (31). In this instance, the important data were the vicinal HCCH and four-bond POCCH couplings. The methyl (R_2, R_3) and R_3 groups were concluded to be equatorial in a fixed chair conformer. The disposition of the exocyclic group R in these and the previously-studied compounds (29, 30) was determined by comparing the values of the cyclic J(POCCH) and J(POCH), respectively, with those for XCII shown below in a manner emphasizing the presence of a six-membered ring in a chair conformation. It should be noted that the pseudo-exocyclic oxygen in XCII is axial relative to the six-membered ring. The differences of the magnitudes of $J(POCH'eq)$ = 6 Hz (XCII) versus 10.8 Hz (XXIX, 30), $J(POCCH_{eq})$ = 0.5 Hz (XCII) versus 3.6 Hz (XXXII A) and $J(POCCH_{ax})$ = 0 Hz (XCII) versus 0.5 Hz (XXXII A) implied to these authors that the





XCII

methoxyl group in XXIX (30) and XXXII A could not be axial and must therefore be equatorial. In other words, as found earlier for the five-membered analogs (17), there exists a great influence of the stereochemical disposition of the phosphorus lone pair on phosphorus-hydrogen coupling constants. The non-methoxyl derivatives were also concluded to have an equatorial group R because each was concluded to be conformationally pure and the POCH and POCCH coupling constants were similar to those for the respective methoxy compounds in most instances.

Stereochemical investigations of pentavalent phosphorus six-membered heterocycles of the 1-phospha-2,6-dioxacyclohexane type are more numerous than those of the preceding cyclic compounds. Notably, almost all of the compounds contain the phosphoryl (P=O) linkage. Reports of solid state structural determinations of XLVIII-LI stand in contrast to the absence of any such studies of the five- and six-membered trivalent phosphorus derivatives. In all four molecules the phosphoryl oxygen was found to be pseudo-equatorial in a distorted chair conformer. The available limited information for XLVIII (27) has previously been presented in this section. In XLIX the bromine atom and bromomethyl group surprisingly are axial (32). However, flattening at the phosphorus end of the ring was reported for XLIX and L (33) and the bond angles and distances reported for LI (34) indicate that this molecule is probably similar. In XLIX, for example, the normal to a least-squares plane through O_2, O_6, C_3 and C_5 makes an angle of 36.7° with the normal to the plane defined by O_2, P_1 and O_6 in contrast to the angle of 52.3° with the normal to the plane defined by C_3, C_4 and C_5. As a consequence of these flattenings, the steric interactions of the pseudo-axial group at phosphorus with the axial hydrogens at C_3 and C_5 are reduced.

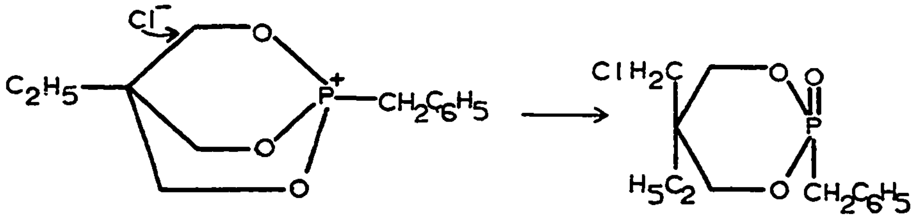
The ^1H and some of the ^{31}P nmr spectra of twenty-eight 4,4-disubstituted-1-phospha-2,6-dioxacyclohexanes and five bicyclic pyrophosphates have been described by Bartle, Edmundson and Jones (35). In the first twenty-eight: R = alkyl, alkoxyl, aryloxyl, alkylamino, halo, or H; Y=0 or S; $R_5 = R_6 = CH_3$ or C_2H_5; $R_5 = CH_3$, $R_6 = ClCH_2$. For several compounds, the resonance due to the methylene protons at C_3 and C_5 was analyzed according to an ABX and/or AMX spin-system approximation, where X is phosphorus. Also, the spectral features in several instances were shown to be consistent with a chair conformation. In a subsequent paper (36), Edmundson and Mitchell examined two ^1H nmr spectral features of fifteen compounds (some of the twenty-eight compounds and several additional 4,4-dimethyl substituted derivatives) in more detail. The first feature was the measurable difference in the widths of the two methyl resonances. Decoupling experiments on one of the compounds, LII, showed that the protons of one of the methyl groups couple strongly to one of the pairs of methylene protons. Noting that enhanced HCCCH couplings have been reported for protons linked by a planar zig-zag arrangement of bonds, these authors attributed the narrow and broad methyl resonances to equatorial and axial methyl groups, respectively. The second feature was the relative positions of the two methyl resonances in the spectra of the compounds possessing an aralkyl group at phosphorus in comparison with the relative positions for the other compounds. Two lines of reasoning, concerned with the "steric acceptability of aralkyl groups" and the dependence of the position of the methyl resonances in deuteriochloroform on the axial-equatorial position of the aralkyl groups, led to the conclusion that the aralkyl groups are equatorial at phosphorus. The effect of benzene compared to deuteriochloroform as a solvent on the absolute and relative chemical shifts of the methyl resonances was also described.

Kainosho and coworkers have presented ^{1}H nmr (37), infrared (38), and dipole moment (39) evidence for a solution equilibrium between two chair conformers for LIII-LXVI (38, 39) in which the preferred conformation possesses an equatorial phosphoryl oxygen. The nmr method was used to establish the chair-like structure of the rings, but the pertinent paper (37) is not yet available. The dipole moments of LIII-LIX were measured and compared to moments calculated for the possible chair conformers with the amino, alkoxyl or phenoxyl groups in several rotameric positions in order to establish the preferred conformer. The observed values for LVI-LIX were clearly in agreement with an equatorial phosphoryl oxygen, but those for LIII-LV were near the middle of the range of calculated values so that additional evidence was required. The similarity of the phosphorus to ring-methylene proton couplings for LIII-LV and LVI strongly indicated that the phosphoryl oxygens in LIII-LV were equatorial also. The infrared spectra of the phosphates LX-LXVI were examined in potassium bromide and carbon tetrachloride in order to determine if the phosphoryl stretching frequency was conformationally dependent. Only one band could be attributed to this vibration in the former medium, but the addition of phenol to each of the carbon tetrachloride solutions caused two bands to shift to lower frequencies, possibly due to hydrogen bonding to the phosphoryl oxygen. The higher frequency band was attributed to stretching of an equatorial phosphoryl linkage because it was of much greater intensity than the lower frequency band for LX-LXIV and the dipole moment evidence for the phosphates LVII-LIX indicated the preferred conformers possessed an equatorial phosphoryl oxygen (39). The intensity ratios of the high to low frequency bands for LXV and LXVI were about 2:1 and 1:1, in agreement with the nmr results (37) and the expected greater proportion of the conformer with an equatorial ortho-substituted phenoxy group at phosphorus.

Many geometrically-isomeric derivatives have been reported but their stereochemical characterization has been limited at best. The synthesis and separation of isomeric phosphates by Denney and Denney (24) and of isomeric thiophosphates by Aksnes, et al. (16) have been mentioned previously. However, the stereochemical nature of these derivatives was not deduced. Hall and Malcolm (40) separated isomeric 1-phenoxy-1-oxo-1-phospha-2,6-dioxacyclohexanes, e.g., LXXXII-LXXXIII and LXXXIV-LXXXV, by thin layer or column chromatography and examined their ^{1}H and ^{31}P nmr spectra. Although the ^{1}H spectra of two isomers were "virtually identical," the ^{31}P resonances were separated by about 1 ppm. Majoral, Munoz and Navech (41) used infrared and ^{31}P nmr methods to study the structures of LIX and LXXXII-LXXXVII. Two ^{31}P resonances were found for each of the isomer pairs but only LXXXVI and LXXXVII could be separated by fractional crystallization. Infrared bands attributable to the phenyl ring were doubled for LIX, LXXXII-LXXXIII and LXXXIV-LXXXV but single for the separated LXXXVI and LXXXVII. Also, only one phosphoryl stretching band was found for LIX, LXXXII-LXXXIII and LXXXIV-LXXXV but those for LXXXVI and LXXXVII were 17 cm^{-1} apart.

These observations and the known solid state structure of L (33) led to two conclusions. On the one hand, the isomers LXXXVI and LXXXVII most likely have the equatorial isopropyl group in chair conformations, but one has an axial and the other an equatorial phenoxy group at phosphorus. On the other hand, LIX, LXXXII-LXXXIII and LXXXIV-LXXXV have rings for which the possibility of inversion causes the phenoxy group to be sometimes axial and sometimes equatorial.

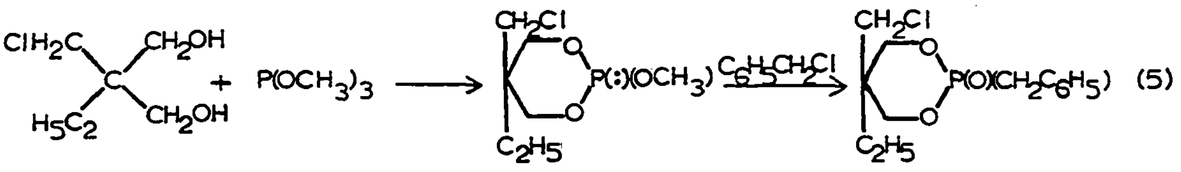
The known stereospecificity of a reaction leading to geometrical isomers can be used to deduce the configuration of the products or, conversely, the configuration(s) of the product isomer(s) can be used to deduce the stereochemical course of the reaction. One of the earlier such investigations was reported by Wadsworth and Emmons in 1962 (42). The action of benzyl chloride on the bicyclic phosphite $P(OCH_2)_3CC_2H_5$, XCVII (C_2H_5), at elevated temperatures gave one of two possible monocyclic isomeric phosphonates as determined by vapor-phase-chromatography. The benzyl and ethyl groups were concluded to be <u>cis</u> because of the bridged structure of XCVII (C_2H_5) and the mechanism of the Arbuzov reaction (28, pp. 37-45) as shown in Equation 4. However, when the re-



(4)

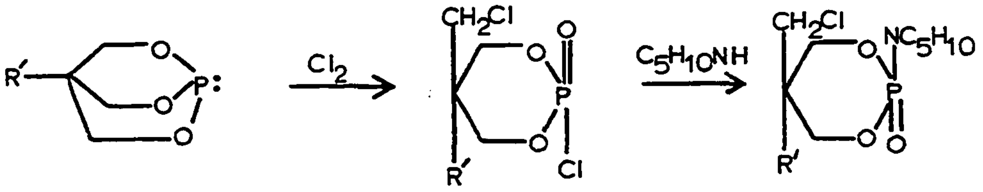
LXVII

actions in Equation 5 were used to prepare the phosphonate, two isomers, LXVII and LXVIII, resulted and could be separated by column chromatography. Furthermore, the identical phosphoryl stretching frequency,



LXVII and LXVIII

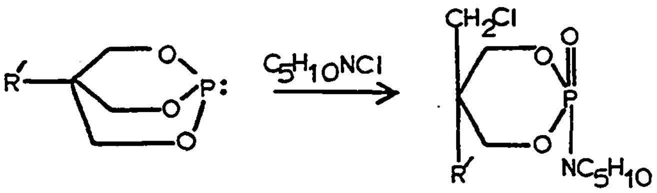
$\nu(P=O) = 1260\ cm^{-1}$, for the two indicated the isomers differed only by the configuration of the ethyl and chloromethyl groups at C_4. In support of this conclusion, only one LXIX was obtained, which had $\nu(P=O) = 1260\ cm^{-1}$, regardless of the preparative route. In contrast to the stereospecificity of the reaction of XCVII (C_2H_5) with benzyl chloride, reaction with chlorine and bromine gave both cis- and trans-1-halo-1-oxo-4-ethyl-4-halomethyl-1-phospha-2,6-dioxacyclohexanes, e.g., LXX and LXXI. On the other hand, Bertrand (43) isolated only one isomer XLIX from the reaction in benzene of bromine with XCVII (CH_3). Wadsworth (44) has used the stereospecificity of the Arbuzov reaction of chlorine and N-chloropiperidine with XCVII (C_2H_5) to elucidate the mechanism of substitution of chlorine at phosphorus in LXXX by piperidine, as shown in Equations 6 and 7. Different isomeric phosphoroamidates, LXXII and LXXIII, were obtained by each route even though this author earlier reported chlorination of XCVII (C_2H_5) to be nonstereospecific. Since the chlorine atom and piperidino group were known to be cis to the ethyl group in LXX and LXXII, respectively, the action of piperidine on LXX



XCVII(C_2H_5) LXX LXXIII

XCVII(CH_3) LXXV

(6)

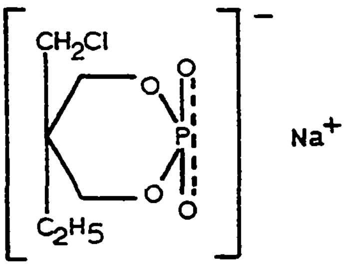


XCVII(C_2H_5) LXXII

XCVII(CH_3) LXXIV

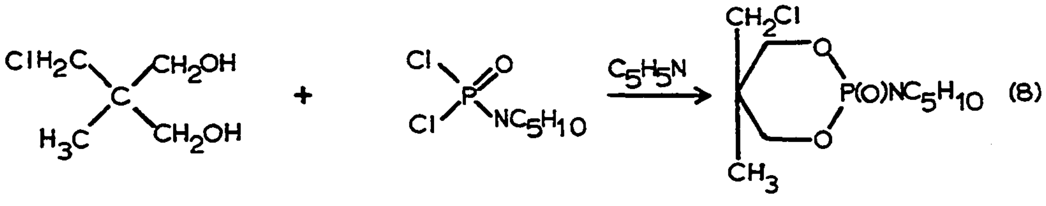
(7)

must have involved an inversion of configuration at phosphorus. The possibility that LXXII and LXXIII are conformers rather than geometrical isomers was ruled out by the observations that heating them separately to 200°C produced no change in their physical properties and that an identical compound CXI was prepared from LXX and LXVII by reactions involving predominately inversion and retention, respectively. Edmundson and Mitchell (45) have studied three methods of preparation of LXXIV and LXXV and their ^{1}H nmr spectra in order to establish the configurations and conformations present. Two of the preparative methods are shown in



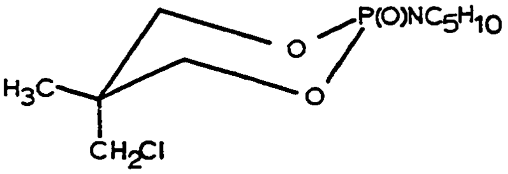
CXI

Equations 6 and 7 and the third in Equation 8. Equations 6 and 7 gave

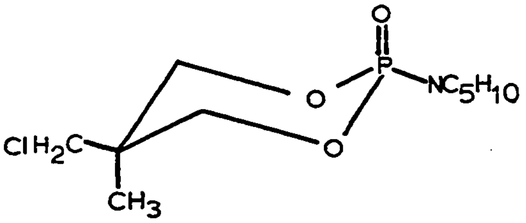


LXXIV and LXXV

single, different isomers, LXXV and LXXIV, respectively, but Equation 8 gave a mixture of the two. The ring methylene proton resonances of LXXV, LXXIV and the phosphorochloridate in Equation 6, LXXVI, were not described but "appeared to be compatible with a chair conformation." Two arguments were employed to establish the dominant dispositions of the exocyclic groups at C_4. First of all, for pairs of geometrical isomers of cyclic aralkyl phosphonates of the 4-halomethyl-4-methyl series, $\Delta\delta_{Me} > \Delta\delta_{CH_2Cl}$ for the trans-phosphoryl oxygen-halomethyl isomer and $\Delta\delta_{Me} < \Delta\delta_{CH_2Cl}$ for the cis-compound, where $\Delta\delta = \delta(CDCl_3) - \delta(C_6H_6)$ for the methyl and chloromethyl groups. However, the $\Delta\delta$ value was shown to be associated with the configuration at C_4, not that at phosphorus. The values of $\Delta\delta$ for LXXIV-LXXVI and the assumption that the chloromethyl group in LXXVI is axial in solution as is the bromomethyl group in the solid state of XLIX allowed the configuration at C_4 in LXXIV and LXXV to be deduced. Secondly, C_4-methyl groups giving broad and narrow resonances in 4,4-dimethyl derivatives have been assigned to axial and equatorial positions, respectively (36). Comparison of the widths of the methyl resonances in LXXIV and LXXV also allowed the C_4-configuration to be determined. In each case, the structures shown below were proposed. The phosphoryl oxygen must then be axial in LXXIV because of the



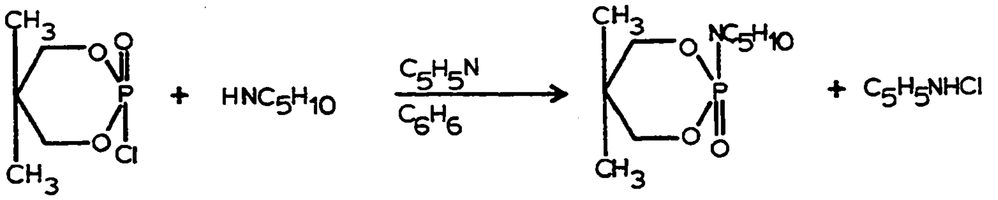
LXXV



LXXIV

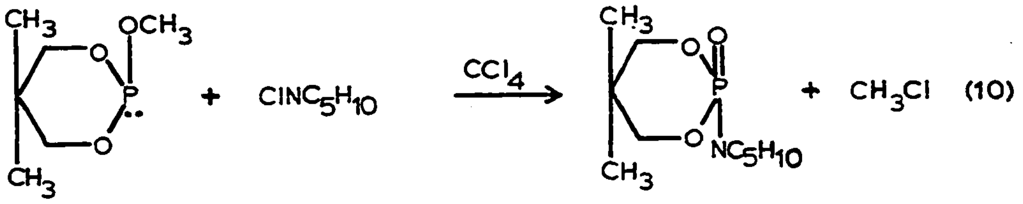
mode of preparation (Equation 7). The authors were not certain of the configuration at phosphorus in LXXV but the stability of LXXIV and LXXV at 200° and the lack of formation of any LXXV from the bicyclic phosphite in Equation 7 indicated that LXXIV and LXXV were not conformers and that, "in all probability," LXXV also possessed an axial phosphoryl oxygen.

The importance of distinguishing between geometrical and conformational isomers has been made clear by the preparation of the two conformers of LXXVII, for which geometrical isomers are not possible (45). Preparation as in Equation 9 yielded a product (LXXVII a) insoluble in boiling light petroleum, whereas preparation as in Equation 10 initially gave more than 95% of a different product (LXXVII b) that



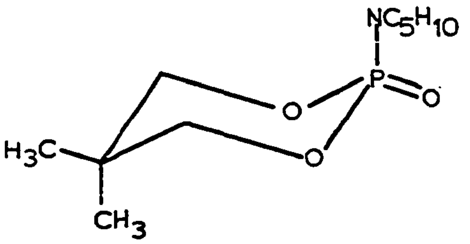
(9)

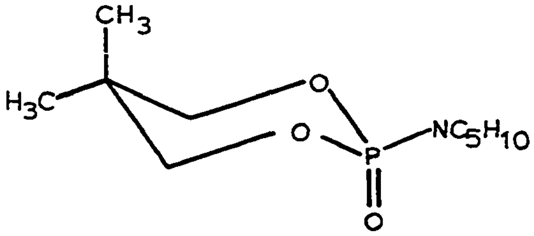
LXXVIIa



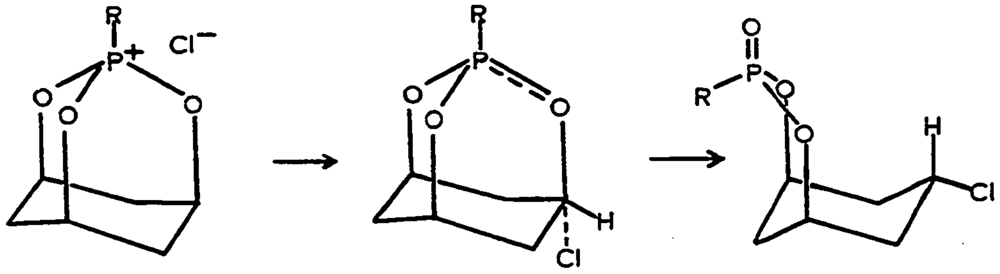
LXXVIIb

yielded LXXVII a upon repeated crystallization from light petroleum. The conversion of LXXVIIb to LXXVIIa was accompanied by the loss of two of the four methyl resonances in the ^{1}H nmr spectrum and by virtually no change in the infrared spectrum. These facts and the relative simplicity of the ^{1}H nmr spectrum of the unstable compound LXXVII led to the conclusion that LXXVII A and B are chair conformational isomers, as shown below. The disposition of the exocyclic groups at phosphorus in either isomer could not be determined.



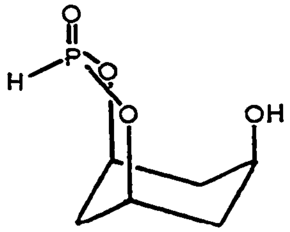


Two other bicyclic phosphites, XCII and CIV, have been used in stereochemical studies of the sort discussed above. Berlin, *et al.* (46, 47) found that the Arbuzov reaction of three aralkyl chlorides with XCII gave just one product in each case. Assuming the mechanism shown in Equation 11 they then analyzed the ^{1}H nmr and infrared spectra and compared the observed dipole moment with moments calculated for two of the possible conformers and proposed a structure with the phosphorus atom in a boat ring and the other six-membered ring in a chair conformation.

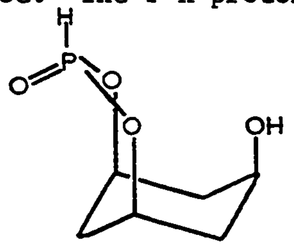


(11)

The hydrolysis of this same bicyclic phosphite, on the other hand, gave two products, CXII and CXIII (48). The stereochemical predictions shown were based on nmr and infrared evidence. The P-H proton was placed opposing and colinear to a methylene proton in CXIII because the observed long-range HPOCCH coupling had been earlier reasoned (49) to require this geometry. The OH group was placed in an axial position in both isomers because no large vicinal coupling attributable to a trans arrangement of the methine proton on the OH-bearing carbon and a methylene proton was found. The configurations at phosphorus were thought to differ in the two isomers because $\Delta\nu(P=O)$ was 33 cm^{-1}. The prediction for CXII was later confirmed by x-ray diffraction analysis (50). The second bicyclic phosphite CIV was recently prepared by Edmundson and Mitchell (51). Reaction with benzyl chloride gave a single product that was formulated as the six-membered ring LXXXVIII on the basis of the



CXII



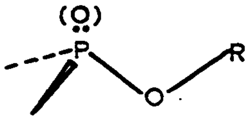
CXIII

evidence: known tendency of five-membered phosphite rings to open when treated with benzyl chloride (52, 53) as opposed to ring-retention with corresponding six-membered phosphite rings (54), stability of the product under aqueous conditions, the product's ^{1}H nmr spectrum, and the accepted mechanism of the Arbuzov reaction. Reaction of CIV with bromine gave the analogous LXXXIX, characterized as the N-cyclohexylphosphoramidate of unstated configuration, and hydrolysis of CIV was believed to have given a six-membered cyclic product.

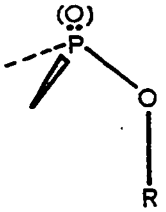
Bicyclic molecules containing phosphorus at one of the bridgehead positions are model compounds because only one conformation is usually possible. Only those having the PO_3 group in an otherwise all-carbon skeleton will be considered. Examples of the bicyclo [2.2.1] heptane (55), bicyclo [2.2.2] octane (56), bicyclo [3.2.1] octane (51) and adamantane (57a) systems are known. No structural determination of a derivative of the first or third types has been reported. Solid state structures of $P(OCH_2)_3CCH_3$[XCVII(CH_3)] complexed to silver as $\{Ag[P(OCH_2)_3CCH_3]_4\}(ClO_4)$ (57b) and to oxygen as $OP(OCH_2)_3CCH_3$ (58), and the structures of the adamantane-phosphite, $PO_3C_6H_9$ (XCII), complexed to sulfur as $SPO_3C_6H_9$ (59) and to nickel as $[Ni(PO_3C_6H_9)_5]$ $(ClO_4)_2$ (57b) are known. The bicyclo [3.2.1] system can exist in more than one conformation and the structure shown in Table 5 for CIV was proposed after a consideration of hydrogen-hydrogen interactions (51) in the possible conformations.

Determination of the stereochemistry of open-chain derivatives containing one or more alkoxyl or aroxyl groups is more difficult than of cyclic derivatives because of the increased freedom of rotation of the groups bonded to phosphorus. An electron diffraction study of trivinyl and triethyl phosphites revealed rotational isomers in the vapor state (60). The predominant isomer in each case has C_{3V} symmetry with a trans-configuration of the PO and CC bonds in each OR group as well as of each CO bond and the bisector of the opposite OPO angle. In one other pertinent structural study, the dihedral angles between the O=P-O and the three POC planes in triphenyl phosphate in the solid state (61) were calculated to be 93°, 154° and 172° (12).

Stereochemical information about the open-chain compounds has been deduced from nmr, dipole moment, infrared and parachor studies. Siddall and Prohaska (62) examined the ^{1}H nmr spectra of 61 esters of arylphosphoric, arylphosphonic, arylphosphinic and phenylphosphonous acids and found that some of the resonances for many of the esters were doubled. Only one structural hypothesis was found which could satisfactorily explain the presence or absence of the doubling and its temperature behavior. It was concluded that rotation about the P-O-C linkages is rapid on the nmr time scale but not all rotamers are equally probable. The conformations in which the R group of a POR group is near rather than away from the phosphoryl oxygen or phosphorus lone electron pair, as shown below, are of some importance because this oxygen or the lone pair was generally the smallest of the groups bonded

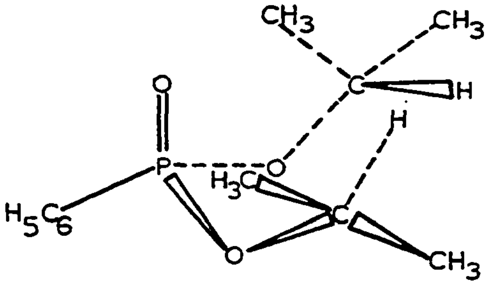


"up" or "folded" form

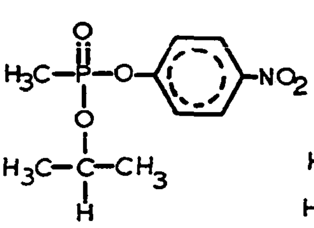


"down" or "extended" form

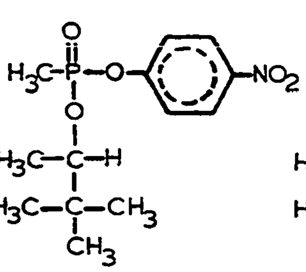
to phosphorus in the compounds investigated. Furthermore, there is in many of the compounds a sterically-favored isomer of rotation about the OC bond. For example in $[(CH_3)_2CHO]_2 P(O)C_6H_5$ the methyl resonance is doubled because one methyl group is near and the other is far from the phenyl group in the favored conformation of the isopropoxyl group in the "up" position as shown below. More recently, Jardine, Gray and Reesor (63) observed peak doubling in the spectra of CXIV-CXVII. The hypothesis of Siddall and Prohaska could not explain all the peak doublings or the coalescence of the doubled resonances of CXIV-CXVI at higher temperatures. Instead, the two resonances were attributed to slowly interconverting "up" and "down" positions of the isopropyl or pinacolyl groups relative to the phosphoryl oxygen. Complexation of CXIV-CXVI with uranyl nitrate eliminated the doubling because it froze the alkoxyl groups in the "down" position. In another related study Frankel, Klapper and



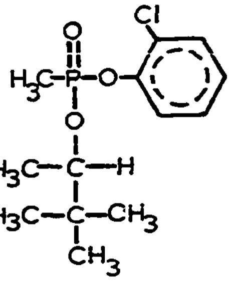
CXIV



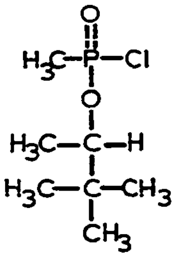
CXV



CXVI



CXVII



Cargioli (64) studied the solvent and temperature dependence of the ^1H nmr spectra of compounds of the type ($\underline{p}$-$NO_2C_6H_4O$) $P(O)CH_3$ ($OCH_2COC_6H_4$-$\underline{p}$-Y) where Y was H, Cl, CH_3, NO_2 and OCH_3. The methylene protons were magnetically nonequivalent in solvents of low dielectric constant and the temperature dependence of the spectra could be fitted with a two-conformer model. The activation energy obtained was comparable to the temperature dependence of the dielectric constant of the medium. Similarly, Finegold (65) found that $CH_3P(S)(OCH_2CH_3)_2$ had two sets of nonequivalent methylenic protons by analysis of the ^{31}P and ^1H nmr spectra; the "critical" nmr parameters were invariant from 27-227°C. Instead of postulating preferred ethoxy orientations, he based his explanation on unequal P-O(R) bond orders. Thus, there is "a resonance stabilization of the molecule in which the anti-bonding electrons of only one of the oxygen atoms contribute to canonical structures involving a conjugated P=S bond" (65, p. 2642). Lastly, Tsuboi and coworkers (66) have used the dihedral angle dependence of POCH coupling constants to conclude that the C-R bond in RCH_2OP systems has a greater chance of taking the trans position with respect to the OP bond around the CO bond than the chance of taking the gauche position.

The stereochemical implications of dipole moments of open-chain organophosphorus compounds were considered as long ago as 1940. Lewis and Smyth (67) vectorially summed the bond moments in triphenyl phosphite assuming free rotation about the PO bonds and obtained good agreement with the observed value. They noted that certain conformations should be sterically impossible but concluded that a sufficiently-wide variety of conformers did exist to approximate a random distribution.

Svirbely and Lander (68) also found the free rotation model satisfactory for calculating the moment of triethyl phosphate. In contrast, Kosolapoff (69) compared the observed moments, from Onsager's equation, of several dialkyl alkylphosphonates with moments calculated by a vector summation method for the "up" or "folded" and "down" or "extended" conformers and concluded that the "extended" form is predominant. Aroney, et al. (70) used O_3P and $O_3P{=}O$ group moments, calculated from the observed moments of the bicyclic molecules XCVII (CH_3) and XCIX (CH_3), a CO bond moment, and the observed moments of several open-chain compounds of the type $P(OR)_3$ and $OP(OR)_3$ to calculate the "effective" angle ϕ of the OC bond with respect to the phosphoryl bond. For example, ϕ for the tri-n-alkyl phosphates was found to be 83° and such that the methyl groups are on the side of the plane of the three non-phosphoryl oxygen atoms nearer the phosphoryl oxygen. Furthermore, the molecules could exist in a mixture of conformations as well as in one "effective" conformation. Ketelaar, Gersmann and Hartog (71) calculated the angle between the phosphoryl link moment and a POR group moment from the observed molecular moments of compounds of several series of the type $(RO)_3PO$, $(RO)_2(R^1O)PO$, $(RO)(R^1O)_2PO$ and $(R^1O)_3PO$ and found a value of 86-88°. They did not interpret this angle in terms of the conformation(s) of the molecules.

The most striking and informative feature of the infrared spectra of compounds containing the phosphoryl linkage is the intense phosphoryl stretching band. This band often appears as a doublet and the possible causes have been reviewed several times (72, 73, 74, p. 201; and 10, p. 54). In some cases splittings of up to 50 cm^{-1} have been found and attributed either to the phosphoryl stretching mode and another vibrational mode or to Fermi resonance of the P=0 and an overtone band. In other cases rotational isomerism or intermolecular dipole-dipole interaction between two phosphoryl bonds has been proposed. Trimethyl phosphate has been extensively studied (75-77) and provides an example of rotational isomerism. One of the more theoretical investigations of rotational isomerism was made by Mayants, Popov and Kabachnik (76). They first calculated $\nu(P=0)$ for several rotamers of trimethyl phosphate keeping the force fields equal. The observed difference in $\nu(P=0)$ of 15 cm^{-1} could not be accounted for in this manner. As a consequence, a difference of about two percent in the P=0 force constants of the rotamers was postulated, possibly due to the presence of a very weak intramolecular interaction between the phosphoryl oxygen and a hydrogen of the methyl groups in one rotamer.

Values of parachor are dependent upon stereochemistry. A "folded" conformation for trialkyl phosphates was found by two groups of workers (78, 79) to give good agreement between calculated and experimental values of the parachors. Also, whereas the three alkyl chains are parallel after the β carbon atom in trialkyl phosphates and thiophosphates, probably only two are parallel in trialkyl phosphites (80).

Several attempts have been made to correlate spectral properties of organophosphorus compounds with the presence or absence of the phosphorus atom in a ring, the ring size and the number of rings. Jones and Katritzky (81) measured ^{31}P chemical shifts of acyclic five-membered and six-membered cyclic phosphorochloridites, phosphites and phosphates and found "no simple relation" between the shift and the ring size. Blackburn, Cohen and Todd (82) determined the ^{31}P chemical shifts of a greater number of five- and six-membered cyclic phosphites and phosphates. The order for phosphites was acyclic (-138 ± 2 ppm) < five-membered (-135.2 ± 2.0) < six-membered (-127.4 ± 3.4) and that for phosphates was five-membered (-15.4 ± 2.0) < six-membered (8.13 ± 1.1) < acyclic (10.5 ± 1.5). The values for the two bicyclic phosphites, XCVIII (CH_3) and XCII, were quite disparate from the mean but the corresponding phosphates, XCIX (CH_3) and XCIV were normal. The order for the phosphates was used to explain the greater reactivity of five-membered esters compared to the others because a greater negative chemical shift indicates less electron-shielding of the phosphorus nucleus and a greater electrophilicity of the atom. Mark (83) has accounted for ^{31}P chemical shifts of trialkyl phosphites of various structural types in terms of the OPO angles. A decrease in the angle was thought to result in greater shielding of the phosphorus nucleus, and an increase to result in deshielding. In the area of infrared spectroscopy, Jones and Katritzky (81) found that values of $\nu(P=O)$ for the five- and six-membered cyclic phosphates were very similar and 25-30 cm^{-1} higher than that of the similar acyclic phosphate. Thus, they concluded there is no correlation with hydrolysis rates. In contrast, Ketelaar and Gersmann (84) found that a decrease in free energy of activation of hydrolysis of six open-chain phosphates paralleled an increase in $\nu(P=O)$. The increase in $\nu(P=O)$ from similar open-chain to monocyclic phosphates has been noted by others (73, 85, 86). The paper by Edmundson (86) contains infrared data for 47 tri- and penta-valent 1-phospha-2,6-dioxacyclohexanes. That by Thomas and Chittenden is a review of

$\nu(P=O)$ for all types of organophosphorus compounds. A further increase in $\nu(P=O)$ from mono- to bi-cyclic phosphates has also been reported (58).

One means of studying the nature of the phosphoryl linkage and the factors influencing it has been the determination of the basicity of the oxygen atom. This subject has recently been briefly reviewed by Bellamy (74, pp. 209-10). Four conclusions, based primarily on the work of Gramstad, et al., deserve emphasis. First of all, the difference between the stretching frequency of the OH bond for free and associated hydrogen of several alcohols, $\Delta\nu(OH)$, is a simple linear function of $K_{assoc}N$, ΔH, ΔF and ΔS, a separate line being required for each alcohol. Secondly, the change in the phosphoryl stretching frequency upon association with alcohols or iodine is not a reliable guide to the strength of association. Thirdly, there is a general trend whereby the higher $\nu(P=O)$ correspond to the less basic oxygens as measured by $\Delta\nu(OH)$. Lastly, $\nu(P=O)$ is not wholly determined by simple inductive effects. More recent articles dealing with association of the phosphoryl oxygen with bis-p-chlorophenylphosphoric acid (87), uranyl nitrate (88), phenol (89-91) and chloroform (92,93) are indicative of the activity in this field. The article by Aksnes and Albriktsen (89) is particularly pertinent. The phenol $\Delta\nu(OH)$ values for 15 compounds, including a five-and six-membered cyclic phosphate and six other cyclic compounds, gave a poorer fit to a straight line than for previously-studied compounds when plotted against log K and essentially no fit when plotted against ΔH and ΔS.

Several pertinent articles and a Ph.D. thesis have come to the attention of the author since the completion of this Review of Literature. Bogat-skii, et al. (94) investigated the possibility of the existence of geometrical isomers in 1-chloro-, 1-methoxy- and 1-ethoxy-4-methyl-4-α-methoxyethyl-1-phospha-2,6-dioxacyclohexanes using ^1H nmr spectra. An analysis of the integrated intensities of the methyl proton resonances revealed isomer ratios of 43:57, 40:60 and 28:72, respectively. The form of the ring-methylene proton resonances indicated that the 1-chloro derivative possesses an axial P-Cl bond in a chair conformation but that the 1-alkoxy derivatives possess an equatorial P-OAlk bond. They hypothesized that the isomer with the exocyclic substituent at phosphorus and the 4-methyl anti was the major one in each case. The arguments for the above conclusions were brief and vague. Bodkin and Simpson (95) have determined that the more stable geometrical isomer of the phosphite XXVI assumes a chair conformation with an equatorial methyl and an axial ethoxyl group. The less stable isomer XXVI B adopts a rapidly-flipping chair conformation at room temperature, but possesses a predominantly-equatorial methyl group at -30° in $CDCl_3$. The thiophosphates derived from XXVI A and B by addition of sulfur and the 1-chloro derivative XLIII A also possess an equatorial methyl group. The methyl group disposition was determined from an analysis of the ^1H nmr spectra. The ethoxyl disposition at phosphorus in XXVI A and B was determined by measuring the dipole moments of the thiophosphates, comparing the moments to those calculated from bond and group moments from the literature for the possible chair isomers and assuming that thiophosphate formation proceeds with retention of configuration at phosphorus. The above compounds were originally studied by Aksnes, et al. (16), who did not establish their stereochemistry. Bentrude, et al. (96) have employed the geometrically-isomeric phosphites XXX A and B to establish that transfer of oxygen from t-butoxyl radicals and sulfur from n-butylthiyl radicals is essentially stereospecific. Comparison of the results of the free-radical oxidations with those of oxidation with t-butyl hydroperoxide and sulfur (S_8), assumed to proceed with retention of configuration at phosphorus, led to the conclusion that the former reactions also proceed with retention.

Edmundson (97) has concluded that the ring of both isomers of 1-oxo-1,4-dimethyl-4-bromomethyl-1-phospha-2,6-dioxacyclohexane is conformationally mobile in $CDCl_3$(-55 to +30°) and $(CD_3)_2CO$(-70° to 30°) from the temperature dependence of the ^1H nmr spectra. In contrast, the ring appeared to be rigid in cis-and trans-1-benzyl-4-chloromethyl-4-methyl-1-oxo-1-phospha-2,6-dioxacyclohexane (-30 to +30°, $CDCl_3$), the corresponding compounds with a tosyl group in place of chlorine (-30 to +30°, $CDCl_3$) and cis- and trans-1-methoxy-4-methyl-4-nitro-1-phospha-2,6-dioxacyclohexane (-50 to +30°, neat). Bentrude and Hargis (98) have analyzed the ^1H nmr spectra of $CDCl_3$ solutions of the compounds[1] X′, XI′, XXI′, XXII′ and the thiophosphate analogs of X′ and XI′. The 4-t-butyl group was concluded to be equatorial in a chair conformation in all of these compounds. However, the magnitudes and variation with temperature of the ring POCH coupling constants of XXI′ suggested that there was also some type of boat form in equilibrium with the chair. The spectrum of the thiophosphate analog of XI′ showed no temperature dependence. The

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[1] The structures of compounds designated by primed Roman numerals are given in Table 14, p. 166.

magnitudes of the ring POCH coupling constants indicated a ring geometry distortion.

The ^{1}H nmr spectrum (100MHz) of a carbon tetrachloride solution of the bicyclic phosphite CV has been analyzed by Robert (99a, pp. 52-7). The results will be presented later along with those found independently by the author.

III. EXPERIMENTAL

A. Materials

All solvents and other materials not mentioned below were reagent grade or better and solvents used in connection with trivalent phosphorus compounds were stored over Linde 3 A Molecular Sieves. Instances of additional purification are noted. Benzene thiol and pentaerythritol were purchased from J. T. Baker Chemical Company ("Baker Grade"); trimethyl phosphite from Aldrich Chemical Corporation, Inc., (97-100%) or Eastman Organic Chemicals (Practical Grade); 2,2-dimethyl-1,3-propanediol (97-100%) and trimethylphosphate (97-100%) from Aldrich Chemical Corporation, Inc.; nitrogen dioxide from The Matheson Company; and diborane from Callery Chemical Company. Phenyl phosphorus dichloride was a sample supplied by Stauffer Chemical Company. Equilibrium and nonequilibrium mixtures of XXXI A and B, from which borane adducts were prepared, were synthesized by McEwen (99b). Samples of X′, XI′, XXI′, XXII′ and the thiophosphate-analog of XI′ were loaned by Bentrude (99c) for the purpose of obtaining their dipole moments. The following compounds, whose ^{1}H nmr and/or infrared spectra were recorded, were prepared by McEwen (99b): XXXI A and B, XXXVI, XXXVII A and B, XXXIX A and B, XLIV, XLV A and B, III′ (Table 14), XIII′, XIX′, XX′, XXIII′, XXIV′, XXV′, XXVI′, XXVIII′, XXIX′ and XXX′; Bertrand (99d) prepared I′, II′, IV′, V′, XVIII′, XXXI′, XXXII′ and XXXIII′ and Mathison (99e) prepared XXXIV′.

B. Nuclear Magnetic Resonance Spectra

All spectra were obtained on samples in spinning 5 mm (od) precision glass tubes. Coupling constants (J) are always given in cycles per second (Hz). The ^{31}P data were obtained by Bertrand (99d). Spectra were obtained at 24.3 MHz on samples at 27.5° with a Varian HR 60 Spectrometer operating at 14,100 gauss. The ^{31}P chemical shifts were obtained either directly from the ^{31}P spectra or from the ^{1}H spectra (Varian HR 60) by the INDOR method and are listed in parts per million (ppm) relative to the chemical shift of 85% phosphoric acid contained in a concentric capillary in the nmr tube. A positive shift is taken to occur at an applied magnetic field greater than that of the standard. Spectra for which ^{31}P-^{1}H or ^{1}H-^{1}H decoupling experiments are reported were obtained on samples at 27.5° at 60 MHz by Bertrand (99d) with a Varian HR 60 spectrometer operating at 14,100 gauss. All other ^{1}H spectra were obtained by McEwen (99b), Bertrand (99d) or the author with a Varian A 60 spectrometer operating at 14,100 gauss or by Cherry (99f) with a Varian HA 100 spectrometer operating at 23,500 gauss on samples at 40° and 30°, respectively, unless specified otherwise. All ^{1}H line positions (δ) are given in ppm relative to internal tetramethylsilane (TMS) unless stated otherwise. A positive shift is taken to occur at an applied magnetic field smaller than that of the standard. ^{1}H nmr spectra were obtained on samples in the absence of a solvent (neat) unless stated otherwise.

C. Infrared Spectra

Spectra were obtained in the 800-4000 cm^{-1} range with a Beckman Model 12 spectrophotometer. The instrument was calibrated by comparing the observed and known band positions in the spectrum of polystyrene versus air. The frequency scale was 25 or 100 cm^{-1}/inch from 800-2000 cm^{-1} and 50 or 200 cm^{-1}/inch from 2000-4000 cm^{-1}. The scanning speed was 80 cm^{-1}/minute or less. Mulls on sodium chloride plates or solutions in demountable cells (Barnes Engineering Company) with sodium chloride windows and, usually, 0.1 mm spacers were used in the 800-4000 cm^{-1} range. Solution spectra were obtained in the double beam mode with solvent in the reference beam unless otherwise indicated. The phenol used to determine phenol shifts was dried by distillation of either the phenol at atmospheric pressure under a nitrogen atmosphere or a water/carbon tetrachloride azeotrope from a carbon tetrachloride solution of phenol. Benzene, bromobenzene, and mesitylene were distilled from sodium; pyridine from barium oxide; and acetonitrile from phosphorus pentoxide.

D. Dipole Moments

The heterodyne-beat apparatus and procedure for obtaining dipole moments have been described elsewhere (100a). Benzene, dried with sodium or $LiAlH_4$, was always employed as the solvent. The indices of refraction were measured with an "Abbe-56" Refractometer (Bausch and Lomb Optical Company) while the temperature was controlled to ±0.2°C with an E. H. Sargent and Company thermostatic, external circulating water bath (catalog No. S-84880). Solutions of water-sensitive compounds were prepared in a nitrogen-filled dry box. The moments of III′, XIX′, XX′, XXIII′, XXIV′, XXV′, XXIX′ and XXX′ were obtained by McEwen (99b); that of XXXII′ by Bertrand (99d) and that of LXXII (CCl_4) by Moore (100b).

E. Preparation of Compounds

All reactions in which CV and its derivatives and compounds containing a P-Cl bond were involved as well as the accompanying isolation and purification steps were carried out under a nitrogen atmosphere. Special care was taken to exclude moisture from nonequilibrium mixtures of geometrical isomers. The main criteria of purity of the compounds were the following: constancy of distillation temperature or melting point, proper integration of ^{1}H nmr resonances and/or absence of unaccountable ^{1}H nmr resonances. The ^{1}H nmr spectra of monocyclic trivalent phosphorus derivatives containing the methoxyl group almost always contain a doublet at slightly-lower field than the main methoxyl doublet. Distillation in several instances with a 16" platinum spinning band column (Nester/Faust Manufacturing Corporation) did not eliminate the impurity. Trimethyl phosphite, arising from rearrangement during distillation, is a likely contaminant and would account for no more than 3% of the distillate. A tertiary base such as pyridine or triethylamine was used in many of the preparations as a hydrogen chloride acceptor; pyridine is not recommended because its hydrochloride is relatively difficult to separate from the desired product by distillation. Ratios of geometrical isomers were determined by comparing the areas of nonoverlapping ^{1}H nmr resonances with the aid of a Varian A-60 integrator or planimeter. ^{1}H nmr spectral descriptions are included in this section if they have not appeared in the literature or are not presented later. Infrared data and dipole moments of many of the compounds are presented later.

1. Meso- and d,l-2,4-pentanediol

Both _ca._ 1:1 mixtures of the diastereomeric alcohols and pure _meso_-2,4-pentanediol were prepared according to a slight modification of the procedure described by Pritchard and Vollmer (101). The isomeric cyclic sulfites were separated with a 16" platinum spinning band column in conjunction with a vacuum regulator (Nester/Faust Manufacturing Corporation); one distillation with reflux ratios no lower than 15:1 gave 96% _meso_-sulfite along with 4% _d,l_-sulfite and distillation of this mixture reduced the latter isomer to less than 1%. The thionyl chloride was freshly purified by a procedure described by Friedman and Wetter (102).

2. 1-Chloro-4,4-dimethyl-1-phospha-2,6-dioxacyclohexane (XXXVIII)

This compound was obtained following a procedure outlined by Edmundson (103). To a well-stirred, ice-cooled ether solution of 44 ml. of phosphorus trichloride (0.50 mole) were 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 XXXVIII was obtained by distillation ($b_{12} = 70^{\circ}$, lit. $b_{13} = 66^{\circ}$ (103)).

3. 1-Chloro-_cis_-3,5-dimethyl and 1-chloro-_trans_-3,5-dimethyl-1-phospha-2,6-dioxacyclohexanes (XLI and XLII, respectively)

These compounds have been reported but their preparation has not been fully described (24). The procedure described for XXXVIII was used to prepare XLI (b_{12} = 72-3°, 35-40% yield) as well as ca. 1:1 mixtures of XLI and XLII (b_{12} = 77-9°) from meso-2,4-pentanediol and ca. 1:1 mixtures of meso- and d,l-2,4-pentanediol, respectively. In one instance the preparation of XLI was modified in that triethylamine instead of pyridine was used as a base. The ^1H nmr spectrum of XLI consists of a C_3C_5-methyl doublet ($\delta = 1.24$, $J = 6.2$), C_4-methylene multiplet ($\delta = 1.59$-1.96) and C_3C_5-methine multiplet ($\delta = 4.41$-5.03). The resonances for XLII are broad at room temperature and are discussed later. In one of the three preparations of a mixture of XLI and XLII the reaction mixture was worked up after about two days instead of a few hours or less, and distillation gave small quantities of two higher-boiling fractions but no XLI or XLII. The ^1H nmr spectrum of each fraction showed a 4:1 ratio of CCH to OCH protons but neither fraction was further characterized.

4. Cyclic phosphites prepared by transesterification

A modification of the general transesterification procedure described by Wadsworth and Emmons (42) was used to prepare the following compounds. Equimolar quantities of trimethyl phosphite and the appropriate diol, triol or tetraol were heated at about 100° until methanol began to reflux. The methanol was removed by distillation at atmospheric pressure at oil-bath temperatures up to 130° and the desired product was obtained by reduced pressure distillation or sublimation. The yields were usually greater than 50%.

a. 1-Methoxy-1-phospha-2,5-dioxacyclopentane (III) Distillation under a pressure of 30 mm took place at 56-8° (lit. b_{35} = 60-2° (104), b_{23} = 55-6° (105)). A higher-boiling fraction, $b_{<1}$ = 80°, solidified in the receiver. Recrystallization of this colorless solid from carbon tetrachloride was accompanied by formation of a yellow oil and exposure to the atmosphere resulted in rapid formation of a colorless liquid. The ^1H nmr spectrum of the solid (C_6H_6) consists of a complex multiplet (δ = 2.9-3.6) featuring intense lines at δ = 3.00, 3.04, 3.22 and 3.24. This compound was not further characterized.

b. 1-Methoxy-1-phospha-2,6-dioxacyclohexane (XXXIV) Distillation under a pressure of 38 mm took place at 76-8° (lit. b_{23} = 65-6° (106), b_{11} = 50-1° (106)). The ^1H nmr spectrum taken neat consisted of a C_3C_5-methylene triplet of multiplets (δ = 4.14-4.65) and multiplet (δ = 3.29-3.91); a methoxyl doublet (δ = 3.48, J(POCH) = 11.7) and C_4-methylene multiplets (δ = 1.93-2.72 and 1.30-1.73).

c. 1-Methoxy-4,4-dimethyl-1-phospha-2,6-dioxacyclohexane (XXIX) Distillation under a pressure of 36 mm took place at 87-8° (lit. b_{18} = 66° (86)).

d. 1-Methoxy-*cis*-3,5-dimethyl-and 1-methoxy-*trans*-3,5-dimethyl-1-phospha-2,6-dioxacyclohexanes (XXXII A and XXXIII, respectively) Preparation of these compounds by transesterification has been reported (24) but not in detail. The phosphite XXXII A (b_{11} = 58-9°) and a *ca*. 1:1 mixture of XXXII A and XXXIII (b_8 = 58°, b_{18} = 75-7°) were prepared from *meso*-2,4-pentanediol and a *ca*. 1:1 mixture of *meso*- and *d,l*-2,4-pentanediol, respectively.

e. 3,9-Dimethoxy-2,4,8,10-tetraoxa-3,9-diphospha-spiro [5.5] undecane - $(CH_3O)\,P(OCH_2)_2\,C(CH_2O)_2\,P(OCH_3)$ (CXVIII) Transesterification of trimethyl phosphite with pentaerythritol is slower than with other alcohols possibly because pentaerythritol is not appreciablly soluble in trimethyl phosphite even at 110°. The product (CXVIII) was sublimed twice at ca. 90° at < 1 mm (m = 124-7°, lit. m = 124-7° (107)).

f. 4-Pentyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.2] octane (XCVII (C_5H_{11})) The preparation and purification of this compound by transesterification have been described elsewhere (88)(m = 44-7°, lit. m = 45-8° (88)).

g. 4-Methyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.2] octane (XCVII (CH_3)) The preparation and purification of XCVII (CH_3) have been described elsewhere (108).

5. 2,6,7-Trioxa-1-phosphabicyclo-[2.2.1] heptane (CV)

This compound was also prepared by transesterification but by a slight modification of the procedure described by Denney and Varga (55); Dow Corning 550 Fluid was used in place of SF-96 silicone oil. The glycerine was purified by azeotropic removal of water with benzene followed by vacuum distillation of the glycerine. Purification of CV was performed as described (55).

6. 1-*t*-Butoxy-4,4-dimethyl-1-phospha-2,6-dioxacyclohexane (XXV)

To a well-stirred ether suspension of 3.50 g of sodium *t*-butoxide (36.4 mmoles), prepared *in situ* from sodium amalgam and *t*-butanol, was added dropwise 6.04 g. of XXXVIII (35.8 mmoles). The ether refluxed during the addition and external heating was applied to reflux the ether for an additional hour. The mixture was filtered and the residue was washed with ether. The ether was removed from the combined filtrates by atmospheric distillation and XXV was obtained in about 30% yield as a solid (m ca. 30°) by distillation at less than 1 mm. The small quantity of product precluded a measurement of the boiling point. The ^1H nmr spectrum consists of methylene multiplets (δ = 3.98-4.30 and δ = 2.95-3.35) a t-butoxy singlet (δ = 1.37) and broad (δ = 1.18) and narrow (δ = 0.68) methyl singlets.

7. 1-Phenyl-4,4-dimethyl-1-phospha-2,6-dioxacyclohexane (XLVI)

This compound was prepared by a modification of the method described by Harwood (109) or Gagnaire, et al. (30). To a well-stirred, ice-cooled ether solution of 19.9 g of C_6H_5 PCl_2 (0.111 mole) were added dropwise 11.6 g of 2,2-dimethyl-1,3-propanediol (0.111 mole) and 17.9 ml of pyridine (0.222 mole). After removal of the pyridine hydrochloride by filtration and after washing of the residue with ether, the solution was concentrated by atmospheric distillation of the ether and XLVI was isolated in greater than 50% yield by distillation (b_6 = 120°, lit. $b_{1.5}$ = 100°, m = 82-3° (109)). Gagnaire, et al. have pointed out the deliquescent nature of XLVI and its reaction with CCl_4, $CDCl_3$, C_6D_6 and CD_3COCD_3 (30). However, a ^1H nmr spectrum of triply-sublimed XLVI in C_6H_6 dried with $LiAlH_4$ showed only approximately 5% impurities.

8. 1-Thiophenoxy-4,4-dimethyl-1-phospha-2,6-dioxacyclohexane (XLVII)

To an ice-cooled, well-stirred ether solution of 4.95 g of XXXVIII (29.4 mmoles) were added dropwise 3.82 g of thiophenol (34.6 mmoles) and 2.98 g of triethylamine (29.4 mmoles) in ca. 20 ml of ca. 3:1 ether/

benzene. The mixture was stirred for an additional 30 minutes at room temperature and then filtered. The residue was washed with ether and the combined filtrates were concentrated to give crude XLVII that was purified by two recrystallizations from a *ca.* 1:1 mixture of hexane and ether (m = 70-5°). Another recrystallization and two sublimations at *ca.* 75° at less than 1 mm did not narrow the melting range, even when the sample was placed in a capillary in a nitrogen-filled dry bag and the capillary was evacuated before being sealed. The solid soon becomes moist in humid surroundings. The ^{1}H nmr spectrum in $CDCl_3$ consists of a phenyl multiplet (δ = 7.08 - 7.55), methylene multiplets (δ = 3.34 - 3.72 and δ = 4.06 - 4.39) and broad (δ = 1.20) and narrow (δ = 0.69) methyl singlets.

9. 1-Methoxy-*trans*-3,5-dimethyl-1-phospha-2,6-dioxacyclohexane (XXXIII) and the isomeric 1-methoxy-*cis*-3,5-dimethyl-1-phospha-2,6-dioxacyclohexanes (XXXII A and B)

Denney and Denney have reported the preparation of a 1.3:1.0:2.9 mixture of XXXII A, XXXIII and XXXII B by the action of sodium methoxide on a mixture of XLI and XLII derived from a *ca.* 4:1 mixture of *meso*- and *d,l*-2,4-pentanediol (24). A tertiary base and methanol were used here in place of sodium methoxide in two adaptations of the procedure described by Aksnes, *et al.* for preparing the unstable isomer XXVI B (16). The ratio XXXII B:A was between 2:1 and 4:1 in four preparations. These nonequilibrium mixtures can be kept for at least a month in a stoppered, nitrogen-filled flask in a Dry Ice chest without appreciable change of the isomer ratio.

a. Procedure A Both a mixture of XXXIII, XXXII A and XXXII B and mixtures of XXXII A and B were prepared by this procedure. For example, 7.10 g of XLI (42.1 mmoles) was added dropwise to an ice-cooled, well-stirred ether solution of 1.36 g of methanol (42.5 mmoles) and 4.31 g of triethylamine (42.5 mmoles). The triethylamine hydrochloride was filtered off and washed with ether and the ether and excess reactants were distilled at reduced pressure below room temperature. A nearly-quantitative yield of a 1:2.3 mixture of XXXII A and B was obtained upon distillation ($b_{10} = 60\text{-}1^{o}$).

b. Procedure B To an ice-cooled, well-stirred ether solution of 5.22 g of XLI (31.0 mmoles) were added dropwise 0.968 g of methanol (31.1 mmoles) and 3.0 g of pyridine (38 mmoles). The remainder of the procedure was as described in Procedure A. The yield was again nearly quantitative.

10. Dimethyl triphenylmethylphosphonate $(C_6H_5)_3CP(O)(OCH_3)_2$

In a modification of the procedure of Arbuzov and Arbuzov (110), approximately 175 ml of a 1:3 acetonitrile/benzene solution of 27.9 g of triphenylmethyl chloride (0.10 mole) and 11.9 ml of trimethyl phosphite (0.10 mole) was heated at 60-70° until gas evolution ceased. The solvents were evaporated at reduced pressure and the product was recrystallized twice from acetone (m = 152-6°, lit. m = 156-7° (110)). Sublimation at ca. 150° at less than 1 mm gave a solid melting at 151.5-3.0°. The ^{1}H nmr spectrum in $CDCl_3$ consists of a triphenylmethyl multiplet ($\delta = 7.06\text{-}7.50$) and methoxyl doublet ($\delta = 3.51$, $J(POCH) = 10.7$).

11. 1-Oxo-1-triphenylmethyl-4,4-dimethyl-1-phospha-2,6-dioxacyclohexane (I′)

This compound was a gift from R. D. Bertrand and was purified by recrystallization from acetone (m = 209-211°, lit. m = 211.5-212° (35)).

12. Isomeric 1-oxo-1-triphenylmethyl-*cis*-3,5-dimethyl-1-phospha-2,6-dioxacyclohexanes (CXIX and CXX)

To 3.50 g of vacuum-dried triphenylmethyl chloride (12.5 mmoles) was added sufficient acetonitrile (twice-distilled from phosphorus pentoxide) to dissolve the solid. The solution was heated to *ca.* 50° and 1.95 g of a 1:2.6 mixture of XXXII A and B (11.8 mmoles total) was added. The solution was held at 70-90° for *ca.* two hours and then evaporated at reduced pressure. A ^1H nmr spectrum of the crude product in $CDCl_3$ contained no methoxyl doublet resonance and indicated a 1:2.3 ratio of isomeric phosphonates. The major isomer was separated from the reaction mixture by fractional crystallization from acetone (m = 203-5°). A ^1H nmr spectrum of a $CDCl_3$ solution of this isomer consists of a triphenylmethyl multiplet at $\delta = 7.1$-7.7, a C_3C_5- methinyl multiplet at $\delta = 3.3$-3.9, a C_4-methylene multiplet at $\delta = 1.3$-2.2 and a C_3C_5-methyl doublet of doublets at $\delta = 1.21$ (J(HCCH) = 6.2, J($POCCH_3$) = 1.4). The minor isomer was considerably more soluble in acetone than the major isomer and was not isolated from the above mixture. The minor isomer was obtained by employing XXXII A instead of a mixture of XXXII A and B in the above procedure. The product was purified by recrystallization from a *ca.* 2:1 mixture of tetrahydrofuran and hexane to give a pale yellow solid (m = 173-5°). The ^1H nmr spectrum of a $CDCl_3$ solution consists of a triphenylmethyl multiplet at δ = 7.0-7.6 with considerably less fine structure than that for the other isomer, a C_3C_5-methinyl multiplet at δ = 4.4-5.0, a C_4-methylene multiplet at δ = 1.2-1.8, and a C_3C_5-methyl doublet of doublets at δ = 1.04 (J(HCCH) = 6.2, J($POCCH_3$) = 1.8). An unsuccessful attempt to isomerize CXIX and CXX was made by heating a solution of each in a 3:1 mixture of acetonitrile and water at 90-100° for 24 hours. The melting point of neither residue was depressed from the values given above.

13. Cyclic phosphates prepared by nitrogen dioxide oxidation of phosphites

In a modification of "Method B" described by Cox and Westheimer (111), nitrogen dioxide was passed (either directly from a tank or first through a tube containing phosphorus pentoxide in the case of a sample prepared (112, pp. 85-9) by G. K. McEwen (99b)) into an ice-cooled, stirred, concentrated solution of a phosphite until a permanent pale green color developed. In all instances except where indicated, carbon tetrachloride was the solvent. The solution was evaporated or the precipitate was filtered and the product purified as described below.

a. 1-Methoxy-1-oxo-1-phospha-2,5-dioxacyclopentane (I) Distillation under 0.6 mm took place at 93-5° (lit. b_1 = 85-6° (113), $b_{0.6}$ = 89-92° (114)). The ^1H nmr spectrum in C_6H_6 consists of a methylene multiplet (δ = 3.85-4.24) and methoxyl doublet (δ = 3.54, J(POCH) = 11.7).

b. 1-Methoxy-1-oxo-1-phospha-2,6-dioxacyclohexane (LXXVIII) Distillation under 0.4 mm took place at 115-8°. The ^1H nmr spectrum in C_6H_6 consists of a C_3C_5-methylene multiplet (δ = 3.77-4.26), a methoxyl doublet (δ = 3.52, J(POCH) = 10.9) and C_4-methylene multiplet (δ = 0.95-2.18).

c. 1-Methoxy-1-oxo-4,4-dimethyl-1-phospha-2,6-dioxacyclohexane (LX or VIII′) This compound was recrystallized from carbon tetrachloride (m = 93.5-94.5°, lit. m = 94° (86)).

d. 1-t-Butoxy-1-oxo-4,4-dimethyl-1-phospha-2,6-dioxacyclohexane (IX′) This compound was recrystallized from carbon tetrachloride.

e. 1-Oxo-1-methoxy-cis-3,5-dimethyl-1-phospha-2,6-dioxacyclohexane (CXXI) This compound was prepared from the stable phosphite XXXII A. A ^{1}H nmr spectrum of the reaction mixture after evaporation of the solvent consists of a C_3C_5-methinyl multiplet at δ = 4.22-4.87, a methoxyl doublet at δ = 3.68 (J(POCH) = 10.8), a C_4-methylene multiplet at 1.5-2.2 and a C_3C_5-methyl doublet of doublets at δ = 1.31 (J(HCCH) = 6.2, J($POCCH_3$) = 2.5). This spectrum contains no resonance corresponding to the phosphite or to another phosphate isomer. This sample can be caused to crystallize by adding ether and cooling in a Dry Ice chest.

f. 1-Oxo-2,6,7-trioxa-1-phosphabicyclo [2.2.1] heptane (CVII) Ether was used as a solvent for the oxidation in place of carbon tetrachloride. Reprecipitation of the crude product from dichloromethane with ether gave a white solid which did not completely dissolve in acetonitrile. All of the organic materials were scrupulously dried: ether with sodium, dichloromethane with magnesium sulfate and acetonitrile with phosphorus pentoxide. The Denneys prepared CVII by this method and reported that it was very sensitive to moisture and decomposed upon heating (55). The ^{1}H nmr spectrum in CH_3CN contains the resonances reported (55) and a broad weak peak at 3.90 although the ratio of intensities of methylene and methine resonances is closer to 5:1 than to the 4:1 ratio reported (55). The infrared spectrum in CH_2Cl_2 contains the reported P=O band at 1346 cm^{-1} (55) and a second sharp, equally intense band at 1355 cm^{-1}.

14. 1-Oxo-4-pentyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.2] octane ($XCIX(C_5H_{11})$)

The preparation of this compound by hydrogen peroxide oxidation has been described elsewhere (88) (m = 136-9°, lit. 134-7° (88)).

15. Trialkyl phosphite boranes

a. Procedure A Carbon dioxide was bubbled through a mixture of sodium borohydride, trialkyl phosphite, and tetrahydrofuran as described by Reetz (115).

1. Trimethylphosphite borane (CII) The ^1H nmr spectrum obtained neat consists of a methoxyl doublet (δ = 3.67, J(POCH) = 10.9) and a $^{11}BH_3$ quartet of doublets (δ = 0.30, $J(^{11}BH)$ = 96.3, $J(P^{11}BH)$ = 19.7, lit. $J(^{11}BH)$ = 97.2 (116)).

2. 1-Borino-1-methoxy-4,4-dimethyl-1-phospha-2,6-dioxacyclohexane (LXXIX) The solid adduct was recrystallized from benzene. The ^1H nmr spectrum in $CDCl_3$ consists of a C_3C_5-methylene multiplet (δ =3.43-4.34), a methoxyl doublet (δ = 3.71, J(POCH) = 11.1), a broad methyl singlet (δ = 1.24), a narrow methyl singlet (δ = 0.85) and a broad $^{11}BH_3$ quartet (δ = *ca.* 0.3).

b. Procedure B Standard vacuum line procedures were employed in the reaction of diborane with the phosphite. The phosphite was dissolved in ether (dried with $LiAlH_4$) and the diborane was purified by trap-to-trap distillation (traps at -112° and -196°). A 5-10% excess of diborane, based on a 1:1 B to P ratio, was condensed in two or three portions onto the phosphite at -196°. The reaction mixture was warmed after each addition to -40° (liquid nitrogen-chlorobenzene slush bath) and stirred with a magnetic jump-stick. The ether and excess diborane were distilled from the product which was not further purified.

1. 1-Borino-1-methoxy-1-phospha-2,5-dioxacyclopentane (CXXII) This adduct melts a few degrees below room temperature. The ^1H nmr spectrum obtained neat consists of a methylene multiplet (δ = 4.04-4.61), a methoxyl doublet (δ = 3.68, J(POCH) = 11.4) and a broad $^{11}BH_3$ quartet ($\delta = 0.37 \pm .05$, $J_{^{11}BH} = 92 \pm 2$).

2. 1-Borino-1-methoxy-1-phospha-2,6-dioxacyclohexane (CXXIII) This adduct is a liquid and its ^1H nmr spectrum obtained neat consists of a C_3C_5-methylene multiplet (δ = ca. 3.8-4.64), a methoxyl doublet (δ = 3.69, J(POCH) = 11.0), a C_4-methylene multiplet (δ = 1.47-2.64) and a broad $^{11}BH_3$ quartet (δ = ca. 0.3).

3. Isomeric 1-borino-1-methoxy-4-methyl-4-chloromethyl-1-phospha-2,6-dioxacyclohexanes (LXXX and LXXXI) Reaction of 3.3:1 and 1:1.8 mixtures of the phosphites XXXI A and B with one equivalent of diborane gave 3.0:1 (damp solid) and 1:1.7 (liquid) mixtures, respectively, of the corresponding adducts LXXXI and LXXX. The ^1H nmr spectrum of the 3.0:1 mixture in $CDCl_3$ includes a methoxyl doublet (δ = 3.76, J(POCH) =

11.0), chloromethyl singlets (δ = 3.78-major, δ = 3.44-minor) and methyl singlets (δ = 0.91-major, δ = 1.30-minor).

4. Isomeric 1-borino-1-methoxy-*cis*-3,5-dimethyl-1-phospha-2,6-dioxacyclohexanes (XC and XCI) The phosphite XXXII A and a 1:2.3 mixture of XXXII A and B with diborane gave a single solid adduct isomer (XCI) and a 1:2.4 liquid mixture of two adduct isomers (XCI and XC), respectively. The solid XCI can be recrystallized from a 3:1 mixture of cyclohexane and benzene (m = 76-77.5°C). The ^{1}H nmr spectrum of XCI in $CDCl_3$ includes a C_3C_5-methinyl multiplet (δ = 4.34-4.90), a methoxyl doublet (δ = 3.71, J(POCH) = 10.8), a C_4-methylene multiplet (δ = 1.57-2.05), and a C_3C_5-methyl doublet of doublets (δ = 1.34, J(HCCH) = 6.3, J($POCCH_3$) = 0.9). Examination of the 1:2.4 mixture as a neat liquid and in a benzene solution permitted separation of the C_3C_5-methyl and methoxyl resonances while the other resonances overlap extensively. In the ^{1}H nmr spectrum of XC, J(POCH) = 11.2 (C_6H_6), J($POCCH_3$) = 0.9 (neat) and J($HCCH_3$) = 6.2 (neat).

5. 1-Borino-4-methyl-2,6,7-trioxa-1-phosphabicyclo [2.2.2] octane (XCVIII(CH_3)) The preparation of XCVIII (CH_3) has been previously described (117) (J(POCH) = 4.2 (neat), lit. 4.2 (116)).

6. 1-Borino-2,6,7-trioxa-1-phosphabicyclo [2.2.1] heptane (CVI) The ^{1}H nmr spectrum in CD_3CN consists of a methine doublet of triplets (δ = 5.50, J(POCH) = 20.0, triplet spacing = 3.1, a methylene multiplet (δ = 3.9-4.6) and a $^{11}BH_3$ quartet of doublets (δ = 0.61, J(^{11}BH) = 102, J(P^{11}BH) = 20). Resonances due to the phosphite (CV) were present in the CD_3CN spectrum (*ca.* 15% of total phosphorus) but not in a benzene spectrum. The adduct does not melt sharply but begins de-

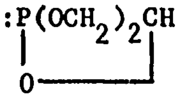
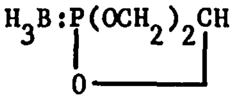
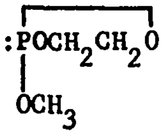
composing in a sealed evacuated capillary tube at *ca*. 80°. The adduct is best stored under nitrogen in a freezer.

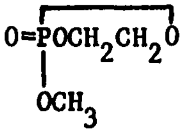
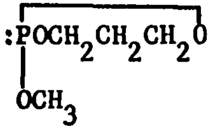
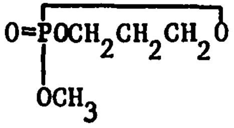
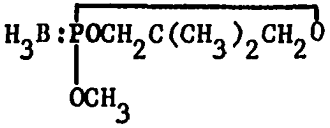
IV. RESULTS AND DISCUSSION

A. Dipole Moments

The dipole moment of a compound containing polar bonds is dependent on the conformation of the molecule. Dipole moments of twenty-three compounds have been determined and will later be compared among themselves, with others and with those calculated by a vector-summation of bond moments in an attempt to deduce the stereochemistries of 1-phospha-2,6-dioxacyclohexanes. The purpose of this Section is to present the experimental results and to discuss some methods of predicting molecular dipole moments. The following data for the twenty-three solutes are given in Table 6: dielectric constant (ϵ) and solute mole fraction (X) for three or four benzene solutions and the solvent benzene at 25.00 ± 0.05°C, the equation for ϵ as a function of X as determined from a least-squares plot, the slope of a plot of index of refraction (n_D) *versus* X, and the orientation polarization (P_0) as calculated from the Cohen-Henriquez equation (118). The resultant dipole moments were calculated from these data with the Debye equation (118). In the cases where the solute is a mixture of geometrical isomers, the resultant moment is a weighted root mean square average of the moments of the components. In order to determine the molecular moments (μ_A and μ_B), resultant moments (μ^1_{obs} and μ^2_{obs}) of two mixtures of different molar component ratios (Y:1 and Z:1) or a mixture (Y:1) and one of the components (Z:1=0) were used to solve the following two simultaneous equations:

Table 6. Dipole moment data

	Solute[a]	Dielectric Constant, ε[b]	Mole Fraction $X\mathrm{x}10^3$	ε=f(X)	$\partial n_D/\partial X$[c]	P_0[d]
CI	$P(OCH_3)_3$	2.326	11.09	4.513X+2.276	-0.17	74.06
		2.301	5.533			
		2.289	2.764			
		2.282	1.380			
		2.275	0.000			
CII	$H_3B{:}P(OCH_3)_3$	2.382	4.671	22.80X+2.276	-.10	339.0
		2.329	2.333			
		2.302	1.165			
		2.276	0.000			
CV	 $:P(OCH_2)_2CH$, O	2.424	10.11	14.67X+2.276	-0.07	219.5
		2.351	5.044			
		2.314	2.517			
		2.295	1.260			
		2.276	0.000			
CVI	 $H_3B{:}P(OCH_2)_2CH$, O	2.833	10.29	54.23X+2.276	-0.098	799.3
		2.556	5.130			
		2.416	2.562			
		2.345	1.279			
		2.275	0.000			
III	 $:POCH_2CH_2O$, OCH_3	2.392	13.13	8.773X+2.277	0.00±.01	128.6
		2.334	6.552			
		2.305	3.272			
		2.291	1.635			
		2.276	0.000			

I	 $O{=}POCH_2CH_2O$ OCH_3	2.648	13.43	27.68X+2.276	-0.067	408.7
		2.461	6.693			
		2.369	3.342			
		2.322	1.667			
		2.275	0.000			
XXXIV	 $:POCH_2CH_2CH_2O$ OCH_3	2.382	9.823	10.77X+2.276	-0.094	162.0
		2.329	4.898			
		2.303	2.449			
		2.289	1.223			
		2.276	0.000			
LXXVIII	 $O{=}POCH_2CH_2CH_2O$ OCH_3	2.731	10.59	42.92X+2.276	-.033	631.9
		2.503	5.279			
		2.390	2.634			
		2.333	1.316			
		2.276	0.000			
LXXIX	 $H_3B:POCH_2C(CH_3)_2CH_2O$ OCH_3	2.702	8.283	51.16X+2.278	-.098	754.3
		2.489	4.121			
		2.384	2.058			
		2.332	1.027			
		2.277	0.000			

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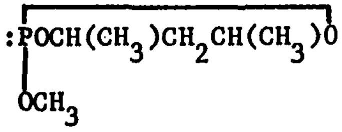
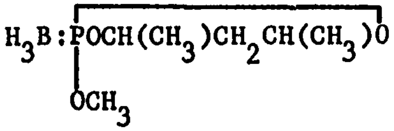
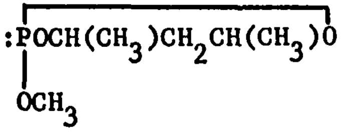
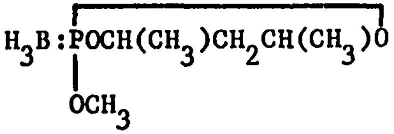
[a] Structural formulas for compounds symbolized by primed Roman numerals are in Table 14.

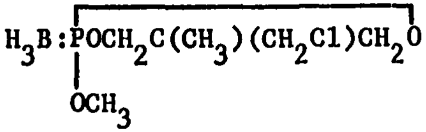
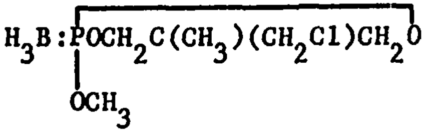
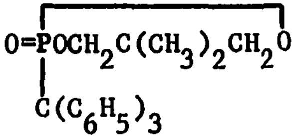
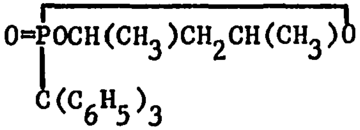
[b] Measured in benzene solution at 25.00 ± 0.05°.

[c] The indices of refraction, n_D, were measured at 25.0 ± 0.2°.

[d] Orientation polarization.

Table 6 (continued)

Solute[a]		Dielectric Constant, ε[b]	Mole Fraction Xx10^3	ε=f(X)	$\partial n_D/\partial X$[c]	P_0[d]
XXXII A	 $:\overline{\underset{OCH_3}{P}OCH(CH_3)CH_2CH(CH_3)O}$	2.425	11.84	12.36X+2.279	-0.17	188.7
		2.351	5.892			
		2.316	2.939			
		2.297	1.467			
		2.278	0.000			
XCI	 $H_3B:\overline{\underset{OCH_3}{P}OCH(CH_3)CH_2CH(CH_3)O}$	2.870	10.79	54.73X+2.279	-0.079	807.0
		2.572	5.368			
		2.425	2.674			
		2.353	1.336			
		2.279	0.000			
XXXII A and B[e]	 $:\overline{\underset{OCH_3}{P}OCH(CH_3)CH_2CH(CH_3)O}$	2.440	10.91	14.79X+2.279	-0.16	223.9
		2.360	5.432			
		2.319	2.710			
		2.298	1.354			
		2.278	0.000			
		2.495	14.36	15.13X+2.278	-0.16	228.4
		2.387	7.124			
		2.333	3.560			
		2.306	1.778			
		2.277	0.000			
XC and XCI[f]	 $H_3B:\overline{\underset{OCH_3}{P}OCH(CH_3)CH_2CH(CH_3)O}$	2.865	11.93	49.27X+2.277	-0.11	728.1
		2.567	5.925			
		2.421	2.954			
		2.350	1.476			
		2.278	0.000			

LXXX and LXXXI[g]	 $H_3B:\underset{OCH_3}{\underset{\vert}{P}}OCH_2C(CH_3)(CH_2Cl)CH_2O$	2.744	9.967	47.13X+2.274	0.00±0.01	691.9
		2.508	4.948			
		2.391	2.466			
		2.333	1.230			
		2.274	0.000			
LXXX and LXXXI[h]	 $H_3B:\underset{OCH_3}{\underset{\vert}{P}}OCH_2C(CH_3)(CH_2Cl)CH_2O$	2.673	9.403	42.30X+2.275	0.00±0.01	621.0
		2.473	4.671			
		2.374	2.328			
		2.325	1.161			
		2.274	0.000			
I′	 $O{=}\underset{C(C_6H_5)_3}{\underset{\vert}{P}}OCH_2C(CH_3)_2CH_2O$	2.435	6.834	23.35X+2.276	+0.47	322.0
		2.359	3.544			
		2.317	1.773			
		2.295	0.837			
		2.276	0.000			
CXIX[i]	 $O{=}\underset{C(C_6H_5)_3}{\underset{\vert}{P}}OCH(CH_3)CH_2CH(CH_3)O$	2.447	6.353	26.84X+2.277	+0.52	371.3
		2.355	2.894			
		2.318	1.552			
		2.295	0.704			
		2.276	0.000			

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[e] Percentage of XXXII B was 49 ± 8% in first set of samples and 50 ± 6% in second set.

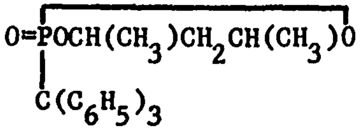
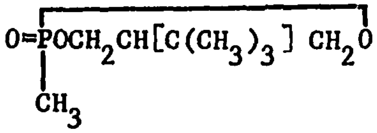
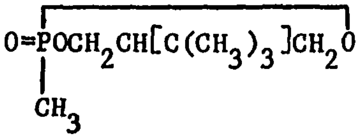
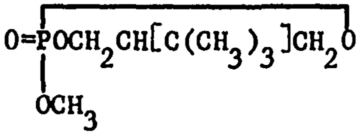
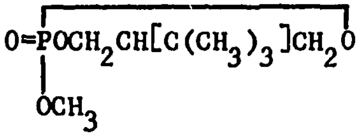
[f] Percentage of XC, derived from XXXII B, was 72 ± 2%.

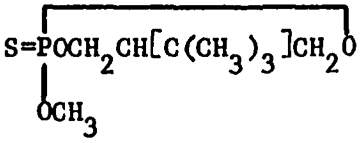
[g] Percentage of LXXX, derived from XXXI B, was 25 ± 2%.

[h] Percentage of LXXX was 63 ± 2%.

[i] Prepared from XXXII A.

Table 6 (continued)

	Solute[a]	Dielectric Constant, ε[b]	Mole Fraction $X\times10^3$	ε=f(X)	$\partial n_D/\partial X$[c]	P_0[d]
CXX[j]	 $O{=}\underset{C(C_6H_5)_3}{P}OCH(CH_3)CH_2CH(CH_3)O$	2.549	6.778	40.33X+2.275	+0.43	573.0
		2.436	4.008			
		2.360	2.100			
		2.321	1.122			
		2.276	0.000			
XXII′	 $O{=}\underset{CH_3}{P}OCH_2CH[C(CH_3)_3]\,CH_2O$	2.590	11.16	28.18X+2.276	-0.053	416.0
		2.437	5.725			
		2.353	2.715			
		2.315	1.380			
		2.275	0.000			
XXI′	 $O{=}\underset{CH_3}{P}OCH_2CH[C(CH_3)_3]CH_2O$	2.750	10.90	43.48X+2.277	-0.036	639.9
		2.519	5.551			
		2.407	2.964			
		2.334	1.309			
		2.276	0.000			
X′	 $O{=}\underset{OCH_3}{P}OCH_2CH[C(CH_3)_3]CH_2O$	2.676	11.21	35.68X+2.276	-0.071	526.7
		2.481	5.754			
		2.388	3.174			
		2.334	1.623			
		2.277	0.000			
XI′	 $O{=}\underset{OCH_3}{P}OCH_2CH[C(CH_3)_3]CH_2O$	2.647	8.433	43.91X+2.277	-0.093	648.6
		2.462	4.190			
		2.371	2.106			
		2.323	1.044			
		2.276	0.000			

CXXIV[k]	 $S{=}\overset{|}{P}OCH_2CH[C(CH_3)_3]CH_2\overset{|}{O}$, P–OCH_3	2.747	11.16	42.20X+2.277	0.00±0.01	619.5
		2.517	5.655			
		2.412	3.183			
		2.356	1.862			
		2.276	0.000			

[j] Prepared from XXXII B.

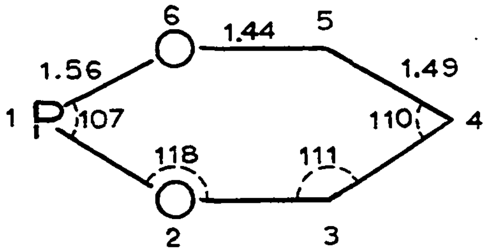
[k] Prepared from XXX A. The *t*-butyl and methoxyl groups are *cis* (98).

$$Y(\mu_A)^2 + (\mu_B)^2 = (\mu^1_{obs})^2$$

$$Z(\mu_A)^2 + (\mu_B)^2 = (\mu^2_{obs})^2$$

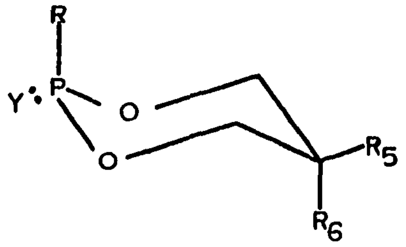
The molecular moments of the twenty-three compounds and of others to be discussed are given in Tables 7 and 8. The moment of XXXII B has an uncertainty of about 0.08 D due to the different isomer ratio XXXII A: XXXII B before and after the measurement of the dielectric constant.

Table 7 also includes moments for the two possible chair conformers for each of the six-membered monocyclic compounds except LXXII as calculated by a vector summation of bond moments. This vector summation requires structural data and a set of bond moments. No structural data are available for a trivalent phosphorus compound or for a BH_3 adduct. As a consequence all of the compounds in solution are assumed to have the ring structure of 1-oxo-1-phenoxy-1-phospha-2,6-dioxacyclohexane (L) (33) in the solid state. The bond angles and distances are shown in the planar figure below. In L, the $O_2P_1O_6$ plane makes an angle of ca. 144°

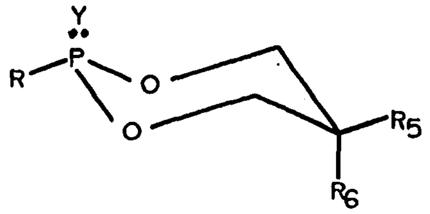


with the $O_2C_3C_5O_6$ plane and the $O_2C_3C_5O_6$ plane makes an angle of ca. 128° with the $C_3C_4C_5$ plane. In addition, the RPY angle (see figure in Table 3 for notation) is assumed to be 114° as in L and the PY and PR bonds are assumed to make angles of 136° and 110°, respectively, with the ring OPO plane as can be calculated from the bond angles and distances for L. The

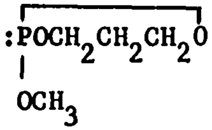
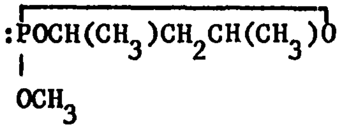
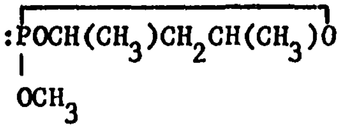
Table 7. Calculated and experimental dipole moments of some 1-phospha-2,6-dioxacyclohexanes

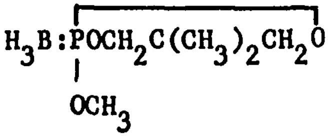
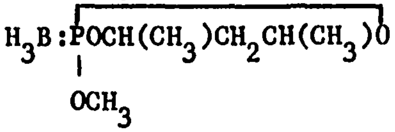
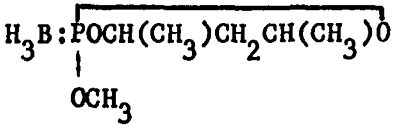
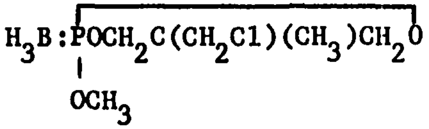
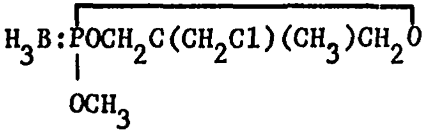
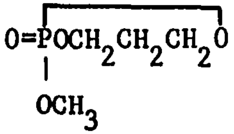


(i)



(ii)

	Compound[a]	Experimental Moment, D[b]	Structure	R	Y	R_5	R_6	Calculated Moment[c] 1	2
XXXIV	 $\underset{OCH_3}{:P}OCH_2CH_2CH_2O$	2.82							
XXXII A	 $\underset{OCH_3}{:P}OCH(CH_3)CH_2CH(CH_3)O$	3.04	(i)	OCH_3	---	H	H	1.6	3.1
			(ii)	OCH_3	---	H	H	2.2	3.4
XXXII B	 $\underset{OCH_3}{:P}OCH(CH_3)CH_2CH(CH_3)O$	3.6							

LXXIX	 $H_3B{:}\overline{\underset{OCH_3}{P}OCH_2C(CH_3)_2CH_2O}$	6.07							
XCI	 $H_3B{:}\overline{\underset{OCH_3}{P}OCH(CH_3)CH_2CH(CH_3)O}$	6.28	(i)	OCH_3	BH_3	H	H	5.8	7.2
			(ii)	OCH_3	BH_3	H	H	4.4	6.2
XC	 $H_3B{:}\overline{\underset{OCH_3}{P}OCH(CH_3)CH_2CH(CH_3)O}$	5.89							
LXXXI	 $H_3B{:}\overline{\underset{OCH_3}{P}OCH_2C(CH_2Cl)(CH_3)CH_2O}$	6.01	(i)	OCH_3	BH_3	CH_2Cl	CH_3	5.8	$\underline{7.1}$
			(i)	OCH_3	BH_3	CH_3	CH_2Cl	6.6	$\underline{7.9}$
LXXX	 $H_3B{:}\overline{\underset{OCH_3}{P}OCH_2C(CH_2Cl)(CH_3)CH_2O}$	5.21	(ii)	OCH_3	BH_3	CH_2Cl	CH_3	$\underline{4.8}$	6.3
			(ii)	OCH_3	BH_3	CH_3	CH_2Cl	$\underline{4.8}$	6.4
LXXVIII	 $O{=}\overline{\underset{OCH_3}{P}OCH_2CH_2CH_2O}$	5.55	(i)	OCH_3	0	H	H	4.4	$\underline{5.8}$
			(ii)	OCH_3	0	H	H	$\underline{3.1}$	5.0

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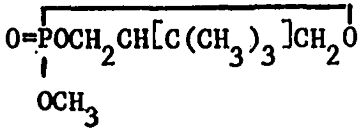
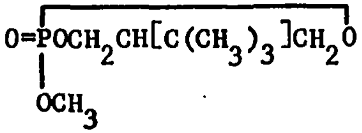
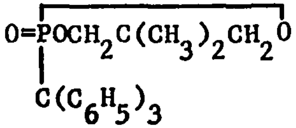
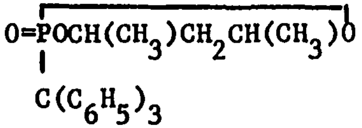
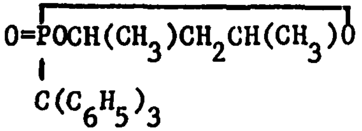
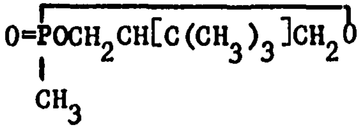
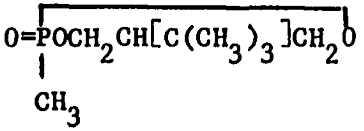
[a] Structural formulas for compounds symbolized by primed Roman numerals are in Table 14. Reasons for structural conclusions are given in the text.

[b] C_6H_6 employed as solvent unless otherwise indicated.

[c] Ring P-0 moments of 1.0 towards oxygen and 0.6 towards phosphorus were employed to determine moments 1 and 2, respectively. The underlined moments are considered "best" values. See text for discussion.

Table 7 (continued)

Compound[a]		Experimental Moment, D[b]	Structure	R	Y	R_5	R_6	Calculated Moment[c] 1	2
X′	 $O{=}\underset{OCH_3}{P}OCH_2CH[C(CH_3)_3]CH_2O$	5.08							
			(i)	OCH_3	0	$C(CH_3)_3$	H	4.4	$\underline{5.8}$
			(ii)	OCH_3	0	$C(CH_3)_3$	H	$\underline{3.1}$	5.0
XI′	 $O{=}\underset{OCH_3}{P}OCH_2CH[C(CH_3)_3]CH_2O$	5.63							
I′	 $O{=}\underset{C(C_6H_5)_3}{P}OCH_2C(CH_3)_2CH_2O$	3.97	(i)	$C(C_6H_5)_3$	0	CH_3	CH_3	5.01	$\underline{6.17}$
			(ii)	$C(C_6H_5)_3$	0	CH_3	CH_3	$\underline{2.96}$	4.66
CXIX[d]	 $O{=}\underset{C(C_6H_5)_3}{P}OCH(CH_3)CH_2CH(CH_3)O$	4.26							
			(i)	$C(C_6H_5)_3$	0	H	H	5.01	$\underline{6.17}$
CXX[e]	 $O{=}\underset{C(C_6H_5)_3}{P}OCH(CH_3)CH_2CH(CH_3)O$	5.29	(ii)	$C(C_6H_5)_3$	0	H	H	$\underline{2.96}$	4.66
XXI′	 $O{=}\underset{CH_3}{P}OCH_2CH[C(CH_3)_3]CH_2O$	4.51							
			(i)	CH_3	0	$C(CH_3)_3$	H	5.01	$\underline{6.17}$
XXII′	 $O{=}\underset{CH_3}{P}OCH_2CH[C(CH_3)_3]CH_2O$	5.60	(ii)	CH_3	0	$C(CH_3)_3$	H	$\underline{2.96}$	4.66

CXXIV[f]	$S{=}\overline{\underset{OCH_3}{P}OCH_2CH[C(CH_3)_3]CH_2O}$	5.50	(i)	OCH_3	S	$C(CH_3)_3$	H	4.03	$\underline{5.61}$
			(ii)	OCH_3	S	$C(CH_3)_3$	H	$\underline{2.89}$	4.72
CXXV[g]	$S{=}\overline{\underset{OC_2H_5}{P}OCH_2CH_2CH(CH_3)O}$	5.36							
			(i)	OC_2H_5	S	H	H	4.03	$\underline{5.61}$
CXXVI[h]	$S{=}\overline{\underset{OC_2H_5}{P}OCH_2CH_2CH(CH_3)O}$	3.19	(ii)	OC_2H_5	S	H	H	$\underline{2.89}$	4.72
XIX′	$O{=}\overline{\underset{CH_3}{P}OCH_2C(CH_3)(CH_2Br)CH_2O}$	5.25[i]	(i)	CH_3	0	CH_3	CH_2Br	5.6	$\underline{6.6}$
			(ii)	CH_3	0	CH_2Br	CH_3	$\underline{3.2}$	4.6
XXIII′	$O{=}\overline{\underset{C_2H_5}{P}OCH_2C(CH_3)(CH_2Br)CH_2O}$	4.75[i]	(i)	C_2H_5	0	CH_3	CH_2Br	5.6	$\underline{6.6}$
			(ii)	C_2H_5	0	CH_2Br	CH_3	$\underline{3.2}$	4.6

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[d] Prepared from XXXII A.

[e] Prepared from XXXII B.

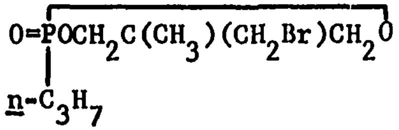
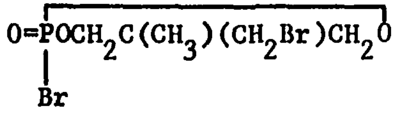
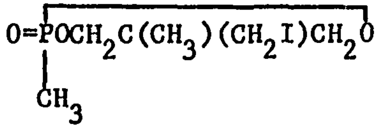
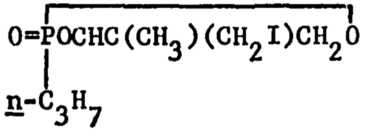
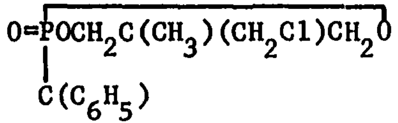
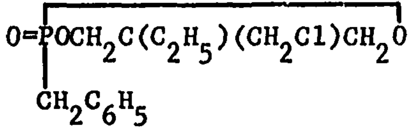
[f] Prepared from XXX A. The *t*-butyl and methoxyl groups are *cis* (98).

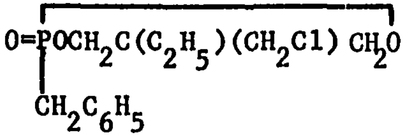
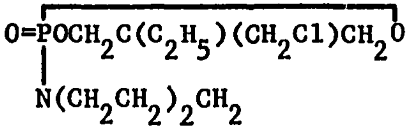
[g] Prepared from XXVI A. The methyl and ethoxyl groups are *trans* (95).

[h] Prepared from XXVI B. The methyl and ethoxyl groups are *cis* (95).

[i] $\partial n_D/\partial X$ was not determined.

Table 7 (continued)

	Compound[a]	Experimental Moment, D[b]	Structure	R	Y	R_5	R_6	Calculated Moment[c] 1	2
XXIV′	 $O{=}\underset{\mid\, \underline{n}\text{-}C_3H_7}{P}OCH_2C(CH_3)(CH_2Br)CH_2O$	4.78^{i}	(i)	$\underline{n}$-C_3H_7	0	CH_3	CH_2Br	5.6	6.6
			(ii)	$\underline{n}$-C_3H_7	0	CH_2Br	CH_3	3.2	4.6
XXXII′	 $O{=}\underset{\mid\, Br}{P}OCH_2C(CH_3)(CH_2Br)CH_2O$	6.59^{i}	(i)	Br	0	CH_3	CH_2Br	4.8	6.1
			(ii)	Br	0	CH_2Br	CH_3	3.0	4.7
XX′	 $O{=}\underset{\mid\, CH_3}{P}OCH_2C(CH_3)(CH_2I)CH_2O$	4.95^{i}	(i)	CH_3	0	CH_3	CH_2I	5.6	6.6
			(ii)	CH_3	0	CH_2I	CH_3	3.2	4.6
XXV′	 $O{=}\underset{\mid\, \underline{n}\text{-}C_3H_7}{P}OCHC(CH_3)(CH_2I)CH_2O$	4.46^{i}	(i)	$\underline{n}$-C_3H_7	0	CH_3	CH_2I	5.6	6.6
			(ii)	$\underline{n}$-C_3H_7	0	CH_2I	CH_3	3.2	4.6
III′	 $O{=}\underset{\mid\, C(C_6H_5)}{P}OCH_2C(CH_3)(CH_2Cl)CH_2O$	4.52^{i}	(i)	$C(C_6H_5)_3$	0	CH_3	CH_2Cl	5.7	6.7
			(ii)	$C(C_6H_5)_3$	0	CH_2Cl	CH_3	3.2	4.7
XXIX′	 $O{=}\underset{\mid\, CH_2C_6H_5}{P}OCH_2C(C_2H_5)(CH_2Cl)CH_2O$	5.30^{i}	(i)	$CH_2C_6H_5$	0	C_2H_5	CH_2Cl	5.7	6.7
			(ii)	$CH_2C_6H_5$	0	CH_2Cl	C_2H_5	3.2	4.7

XXX′	 $O{=}\underset{CH_2C_6H_5}{\underset{\vert}{P}}OCH_2C(C_2H_5)(CH_2Cl)CH_2O$	3.42^{i}	(i)	$CH_2C_6H_5$	0	CH_2Cl	C_2H_5	4.8	5.8
			(ii)	$CH_2C_6H_5$	0	C_2H_5	CH_2Cl	3.0	4.6
LXXII	 $O{=}\underset{N(CH_2CH_2)_2CH_2}{\underset{\vert}{P}}OCH_2C(C_2H_5)(CH_2Cl)CH_2O$	$5.02^{i,j}$	(i)	NC_5H_{10}	0	C_2H_5	CH_2Cl		
			(ii)	NC_5H_{10}	0	CH_2Cl	C_2H_5		

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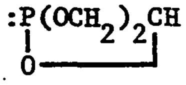
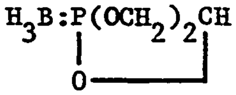
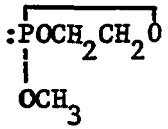
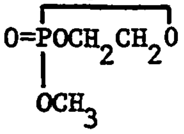
[j] CCl_4 employed as solvent.

Table 8. Miscellaneous experimental dipole moments

Compound		Dipole Moment,D[a]	Reference
CI	$:P(OCH_3)_3$	1.90 1.81	 70
CIII	$O{=}P(OCH_3)_3$	3.18	70
CII	$H_3B{:}P(OCH_3)_3$	4.07	
XCVII(CH_3)	$:P(OCH_2)_3CCH_3$	4.15^b 4.13	119 120
XCIX(CH_3)	$O{=}P(OCH_2)_3CCH_3$	7.10^b	119
XCVIII(CH_3)	$H_3B{:}P(OCH_2)_3CCH_3$	8.60^b	117
	$S{=}P(OCH_2)_3CCH_3$	6.77^b	119
CV	 $:P(OCH_2)_2CH$ O	3.28	
CVI	 $H_3B{:}P(OCH_2)_2CH$ O	6.25	
III	 $:POCH_2CH_2O$ OCH_3	2.51	
I	 $O{=}POCH_2CH_2O$ OCH_3	4.47	

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[a] C_6H_6 employed as solvent unless indicated otherwise; 25°.

[b] $O(CH_2CH_2)_2O$ employed as solvent.

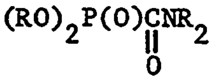
angles about C_4, and the CCCl, CCBr, and CCI angles are assumed to be 110°. The POC angle of an exocyclic $POCH_3$ group is given a value of 120°, which is between the values of 119° and 123° found in the solid state structures of I and II, respectively. In reality, the trivalent phosphorus compounds and the BH_3 adducts probably have RPO, OPO, YPR, YPO and POC angles that are different than those of the phosphates. Indicative of the dependence of bond angles on the nature of the Y group are the average POC and OPO angles of 122° and 100°, respectively, for the transition metal complex $C(CH_3)$ (57b) and 115° and 104°, respectively, for the phosphate $XCIX(CH_3)$ (58). Similarly, the average POC and OPO angles are 116° and 103°, respectively, for the transition metal complex XCVI (57b) and 113° and 105°, respectively, for the thiophosphate XCV (59).

The set of bond moments is given in Table 9.

Table 9. Bond moments

Bond	Moment, D	Bond	Moment, D
C-H	0.0	P-O (ring)	1.0
C-C	0.0	or	
C-O	1.16	O-P (ring)	0.6
C-Cl	1.86	P=O	2.95
C-Br	1.6	$P-BH_3$	4.45
C-I	1.6	P=S	2.62
C-P	1.0		
P-Br	0.39		
P-O (exocyclic)	1.0		

The negative end of the bond dipoles is toward the atom at the right end of the bond. A moment is said to be directed towards a particular atom if the negative end of the dipole is nearer that atom than the other. The term "bond moment" is used here with two meanings. In both definitions it is a vector. The magnitude of the first kind of bond moment is ideally the product of the separation of the centers of positive and negative charges and the magnitude of either charge. The negative charge is due to the valence shell bonding and nonbonding and non-valence shell electrons. However, if one or both of the bonded atoms are bonded to other atoms, the contributions of these electrons are reduced accordingly. For example, the negative charge contribution to the C-O bond moment in dimethyl ether includes one-half of the oxygen and one-fourth of the carbon non-valence shell electrons, the valence shell bonding electrons in one C-O bond and one-half of the oxygen valence shell nonbonding electrons (rather than one lone pair of electrons). The positive charge is due to protons located at the bonded nuclei. The magnitude of each nuclear charge is equal to the negative charge contributed by each atom as outlined above and would be 1.5 for carbon and 4 for oxygen in dimethyl ether. These bond moments are usually empirically determined by resolving the measured moment of a molecule of known or assumed structure into component bond moments. Secondary moments may be induced by the primary bond moments and these primary moments are dependent on the electronic structure of the molecule. Therefore, caution is required when using a bond moment derived from one molecule to predict the molecular moment of another. Empirically derived bond moments are assumed to be parallel to the respective bonds. Although this assumption has been made in all the vector summations of bond moments thus far located in the literature, it is invalid for P-O and C-O moments for reasons to be presented later. Thus, bond moments function only as an effective value when this assumption is incorrect and cannot be easily interpreted in terms of charge separation. Knowledge of the position of the bond moments with respect to the bonded atoms is not needed in the following discussion. Another type of bond moment is better called a bond-formation moment. The P=O, P-BH_3 and P=S moments are examples of this type and are the differences between the molecular moment of a bicyclic phosphite (XCVII(CH_3)) and the moments of the corresponding phosphate, borane adduct and thiophosphate, respectively. These moments do not include the phosphorus lone pair moment as it exists in the phosphite because it is incorporated among the P-Br, P-O, etc. bond moments. On the other hand, these moments do include any change in molecular charge distribution that occurs upon formation of the P=O, P-BH_3 and P=S bonds. Also, they are directed towards the acceptor atom or group of atoms and are parallel to the bond. The P-BH_3 moment also includes the B-H moments. The P=O and P=S moments are smaller than the values of 3.3±0.1 and 3.0±0.1 D, respectively, selected by Estok and Wendlandt (121) as the most probable when these bonds are not appreciably influenced by induction. The smaller values will be used because they were derived from molecules similar to those being investigated.

An explanation of the sources of the other bond moments listed above is now in order. Smyth has discussed the difficulties assigning a C-H bond moment (122, pp. 239-243). He discusses how values ranging from 0.4 D in one direction to 0.4 D in the other have been proposed. A value of 0.0 D is arbitrarily used here instead of 0.4 D directed towards carbon which was chosen by Smyth. The C-Cl, C-Br and C-I moments are taken as the molecular moments of CH_3Cl, CH_3Br and CH_3I, respectively, in benzene (123). The C-O moment was calculated from the molecular moment, 1.32D (124), and the COC angle, 111° (125), of dimethyl ether. The fact that COP angles in alkyl phosphorus esters are 115-123° indicates that the hybridization of the oxygen valence orbitals is not the same in these compounds and in dimethyl ether. Thus, the C-O moment derived from dimethyl ether is undoubtedly incorrect but will be used to calculate the moments of phosphorus compounds simply because no better value is available. The P-Br moment was calculated from the molecular moment of 0.52D (123) and the BrPBr angle of $101.5 \pm 1.5^\circ$ (126) of PBr_3 and includes one-third of the phosphorus lone pair moment. The C-P moment is an average of alkyl-P moments calculated by Kodama, et al. (127) from structural and dipole moment data for several mono and trialkyl phosphines and includes one-third of the phosphorus lone pair moment. This moment is directed towards phosphorus because the moment of $P(\underline{p}\text{-}C_6H_4Cl)_3$, 0.65 D (123), is less than that of $P(C_6H_5)_3$, 1.40 D (123). Kosolapoff has cited a C-P moment of 0.9 D implicitly directed towards phosphorus (69) but in the English translation of the Russian source of this moment (128) the direction is stated explicitly to be towards carbon in compounds of the type  $(RO)_2P(O)\underset{\underset{O}{\|}}{C}NR_2$ wherein R is an alkyl group. Other translations of Russian papers include values for the P-C moment of 0.7 D (129) and 0.8 D (130) directed towards carbon in a P-alkyl group in molecules such as $RP(O)(OC_2H_5)_2$ and $C_2H_5P(O)H(OR)$ but 0.8 D directed towards phosphorus in a P-CCl_3 group in $(RO)P(O)(C_2H_5)(CCl_3)$ (130). The Russian values depend on the validity of the other bond moments in the molecules investigated. Unfortunately, the justification of these moments is given in a Russian Ph.D. Thesis (131) which is not available. The P-O (ester) moment of 1.2 D directed towards oxygen may have been taken from the work of Lewis and Smyth (67) and, if this is true, it was derived from a freely-rotating model of $P(OC_6H_5)_3$ by a vector summation calculation. The Russians have employed this value in molecules for which rotation about the P-O bonds was considered to be restricted. This procedure will later be shown to be incorrect and, for this reason, the Russian P-C moment will not be used. The P=O, P-BH_3 and P=S moments were discussed earlier.

Three entries for the P-O moment are given in the list above. Each of these includes one-third of the phosphorus lone pair moment and one-half of the resultant oxygen lone pairs moment. The oxygen is covalently bonded to an alkyl group and, thus, these P-O moments should be distinguished from the P=O moment. The value for the exocyclic P-O moment and the first of the ring P-O moments was derived by the method of Zahn as described by Partington (132, p. 485) from the moment of trimethyl phosphite (Table 8), the H-C and C-O moments given above, a POC angle of 120° and an angle of 66° between each of the P-O bonds and the three-fold rotational axis of the PO_3 group. The use of Zahn's method requires the assumption that the methyl groups are freely rotating about the P-O bonds. The resultant molecular moment is then a root mean square average of all of the possible conformer moments. The molecular moment of trimethyl phosphite is: $\sqrt{\mu^2_{k_1k_2k_3}} = \sqrt{\mu_0^2 + \mu_{k_1}^2 + \mu_{k_2}^2 + \mu_{k_3}^2} =$ $\sqrt{\mu_0^2 + 3\mu_k^2}$, wherein μ_0 is the magnitude of the vectorial sum of the non-rotating bond moments and the components of the rotating moments (C-O) parallel to the respective rotational axes k_1, k_2 and k_3 (the three PO bonds) and μ_k is the magnitude of the component of the rotating moment perpendicular to the k^{th} rotational axis. The proper substitutions can be made in the above equation to give: $\sqrt{\mu^2_{k_1k_2k_3}} =$ $\sqrt{[3(\text{PO}-\text{CO} \cos 60^\circ)\cos 66^\circ]^2 + 3(\text{CO} \sin 60^\circ)^2}$. Solution of this equation for the PO moment gives values of 0.98 D and 0.18 D directed towards oxygen. The first value corresponds to a molecular moment directed on the average from the phosphorus atom towards the methoxyl groups and the second to a moment in the opposite direction. A P-O moment of 1.2 D directed towards oxygen has been used by Russian workers, as pointed out earlier, and others (67, 69, 133) when treating noncyclic derivatives. This number differs from that calculated above because Lewis and Smyth (67) used triphenylphosphite with a moment of 2.02 D, an oxygen valency angle of 110°, a phosphorus valency angle of 100° and an OCH_3 group moment of 1.0 D towards oxygen in order to calculate it. They used an equation derived by Eyring (134) for a molecule with freely rotating phenyl groups but the above equation yields the same P-O moment when these same data are used. These authors did not mention the second value of the P-0 moment that is possible but did point out that 1.2 D is the difference between the H-0 and H-P moments, both directed away from hydrogen; the similarity between a Y-Z moment and the difference between H-Y and H-Z moments had earlier been empirically established (135). It is noteworthy that the value of 1.0 D can be used to calculate the moments of trimethyl phosphate (CIII) and trimethyl phosphite borane (CII) to within 0.2 D of the experimental values (Table 8) if the data assumed for trimethyl phosphite, the P-BH_3 and P=0 moments listed above and a free-rotation model are employed. Use of the value of 0.18 D for the P-0 moment gives molecular moments that are 0.7 D and 1.1 D, respectively, greater than the experimental values. Either value of the P-0 moment could also conceivably be derived from a model with no rotation or one with less than completely free rotation. As noted earlier there is considerable infrared evidence for rotational isomerism for trimethyl phosphate in many solvents. Also, Brown et al. (119) found that the moment of triethyl phosphite decreased 0.22 D from 25° to 35° in dioxane whereas that of the bicyclic phosphite XCVII(CH_3) varied only 0.02 D. In the gas phase, an electron diffraction study of triethyl phosphite revealed the presence of rotational isomers (60). Thus, a model with partially restricted rotation seems most reasonable. The fact that the moments of trimethylphosphite and its oxo and borane derivatives can be calculated with the same value of the P-0 moment may be due to similar stereochemical preferences among these molecules or to chance. Franklin (136) calculated the moments of twelve central-atom molecules, e.g., $(C_2H_5O)_3SiH$, $(ClCH_2)_4C$ and $(C_2H_5O)_3PO$, using the free-rotation model and found no agreement with experimental values. The error for triethylphosphate was only 0.2 D but differences of 1 D were more typical. He pointed out that dipole-dipole and steric interactions would tend to exclude conformations with large moments, in agreement with the fact that most of the observed values were lower than the calculated values. Svirbely and Lander (68) found good agreement between the experimental moment of triethylphosphate and the moment calculated for a free-rotation model. However, their method of calculation was incorrect because the root mean square average of the rotating ethoxyl bond moments was calculated first and then added vectorially to the P=0 and PO_3 moments; the ethoxyl contribution was considered to be parallel to the P=0 bond on the average. This procedure is not equivalent to that described earlier for trimethylphosphite.

A P-0 moment of 1.0 D towards oxygen has been used to calculate the moments of the monocyclic compounds in order to arrive at the values listed in Table 7 under "Calculated Moment 1." About the only justifications for these calculations are the possibilities that the weighted root mean square average moment of the conformers that do exist for trimethylphosphite approximates the free rotation average and that the directions and the magnitudes of the P-0 and C-0 moments are independent of rotation about the P-0 and C-0 bonds. These are admittedly relatively poor assumptions, but since many workers have used values for the P-0 moment of 1.2-1.4 D to calculate moments of molecules in which rotation was considered to be both restricted and free, the results are being presented and will be discussed later. The molecular moments have been calculated for the structures at the top of Table 7. The structures differ in the axial and equatorial disposition of the exocyclic groups. All of these groups were assumed to be freely rotating about the bond connecting them to a ring atom. Thus, the method used to calculate the moment of trimethylphosphite was used here also. All of the bond moments were first resolved into fixed and rotating components. Secondly, the fixed components were resolved into x, y and z components according to the Cartesian coordinate system show below. The xz plane is the symmetry plane of the ring atoms, and the axial bond at phosphorus is the z-axis. Thirdly, these x, y and z components were added to give μ_x, μ_y and μ_z. Finally the molecular moment, μ_{mol}, was written as the square root of the sum of the squares of the magnitudes of these component sums and each independently rotating component. If two components were rotating about the same axis with a constant angle between them, which was not the case in these calculations, they would first be vectorially added before being squared. Now $\mu_{mol} = \sqrt{(\mu_{rot1})^2 + (\mu_{rot2})^2 + \dots + (\mu_{rotk})^2 + (\mu_x)^2 + (\mu_y)^2 + (\mu_z)^2}$ if there were k independently-rotating components. The bond moment components for the two structures in Table 7 are listed in Table 10. These were determined from the bond moments and structural data given earlier. The components of both the two ring P-O

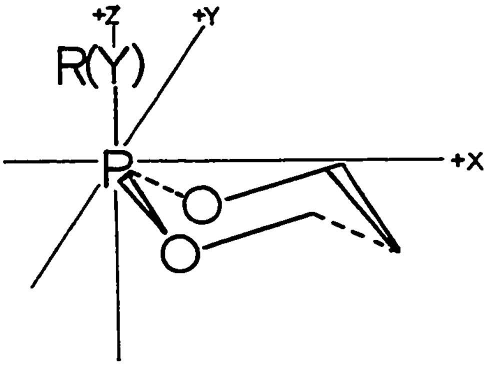
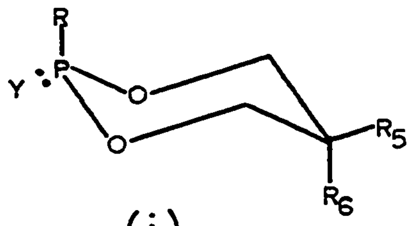
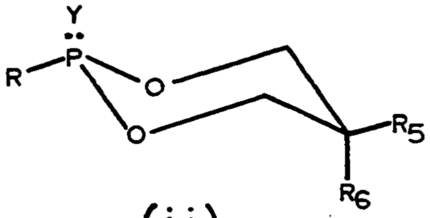


Table 10. Bond moment components for 1-phospha-2,6-dioxacyclohexanes



(i)



(ii)

		Components, D[a]				
	Bond	Structure(i)		Structure (ii)		
Bonds[b]	Moment, D	X	Z	X	Z	Rot.[c]
2 C-O (ring)[d]	1.16	-2.23	-0.64	-2.28	0.40	
C-O (exo)	1.16	0.00	-0.58	0.52	0.23	1.00
C-Cl (ax)	1.86	0.00	-0.63	-0.29	-0.57	1.75
C-Cl (eq)	1.86	0.60	0.21	0.63	-0.08	1.75
C-Br or C-I (ax)	1.6	0.00	-0.54	-0.25	-0.49	1.50
C-Br or C-I (eq)	1.6	0.52	0.18	0.54	-0.07	1.50
C-P (R)	1.0	0.00	-1.0	0.91	0.41	
P-Br (R)	0.39	0.00	0.36	-0.33	-0.15	
2 P-O (ring)[d]	1.0	1.12	-0.41	0.83	-0.85	
2 O-P (ring)[d]	0.6	-0.67	0.25	-0.50	0.51	
P-O (exo)	1.0	0.00	1.00	-0.90	-0.40	
P=O (Y)	2.95	-2.70	-1.20	0.00	2.95	
$P-BH_3$ (Y)	4.45	-4.06	-1.81	0.00	4.45	
P=S (Y)	2.62	-2.40	-1.07	0.00	2.62	

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[a] All y components are zero.

[b] Exo = exocyclic, ax = axial, eq = equatorial, R = R group at phosphorus, Y = Y group at phosphorus.

[c] Rot. = rotating component.

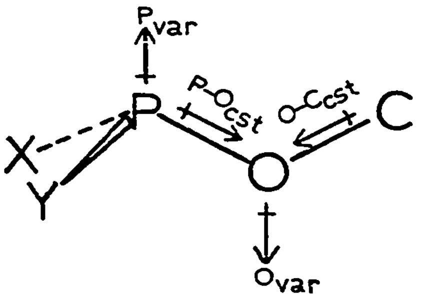
[d] The two ring bond moments have been added.

and the two ring C-O moments were added because in each case the y components cancel and the x or z components are equal. All of the other y components in Table 10 are also zero.

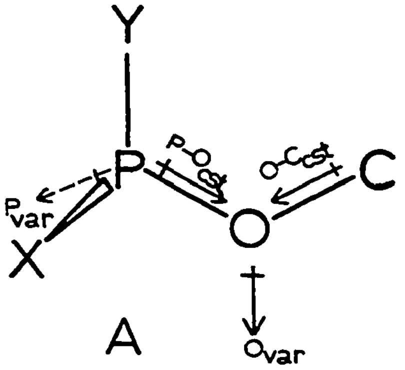
The second value for the ring P-O moment of 0.6 D towards phosphorus has been derived by two groups of workers from a consideration of the moment of the bicyclic phosphite XCVII(CH_3) (120, 137). This molecule would seem to be an ideal model because its stereochemistry is fixed. The molecular moment, bond angles from the solid-state structure of the corresponding phosphate XCIX(CH_3) (58) and C-O and C-H moments given above can be used in the following equation for the molecular moment to obtain the P-O moment: $4.15 = 3(\text{C-O}) + 3(\text{P-O}) \cos 66^\circ$. The molecular moment has the same direction as the C-O moments because the difference between the moments of the phosphate and phosphite, taken in the same direction, is 2.95 D and is in the range of P=O moments surveyed by Estok and Wendlandt, 2.5 - 3.5 D (121). A phosphite moment in the opposite direction would give a P=O moment of 11.25 D. The large phosphate moment of 7.10 D is certainly directed towards the phosphoryl oxygen and, consequently, the phosphite moment is directed towards the phosphorus lone pair of electrons. Surprisingly, the P-O moment is directed towards phosphorus, contrary to the electronegativities of the two atoms. The explanation of this result and a discussion of the calculated molecular moments based on this value of the P-O moment must be deferred until the C-O and P-O moments have been more fully discussed.

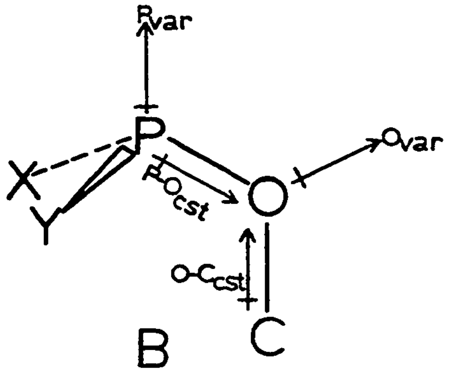
The C-O and P-O moments are difficult to determine because they vary as the lone pairs of electrons rotate about the bonds. These moments can be arbitrarily resolved into two and three component vectors, respectively.

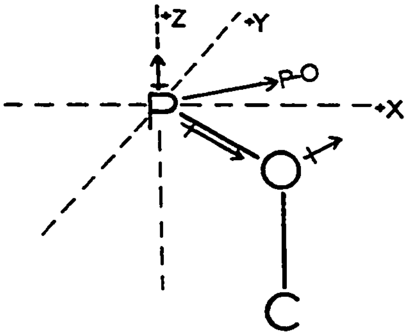
In each case there is a component parallel to the bond which includes all of the electrons and protons contributing to the bond moment except the valence shell nonbonding electrons and an equal number of protons. This component will be called the constant part, e.g., $P\text{-}0_{cst}$. The second component of the C-0 moment is due to the oxygen lone pairs. It has the direction of the vector sum of the two oxygen lone-pair moments and has one-half of its magnitude. Thus, it bisects the POC or COC angle, depending on the second atom bonded to oxygen, and lies in the POC or COC plane, respectively. This component will be called $1/2\ 0_{var}$. In the case of the P-0 moment, there is not only a $1/2\ 0_{var}$ component but also a $1/3\ P_{var}$ component due to the phosphorus lone-pair. This latter component has the same direction as the phosphorus lone-pair with respect to the phosphorus nucleus and has a magnitude one-third of that of the lone-pair moment. These several components are pictured below.

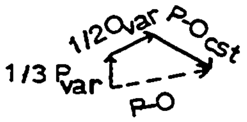


The lengths of the vectors and the direction of $P\text{-}0_{cst}$ and $0\text{-}C_{cst}$ are unknown and are arbitrarily shown. The phosphorus lone-pair orbital is believed to be directed, i.e., not centered on the phosphorus nucleus, because XPY, XP0 and YP0 angles are usually greater than 90° but less than 120°. Thus, P_{var} should not be zero. Likewise, 0_{var} should be nonzero; however, a POC angle of 120° indicates possible sp^2 hybridization of the oxygen valence orbitals and one of the oxygen lone pairs would then be in a p orbital perpendicular to the POC plane. Since the C-O and P-O moments are sums of two or three nonparallel vectors, these moments are not parallel to the respective bonds. An exception might exist if 1/3 P_{var} and 1/2 O_{var} are of equal magnitude and antiparallel. More importantly, O_{var} can rotate about $O\text{-}C_{cst}$ and O_{var} and P_{var} can rotate independently about $P\text{-}O_{cst}$. Examples of this are shown below. The magnitude of the C-O moment will not change with rotation but the direction will. The P-O moment not only will change in direction but also in magnitude. The changes that occur in either the C-O or P-O moment will depend on the magnitudes of O_{var} or O_{var} and P_{var}, respectively. The orientation shown in B above corresponds to that in the bicyclic phosphite XCVII(CH_3). In this orientation the variable vectors add to give the greatest total possible; consequently, the P-O moment will probably have its maximum value. The conclusion that the P-O moment is directed towards phosphorus (120) is a consequence of the invalid assumption that the bond moment is parallel to the bond. This can be understood by considering the drawing below. Here, the POC plane lies in the xz plane and the z axis is coincident with the P_{var} vector. The P-O moment is shown on



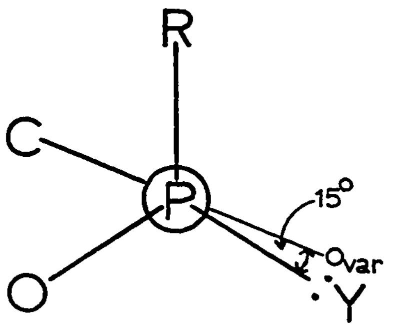




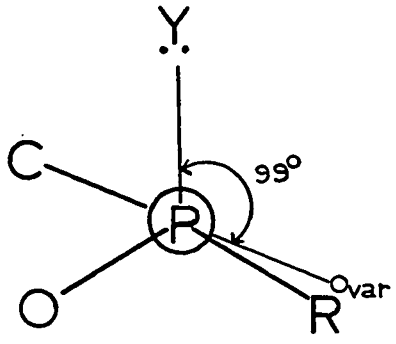


the right as the sum of 1/3 P_{var}, 1/2 O_{var} and P-0_{cst}. Now the three P-0 bond moments in XCVII(CH_3) will have the same magnitude and each will lie in its respective POC plane. Due to the C_{3v} symmetry of the molecule, the x and y components of the three P-0 moments will exactly cancel. The z components will not cancel and will reinforce the C-0 moments if the P-0 moments are directed above the xy plane, as the moment in the drawing is. If the P-0 moments were assumed to be parallel to the bonds, they would have to be directed towards phosphorus in order to reinforce the C-0 moments. Clearly, the P-0 moment in the drawing is directed towards oxygen and would be unless it made an angle greater than 66° with the xy plane. Any P-0 moments between 0° and 66° above this plane and of the proper magnitude could add to the C-0 moments to give a molecular moment of 4.15 D. In reality, therefore, the P-0 moment may be directed towards oxygen.

The moments listed in Table 7 under "Calculated Moment 2" were determined in the same manner as those under "Calculated Moment 1" except that the ring P-0 moments were given a value of 0.6 D towards phosphorus. The exocyclic P-0 moment was not changed from 1.0 D towards oxygen. This procedure is not entirely satisfactory because the 0.6 D moment is an effective P-0 moment for a :P($OC)_3$ group with a stereochemistry like that in the bicyclic phosphite. A useful way to classify this stereochemistry is in terms of the dihedral angle between 0_{var} and P_{var} or the P:Y bond which is 0° in XCVII(CH_3). If this moment is to be used to calculate moments of the monocyclic molecules, the dihedral angles should be 0°. In fact, they are about as shown below in the Newman projections along one of the ring P-0 bonds of structures (i) and (ii), respectively (Table 10); P_{var} and the P-Y bond are parallel. The P-0 moment for structure (i) should be near the maximum but that for structure (ii) should be less because the P_{var} and 0_{var} moments are more in opposition. Since 99° is close to the average of 90° for free rotation about the P-0 bond, a value of 1.0 D towards oxygen may be more appropriate for structure (ii). Of course, 1.0 D is probably not correct for free rotation, but the error is unknown. Given the assumption that the exocyclic groups in the monocyclic compounds are freely rotating, the molecular moments under "Calculated Moment 2" are probably better approximations than those under "Calculated Moment 1" for structure (i) and *vice versa* for structure (ii). Predictions of the stereochemistry of the mono-



(i)



(ii)

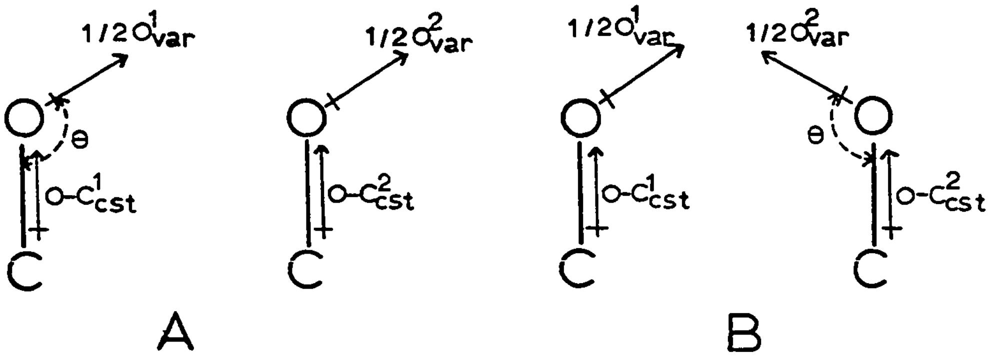
cyclic compounds will be made after the nmr and infrared evidence has been presented.

Thus far, the fact that P-O and C-O moments change with rotation of substituents about the bonds has been discussed and an attempt has been made to calculate molecular moments using P-O moments appropriate to the stereochemistry. However, the calculations were carried out assuming that the C-O and P-O moments are parallel to the bonds. As a result, at least one additional error remains which can be illustrated by the following example. In the drawing below, cases A and B correspond to two different relative orientations of two 1/2 O_{var} vectors. The vector-sum $O\text{-}C^1_{cst} + O\text{-}C^2_{cst} + 1/2\ O^1_{var} + 1/2\ O^2_{var}$ has a magnitude of

$$\sqrt{(2\ O\text{-}C_{cst})^2 + (O_{var})^2 - 2(2\ O\text{-}C_{cst})(O_{var})\cos\theta}$$ in case A and

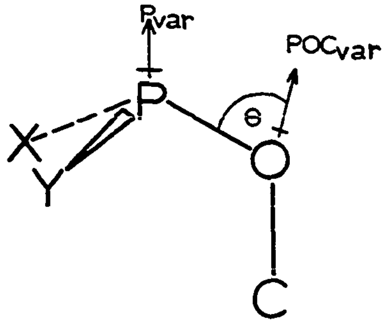
$$\sqrt{(2\ O\text{-}C_{cst})^2 + (O_{var})^2\cos^2\theta - 2\ (2\ O\text{-}C_{cst})\ (O_{var})\cos\theta}$$ in case B and

and has a different direction in the two cases. However, a summation with C-O bond moments assumed parallel to the bonds would give the same result in both cases. Thus, knowledge of the magnitudes of $O\text{-}C_{cst}$, $O\text{-}P_{cst}$, O_{var} and P_{var} would allow calculation of more accurate bond

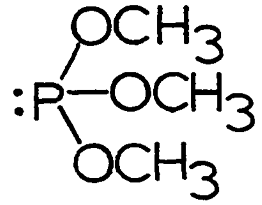


moments and, consequently, more accurate molecular moments.

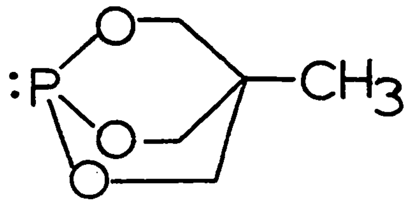
An empirical approach to the determination of the components of the C-0 and P-0 moments would require the existence of four molecules that contain the C-0 and P-0 bonds. The molecular moments would be expressed in terms of the four unknown component moments and the resulting set of equations would be solved for the unknowns. However, these equations must be independent. That is, the spatial relationship of the unknown vectors must be different in the four molecules in order for a solution to be possible. In fact, rotation about the P-0 bond in a :POC group does not change the spatial relationship of the $O\text{-}C_{cst}$, O_{var} and $P\text{-}O_{cst}$ vectors. Their vector sum changes direction but not magnitude. The orientation of P_{var} with respect to this vector sum, POC_{var}, does change with rotation, however. The unknowns then become the angle θ and the magnitudes of P_{var} and POC_{var} as shown below. The POC_{var} vector



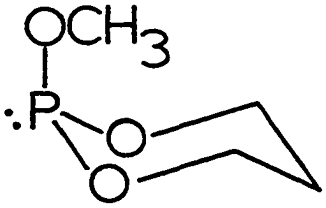
lies in the POC plane. Molecules for which moments might be written in terms of these unknowns are shown next. The bonding in these molecules is considered similar enough that the unknowns have the same value in all four. Evidence to be presented later indicates qualitatively that there are differences in bonding but the effect of these differences on charge distribution cannot presently be evaluated. The unknown stereo-



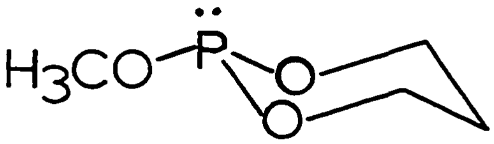
CI



XCVII(CH$_3$)



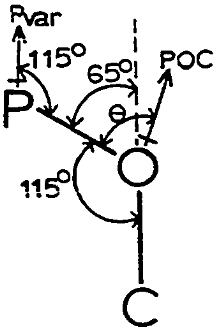
(i)



(ii)

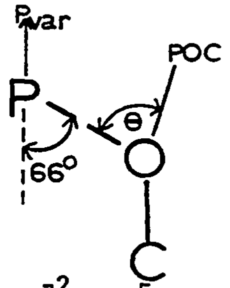
chemistry of CI has already been discussed. Evidence in addition to that given in the Review of Literature will be presented later for the axial disposition of the methoxyl group in a chair conformation as the most stable conformation of monocyclic derivatives such as XXXIV, XXXII A and XXIX. Also, the moment of a phosphite isomer (XXXII B) in which the methoxyl group at phosphorus is believed to be equatorial is available. In none of these cyclic compounds is the orientation of the methoxyl group with respect to rotation around the OP bond known. Ideally, the stereochemistry of these molecules should be completely defined before the unknown moments are determined. Much less satisfactorily, assumptions of the stereochemistry can be varied until three molecular moment equations are consistent. "Consistency" in this context means that no matter which two equations are solved for one unknown in terms of one of the others, the same equation results. This definition will be made clearer shortly. The problem with this method is that an infinite number of stereochemical possibilities exist and it is never certain that more than one combination of stereochemical assumptions will not give a consistent set of equations. In fact, it may not be possible to find one satisfactory combination without a great deal of trial and error. As a result, either an independent method of determining θ and the magnitudes of POC_{var} and P_{var} should be found, or the stereochemistry of these compounds should be determined by some other means. Some progress in the determination of the stereochemistry will be described later, but no attempt has been made to implement the first suggestion.

Expressions for the molecular moments of CI, structures (i) and (ii) ($R = OCH_3$, Table 7) and XCVII(CH_3) in terms of θ and the magnitudes of POC_{var} and P_{var} have been written and analyzed to test the possibility that rotation is free in CI and monocyclic trialkyl phosphites like XXXIV, XXXII A and XXXII B. The expression for the bicyclic phosphite is given in Equation 12 along with the necessary structural assumptions.

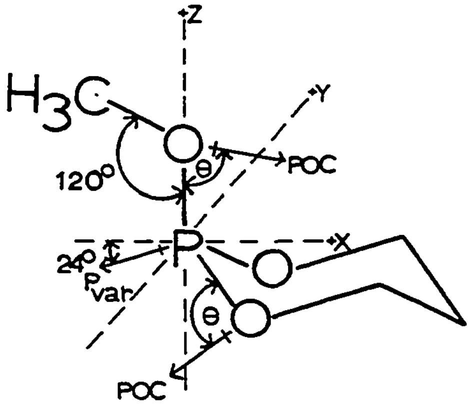


$$4.15 = P_{var} + 3(POC)\cos(\theta-65) \qquad (12)$$

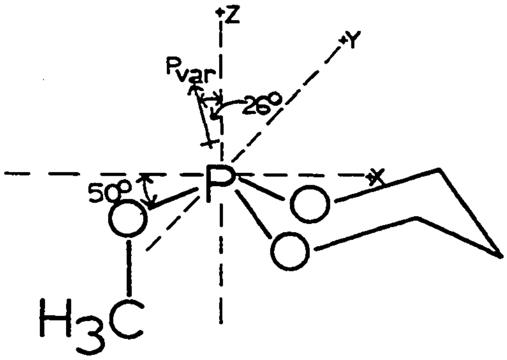
Similarly, Equations 13-15 correspond to trimethylphosphite, structure (i) and structure (ii), respectively. These last three equations were derived in the same way as those of the moments in Table 7. The coordinate system was oriented as previously shown (p. 85) for structure (i) but was



$$(1.83)^2 = [P_{var} + 3(POC)\cos\theta\cos 66]^2 + 3[(POC)\sin\theta]^2 \qquad (13)$$



$$\begin{aligned}(2.93)^2 = {} & [-P_{var}\cos 24^\circ + POC(-1.13\cos\theta - 1.61\sin\theta)]^2 \\ & + [-P_{var}\sin 24^\circ - POC\cos\theta + POC(.414\cos\theta - .724\sin\theta)]^2 \\ & + [POC\sin\theta]^2 \end{aligned} \qquad (14)$$



$$(3.6)^2 = [-P_{var}\sin 26^\circ + POC\cos\theta\cos 50^\circ + POC(-1.13\cos\theta - 1.61\sin\theta)]^2 + [P_{var}\cos 26^\circ + POC\cos\theta\sin 50^\circ + POC(.414\cos\theta - .724\sin\theta)]^2 + [POC\sin\theta]^2 \qquad (15)$$

rotated 26° clockwise for structure (ii). The molecular moment of 2.93 D for structure (i) is an average of those of XXXIV(2.82 D) and XXXII A (3.04 D). The ring atomic unit cell positions given in reference 33 for L were used to determine the x and z components of the ring POC vectors. The ring of L was first translated and rotated so that the coordinate system was oriented as described above. Then equations were written for one of the ring POC planes and cosines of two angles defined by the P-O bond and adjacent POC vector and the POC vector and adjacent O-C bond. These equations were combined and solved for the direction cosines of the POC vector and finally for the x and z components in terms of θ and the magnitude of POC. If Equation 12 is solved for P_{var} in terms of θ and POC and this expression for P_{var} substituted in Equation 13, POC can be expressed in terms of θ as $(1.09 + 0.400i)/\sin\theta$. This result was checked by substituting it into Equation 13, solving for P_{var} in terms of θ, substituting the expressions for POC and P_{var} into Equation 12 and finding an equality. The above procedure was followed with Equations 12 and 14 and 12 and 15 and POC was found to be $(2.08 \pm 0.450i)/\sin\theta$ and $(0.987 \pm .770)/\sin\theta$, respectively. Thus, the three pairs of equations do not yield the same value of POC as a function of θ and, in this sense, the four equations are not consistent. That is, the assumptions made to derive one or more of the equations are not all correct. The pairs of Equations 12 and 13 and 12 and 14 yield imaginary values of POC, due most likely to restricted rotation of the methoxyl groups in CI and structure (i). Even if the C-H moments in XCVII(CH_3) and CI are assumed to be 0.4 D towards carbon instead of 0.0 D, combination of the modified Equations 12 and 13 gives a POC magnitude of $(0.730 \pm 0.396i)/\sin\theta$, still imaginary. A real value of POC is obtained when Equations 12 and 15 are combined but this is not proof that the methoxyl group in structure (ii) is freely rotating. If Equations 13 and 14 are written assuming that the methoxyl groups are all fixed with a P_{var}, O_{var} dihedral angle of 180°, Equations 16 and 17, respectively, result.

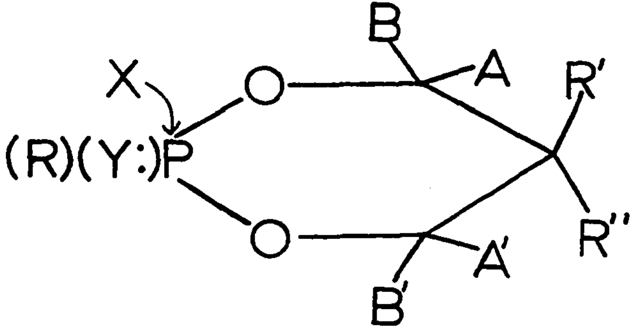
$$\pm 1.83 = 3\cos(114-\theta)\ \mathrm{POC}\text{-}P_{var} \qquad (16)$$

$$(2.93)^2 = [-P_{var}\cos 24^\circ + \mathrm{POC}\sin\theta - \mathrm{POC}(1.13\cos\theta + 1.61\sin\theta)]^2 + [-P_{var}\sin 24 - \mathrm{POC}\cos\theta + \mathrm{POC}(.414\cos\theta - .724\sin\theta)]^2 \qquad (17)$$

Equations 12 and 16 and Equations 12 and 17 can then be combined to give values of POC of $1.09/\sin\theta$ or $0.425/\sin\theta$ and $(2.12 \pm 1.46)/\sin\theta$, respectively. These solutions are also real but are not the same for the two pairs. This illustrates the difficulty mentioned earlier of finding a consistent set of equations which might possibly be indicative of the correct molecular stereochemistries. It may be necessary to express one or more of the molecular moments as a weighted average of those of several conformers.

B. Methods of Analysis of NMR Spectra

The purpose of this section is to describe the methods of analysis of the commonly-encountered nmr spectra. The primary reference is the book by Pople, et al. (138, pp. 132-51). Deceptively simple spectra are discussed by Abraham and Bernstein (139). The phosphorus nucleus and the OCH_2 protons of a chair or boat conformation of a 1-phospha-2, 6-dioxacyclohexane comprise an $AA'BB'X$ spin system. The nuclei are labeled in the structure below. In the following analysis, nuclei of R, R', R'' and Y are assumed to couple negligibly to the methylene protons. In practice, nuclei in R and Y apparently do not couple and any other couplings greater than a few tenths of a Hertz can be eliminated by saturating the responsible nuclei in R' and R''. The difference in chemical shift of X and any of A, A', B and B' is termed ν_{AX} (frequency units), for example, and is very great compared to any spin-spin couplings between X and the other nuclei. The A and A' nuclei have the same chemical shift relative to tetramethylsilane, $\nu_A = \nu_{A'}$, as do also the B and B' nuclei. This is due to the apparent molecular plane of symmetry passing through P_1, C_4 and the exocyclic bonds to these atoms. The A and A' nuclei, or B and B', are different because A and A' do not generally couple equally to B and B', i.e., $J_{AB} \neq J_{A'B}$ and $J_{AB'} \neq J_{A'B'}$.



The AA′BB′ part of the spectrum can be analyzed as the AB part of an ABX spectrum if all couplings between primed and unprimed nuclei, e.g., $J_{AA'}$ and $J_{AB'}$, are small relative to J_{AB} (= $J_{A'B'}$) and ν_{AB}. In this case, the AB pair does not couple appreciably to the A′B′ pair and both give the same spectrum. The ABX approximation has been used in the analysis of many of the spectra. The X parts of the spectra usually were not obtained or were poorly resolved; therefore, they are not discussed in this section. The AB part of an ABX spectrum contains eight lines and is illustrated in Figure 1. The spacings between lines 1, 3; 2, 4; 5, 7; and 6, 8 are equal to J_{AB}. The parameters $2\,D_{\pm}$ and $2\,\phi_{\pm}$ are defined below. Lines 1, 3, 5, 7 and 2, 4, 6, 8 comprise two

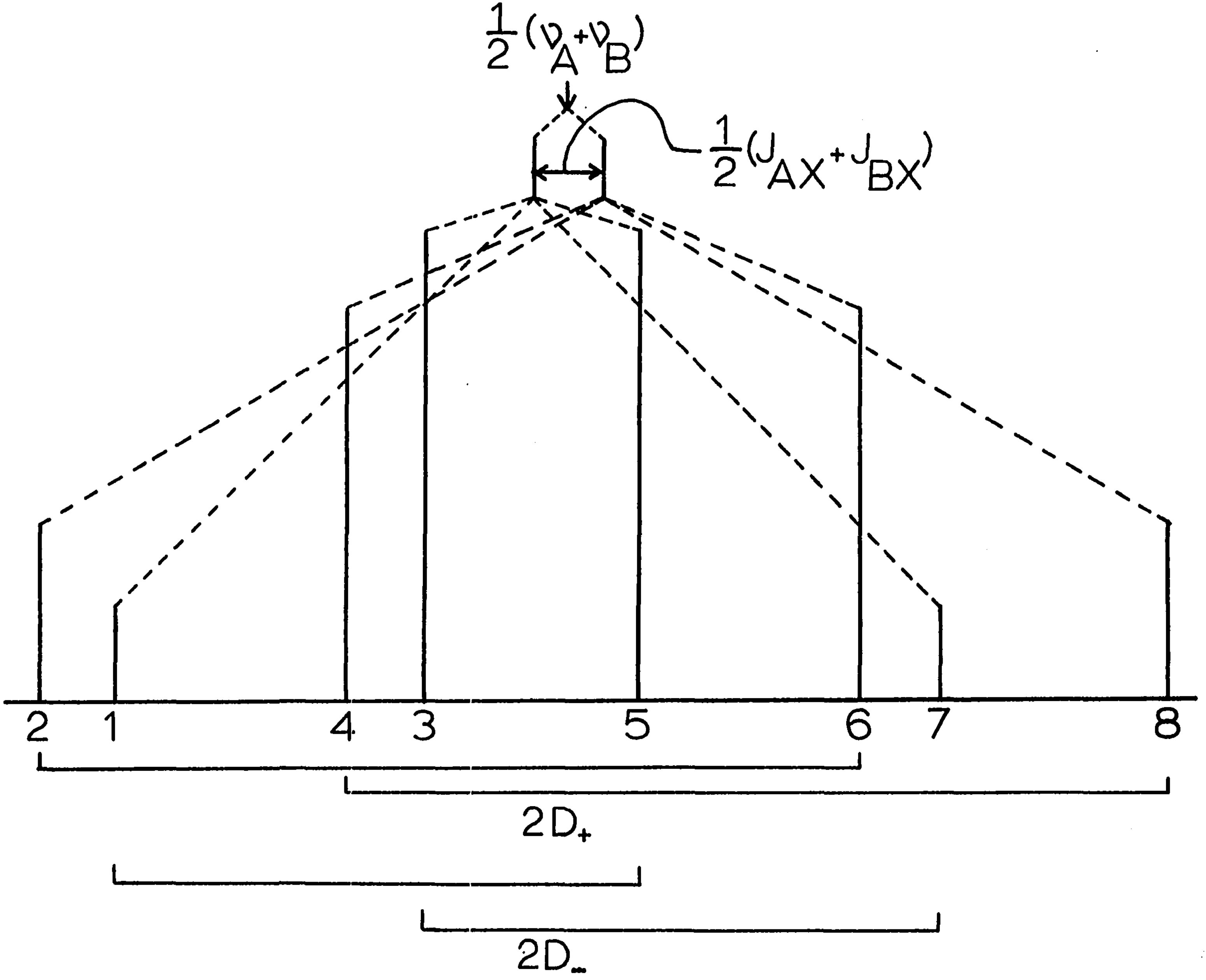
$$2D_{\pm} = \left\{[\nu_{AB} \pm \tfrac{1}{2}\,(J_{AX} - J_{BX})]^2 + J_{AB}{}^2\right\}^{\frac{1}{2}}$$

$$\cos 2\phi_{\pm} = [\nu_{AB} \pm \tfrac{1}{2}\,(J_{AX} - J_{BX})]/(2\,D_{\pm})$$

$$\sin 2\phi_{\pm} = J_{AB}\,/\,(2\,D_{\pm})$$

symmetrical but not generally identical quartets. The separation of the quartet centers is $\frac{1}{2}\,(J_{AX} + J_{BX})$ and the average of the centers is $\frac{1}{2}\,(\nu_A + \nu_B)$. When lines of each of the sets 2, 1, 7, 8 and 4, 3, 5, 6 are apparently of the same intensity, two quartet assignments are possible. In these cases, the spectral parameters were determined for both assignments. In some instances, the correct assignment was determined by noting which pair of values of $2D_+$ and $2D_-$ could be used to calculate the AB part of the spectrum observed when a different external field was applied. In other instances, unreasonable values of J_{AX} and J_{BX} were obtained from

Figure 1. The AB part of an ABX spectrum


$\frac{1}{2}(\nu_A+\nu_B)$
$\frac{1}{2}(J_{AX}+J_{BX})$
2
1
4
3
5
6
7
8
$2D_+$
$2D_-$

one quartet assignment, i.e., one or both were very large or they were of opposite sign (see Section IV. J.1). For each quartet assignment, $2D_+$ and $2D_-$ cannot be distinguished and only the magnitudes of (D_+, D_-), $(J_{AX} + J_{BX})$, J_{AB}, and $(\nu_A + \nu_B)$ can be determined. Two magnitudes of $\nu_{AB} \pm \frac{1}{2}(J_{AX} - J_{BX})$, x and y, can be found from J_{AB}, D_+ and D_-. Then, two sets of magnitudes of ν_{AB} and $(J_{AX} - J_{BX})$ can be deduced as follows:

$$\nu_{AB} = \frac{1}{2}(x + y) \qquad J_{AX} - J_{BX} = x - y$$

$$\nu_{AB} = \frac{1}{2}(x - y) \qquad J_{AX} - J_{BX} = x + y$$

The correct set was determined by using the magnitudes of $(J_{AX} - J_{BX})$ and $(J_{AX} + J_{BX})$ to calculate two pairs of J_{AX} and J_{BX}. Almost always, one pair was unreasonable by the criteria noted above. In a few instances, the correct pair was determined by noting which could be used to calculate the spectrum observed at another external field.

Examples of two deceptively-simple methylene proton resonances are shown in Figure 2. In these spectra, one or both of the quartets have apparently collapsed to a single line. The outer lines of each collapsed quartet seemingly have zero intensity. In general, the separation of the innner lines of a quartet is:

$$W_{\pm} = J_{AB} - 2D_{\pm} = J_{AB} - \left\{\left[\nu_{AB} \pm \frac{1}{2}(J_{AX} - J_{BX})\right]^2 + J_{AB}{}^2\right\}^{\frac{1}{2}} .$$

If $\nu_{AB} \pm \frac{1}{2}(J_{AX} - J_{BX}) = Y_{\pm}$, then the above equation can be rearranged to give:

$$Y_{\pm} = \left[W_{\pm}{}^2 \pm 2W_{\pm} J_{AB}\right]^{\frac{1}{2}} .$$

Figure 2. Two deceptively-simple methylene ^{1}H nmr resonances

a. The expanded methylene resonance of 1-hydro-1-oxo-4,4-dimethyl-1-phospha-2,6-dioxacyclohexane (XXXIV′) in C_6H_6 (1.1M). The intense apparent singlet at the left has been compressed by insertion of the top portion in the lower portion.

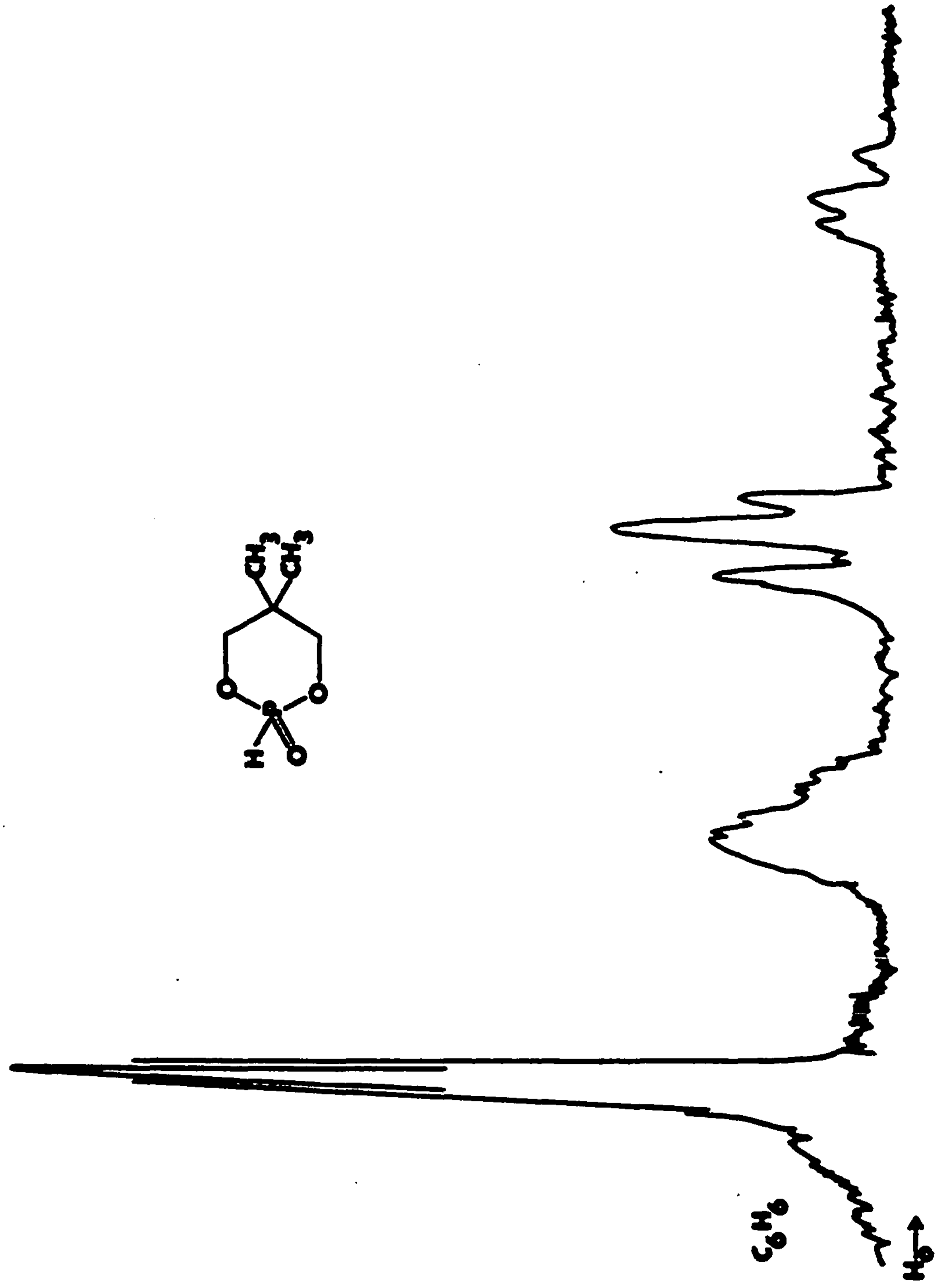
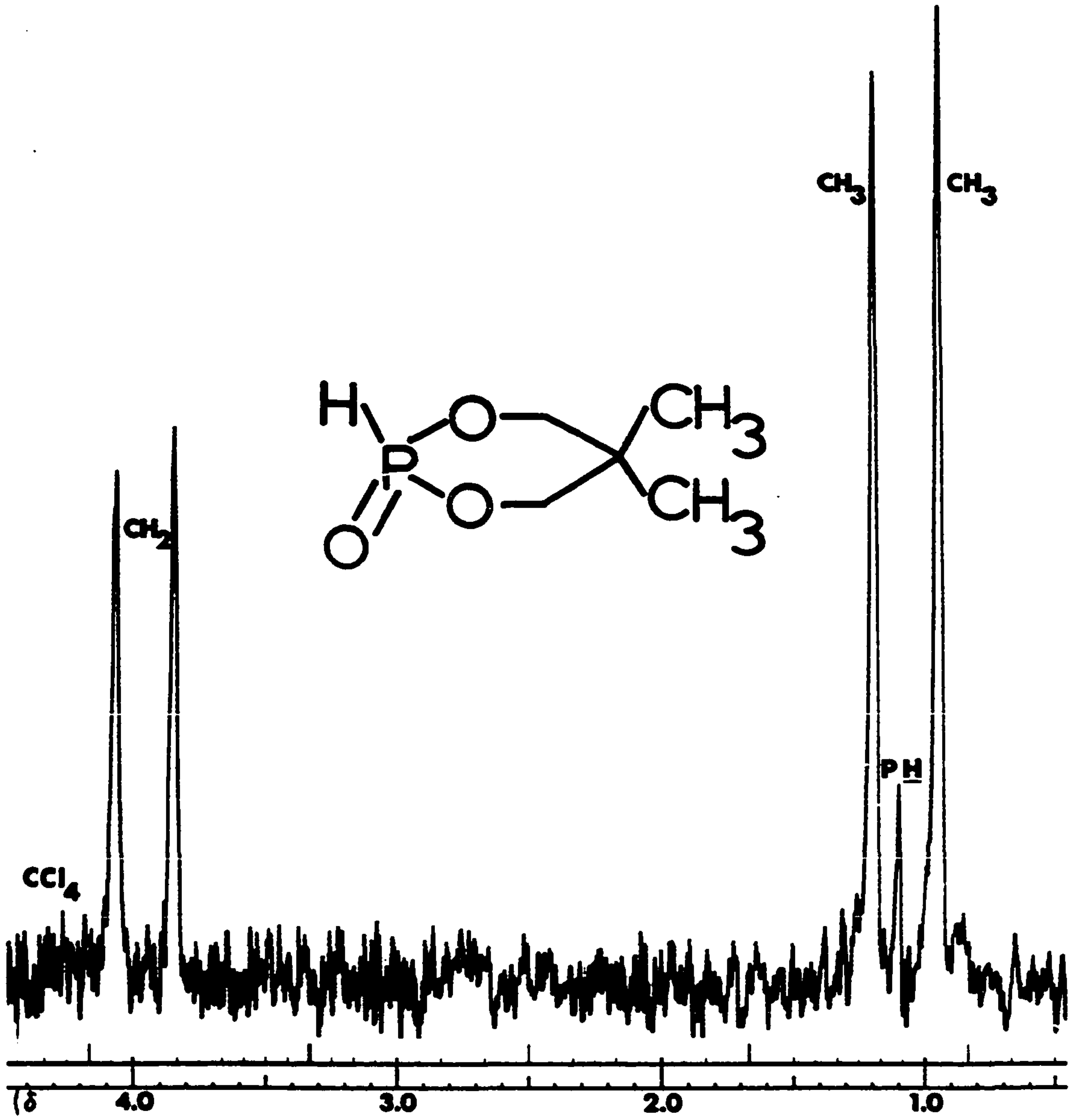

CH3
CH3
O
O
P
H
O
C6H6
H0

Figure 2 (continued)

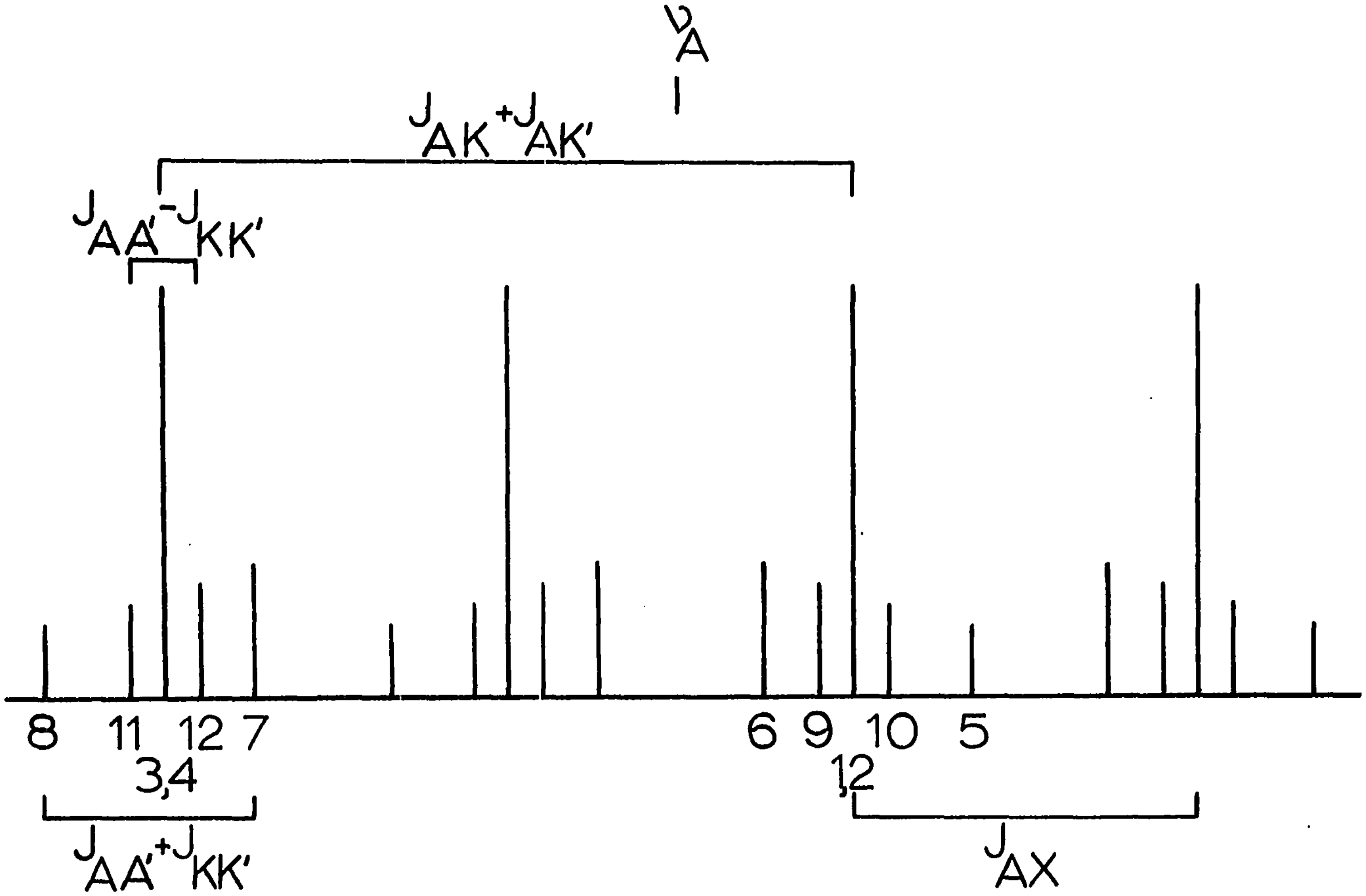
b. The spectrum of XXXIV$'$ in CCl_4 (0.070 M). The methylene (CH_2) resonance consists of two apparently-single lines. The low-field half of the PH-proton resonance is not shown.


H
P
O
O
O
CH3
CH3
CH3
CH3
CH2
CCl4
PH
δ
4.0
3.0
2.0
1.0

The sum or difference applies to both Y_+ and Y_-, but, in the cases to be dealt with here, one root is imaginary. If W_+ and W_- were exactly zero, then $\nu_{AB} = \frac{1}{2}(J_{AX} - J_{BX}) = 0$ and two collapsed quartets would be observed. If W_+ or W_- were exactly zero, then Y_+ or Y_-, respectively, equals zero and one collapsed quartet would be observed. However, the ability to determine whether a quartet has collapsed is dependent on the resolving power of the spectrometer. In practice, ν_A, ν_B, J_{AX} and J_{BX} have large uncertainties when one of these deceptively simple spectra is encountered. For example, if in the two-line case, i.e., two collapsed quartets, $W_{\pm} = 0.3$ Hz, $J_{AB} = -11$ and ν_{AB} is arbitrarily made zero, then $Y_{\pm} = 2.6$ and $(J_{AX} - J_{BX}) = 5.2$. The intensity of the outer lines of the quartets would be 1.3% of the intensity of the inner lines. The assumption that the quartets are completely collapsed would lead to $(J_{AX} - J_{BX}) = 0$. If, in the five-line case, i.e., one apparently collapsed quartet, $W_- = 0.3$, $J_{AB} = -11$, $\nu_{AB} = 10$ and $J_{AX} + J_{BX} = 24$, then $Y_- = 2.6$, $J_{AX} = 19.4$ and $J_{BX} = 4.6$. The intensity of the outer lines of the "collapsed" quartet would be the same as in the previous case. If W_- had been zero, then $J_{AX} = 22.0$ and $J_{BX} = 2.0$. Since the quality of many of the spectra does not allow distinction of lines closer than about 0.5 Hz, the determination of J_{AX} and J_{BX} must be considered highly uncertain when a seemingly collapsed quartet is encountered. Abraham and Bernstein (139) have pointed out that, under circumstances similar to those encountered here, the width at half height ($W_{\frac{1}{2}}$) of the component lines of the quartet will limit the certainty of the analysis. This half-width was seldom less than 1 Hz. If the central line of a seemingly collapsed quartet had $W_{\frac{1}{2}} = 1.3$ and the components of a second noncollapsed quartet in the same spectrum had $W_{\frac{1}{2}} = 1.0$, then W should be 0.3 and an approximate analysis should be possible. Unfortunately, the uncertainty in the half-width difference is probably no less than 0.2. Also uncertain is the effect of long-range couplings on the width of the apparent single line and these interactions have not been taken into account in this ABX analysis. The values of J_{AX} and J_{BX} can be determined if a change of conditions changes ν_{AB} but not J_{AX} and J_{BX}. However, the latter condition does not hold for many of the substituted 1-oxo-1-phospha-2,6-dioxacyclohexanes. Therefore, $(J_{AX} + J_{BX})$, but not J_{AX} and J_{BX} separately, can be accurately found from one of the above deceptively-simple spectra.

Many of the methylene proton resonances contain lines in addition to those expected for an ABX spin system; examples appear in Figures 2, 4 and 9. These are due to long-range HCCCH couplings. If ν_{AB} is at least several times greater than J_{AB}, the spectrum can be analyzed using an $AA'KK'X$ approximation. The AA' part of an $AA'KK'X$ spectrum is shown in Figure 3. For this spectrum: $J_{AA'} = 1$, $J_{KK'} = 2$, $J_{AK} = -10$, $J_{AX} = 5$, and $J_{AK'} = 0$. The AA' and KK' parts are symmetrical about their centers. The only difference between the two parts is the spacing J_{AX} and J_{KX}. Two pairs of identical sets of peaks can be found in each part. The two sets in each pair are separated by J_{AX} or J_{KX}. The splittings $(J_{AA'} + J_{KK'})$ and $(J_{AA'} - J_{KK'})$ cannot be distinguished from the spectrum. The separations 5-7, 6-8 are $[(J_{AA'} + J_{KK'})^2 + (J_{AK} - J_{AK'})^2]^{\frac{1}{2}}$ and 9-11, 10-12 are $[(J_{AA'} - J_{KK'})^2 + (J_{AK} - J_{AK'})^2]^{\frac{1}{2}}$. Thus, from the line positions in the $AA'KK'$ part, the

Figure 3. The AA$'$ part of an AA$'$KK$'$X spectrum


ν_A
$J_{AK}+J_{AK'}$
$J_{AA'}-J_{KK'}$
8
11
3,4
12
7
6
9
1,2
10
5
$J_{AA'}+J_{KK'}$
J_{AX}

magnitudes of all the coupling constants can be determined. However, $J_{AA'}$ cannot be distinguished from $J_{KK'}$, nor J_{AK} from $J_{AK'}$. In the molecules that were studied, J_{AK} is expected to be much larger than $J_{AK'}$.

As ν_{AK}/J_{AK} decreases, the spectrum becomes the AA′BB′X type and is extremely difficult to analyze for all of the parameters by hand calculations. Since the long-range couplings are not expected to be greater than 3 Hz many spectra of this type were analyzed using the ABX approximation. The extra lines could usually be identified and were ignored. In these cases, the long-range couplings could, of course, not be determined. A few of these same spectra were analyzed as AA′BB′X spectra using the LAOCN 3 iterative least-squares computer program of Castellano, et al. (140). Trial coupling constants and chemical shifts were first used to calculate line positions. Then, the parameters were varied iteratively until the calculated line positions converged as closely as possible to those observed. The differences in the parameters as determined by the two methods were less than 1 Hz.

The spectrum of CV is an AA′BB′MX type and was analyzed with the aid of LAOCN 3. Discussion of the analysis of this spectrum, others not frequently encountered and those of the types discussed above appear throughout the remainder of this dissertation.

C. Description and Analysis of ^{1}H NMR Spectra of 1-R-1-phospha-2,6-dioxacyclohexanes

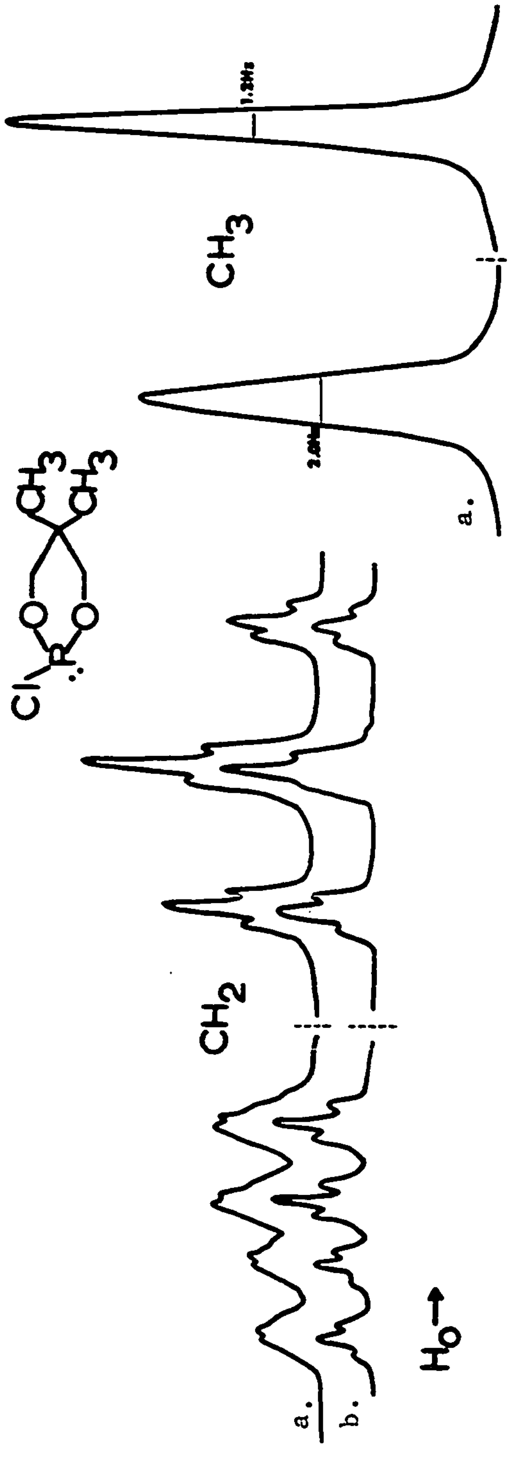
1. 1-R-4,4-dimethyl-1-phospha-2,6-dioxacyclohexanes

The ^{1}H nmr spectra of the compounds in Table 2 having $R_5 = R_6 = CH_3$ (except XXXV) have several common features which are exemplified in Figure 4a, the spectrum of the chloro derivative XXXVIII. In all cases,

Figure 4. The ^1H nmr spectrum of 1-chloro-4,4-dimethyl-1-phospha-2,6-dioxacyclohexane

a. The ring-methylene proton resonance and the two 4-methyl resonances. The widths at half height ($W_{1/2}$) are shown for the expanded latter two resonances.

b. The ring-methlene proton resonance when the protons giving the broader methyl resonance are decoupled.


Cl
P
O
O
CH3
CH3
CH3
1.2Hz
2.0Hz
a.
CH2
a.
b.
Ho→

the two methyl resonances are separated by at least 0.42 ppm and the one at lower field is broader. The methylene resonance consisting of two non-overlapping halves appears at still lower fields. The low-field half is distinguished by its broadness relative to the high-field half which consists of sharp unsymmetrical triplets. When the protons associated with the broader methyl resonance are decoupled from the methylene protons a spectrum similar to that shown in Figure 4b results. The sharp unsymmetrical triplets are now evident in both halves of the methylene resonance. Decoupling of both methyl groups gives a methylene resonance essentially the same as in Figure 4b.

Gagnaire, et al. recently reported the analyses of the ^{1}H nmr spectra of XXIV, XXIX, XXXV, XXXVI, XXXVIII and XLVI (29, 30). For XXIV, XXIX, XXXVI and XXXVIII, irradiation of the broader methyl proton resonance led to a methylene resonance which was treated as the superposition of two subspectra, one corresponding to the α spin state of phosphorus and the other to the β spin state. Because the chemical shift between the high-field AA' and low-field KK' methylene protons is large relative to the couplings of the protons to phosphorus, these $AA'KK'$ subspectra are practically identical and, as a result, the relative signs of $J(POCH_A)$ and $J(POCH_K)$ could not be determined; however, their magnitudes could be found (Figure 3). Also, the magnitudes of $J(H_AH_{A'}) + J(H_KH_{K'})$ (apparently equal to $J(H_AH_{A'}) - J(H_KH_{K'})$) and $J(H_AH_K) + J(H_AH_{K'})$ could be determined (Figure 3). The magnitudes of $J(H_AH_{A'})$ and $J(H_KH_{K'})$ could not be determined with much accuracy because the components of the triplets (Figure 4b) were spaced too closely. However, examination of the ^{13}C satellites from ^{13}C in natural abundance revealed that $J(H_KH_{K'})$, $J(H_AH_{K'})$ and $J(H_{A'}H_K)$

were practically zero. The spectra of XXXV and XLVI differ from the others because the chemical shift between AA$'$ and KK$'$ is considerably smaller. Comparison of spectra at 100 and 60 MHz allowed them to conclude that the coupling constants between the methylene protons and phosphorus are of the same sign. In addition, the similarity of the magnitude of the coupling constants of the others to those of XLVI led them to assume that all are of the same sign.

The parameters found by Gagnaire, et al. refer either to solutions in CS_2 (XLVI) or at infinite dilution in CCl_4. Spectra of XXV (neat), XXXVIII (neat) and XLVI (C_6H_6) have been obtained with the methyl protons decoupled and have been analyzed as AA$'$BB$'$X spectra with the aid of the LAOCN 3 program to determine if the parameters differ from those found under different conditions.[2] Final parameters, degree of convergence and other pertinent information have been collected in Table 11; also included are results of spectral analysis of other compounds that will be discussed later. The accuracy of the magnitudes of $J(H_AH_{A'})$ and $J(H_BH_{B'})$ may not be very great because they were determined assuming that the outer components of the triplets (Figure 4b) are single lines and, although this appears to be the case, the small intratriplet spacing of about 1.5 Hz makes any splitting difficult to observe. The good agreement between calculated triplet line-intensity ratios and observed line-height ratios, e.g., 3% error for XXV, suggests that the outer lines are single. The larger long-range coupling J(HCCCH) is

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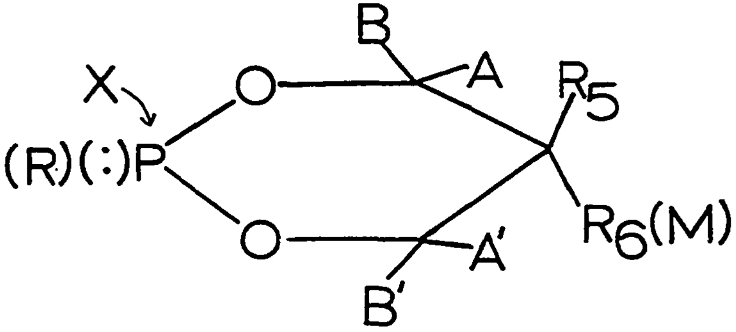
[2] Analysis of the spectra of XXV and XXXVIII was performed by Bertrand (99d).

Table 11. Results of spectral analysis of some 1-R-1-phospha-2,6-dioxacyclohexanes and 2,6,7-trioxa-1-phosphabicyclo [2.2.1] heptane (CV)



		Chemical Shifts, Hz[a]			Coupling Constants, Hz[a]			
		δ_A	δ_B		J_{AB}[c]	J_{AX}[d]	J_{BX}[d]	
Cmpd.	Solvent	$\delta_{A'}$	$\delta_{B'}$	$J_{AA'}$[b]	$J_{A'B'}$	$J_{A'X}$	$J_{B'X}$	J_{MX}[d]
XXV[h]	----[i]	189.19 (0.02)	249.42 (0.02)	2.89 (0.03)	-10.46 (0.03)	10.68 (0.04)	3.00 (0.04)	
XXX A[j]	CDCl$_3$[k]	232	254	< 2.0	-10.6	11.0	2.89	
XXX B[j]	CDCl$_3$[k]	235	264	< 2.0	-11.6	8.40	5.03	
XXXVIII[h]	----[i]	211.59 (0.015)	257.48 (0.015)	2.79 (0.025)	-10.80 (0.02)	11.16 (0.03)	5.73 (0.03)	

---

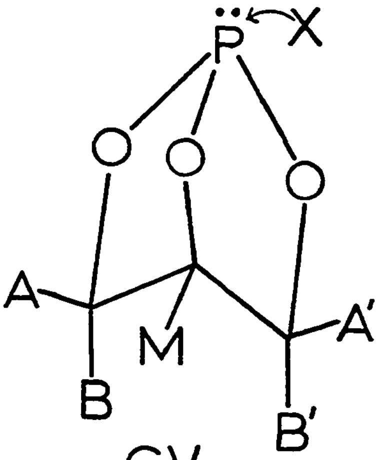
[a] Number in parentheses is probable error in Hz. Probable errors for XXX A, B and XL A < 1.0 Hz (25).

[b] Assumed positive.

[c] Assumed negative (141, pp. 172-4).

[d] Assumed positive (31).

[e] Assumed positive (141, pp. 172-4). (Footnotes continued next page)



CV

Coupling Constants, Hz[a]		RMS Error	Max Error[f]	Peaks Observed[g]	Transitions Calcd.	Transitions Used For Iteration
J_{AM}^{e}	J_{BM}^{e}	Hz.				
$J_{A'M}$	$J_{B'M}$					
		0.144	0.29	19	58	58
3.71	11.9					
4.90	4.65					
		0.094	0.27	21	48	48

Table 11 (continued)

		Chemical Shifts, Hz[a]			Coupling Constants, Hz[a]			
		δ_A	δ_B		J_{AB}[c]	J_{AX}[d]	J_{BX}[d]	
Cmpd.	Solvent	$\delta_{A'}$	$\delta_{B'}$	$J_{AA'}$[b]	$J_{A'B'}$	$J_{A'X}$	$J_{B'X}$	J_{MX}[d]
XL A[j]	$CDCl_3$[k]	255	274	< 2.0	-10.9	11.3	5.24	
XLVI[h]	C_6H_6[i]	197.29 (0.02)	215.65 (0.02)	2.51 (0.04)	-10.59 (0.03)	10.02 (0.04)	2.85 (0.04)	
CV[l,m]	----[i]	211.63	225.66	3.40 (0.01)	-8.12 (0.01)	0.29 (0.015)	3.83 (0.014)	15.90 (0.015)
---[n]	CCl_4			±3.5	-8.2	0.4	3.8	15.7

(Footnotes continued from preceding page)

[f] Sweep width, Hz/cm: 0.37 for XXV and XXXVIII, 1.98 for XLVI and 0.27 (^1H) and 3.8 (^{31}P) for CV; one scan for each compound.

[g] Includes shoulders.

[h] $J_{AB'}$, $J_{A'B}$, $J_{BB'} < 0.15$.

[i] XLVI approximately 1.7M; all samples 27.5°C; Varian HR 60.

[j] $J_{AB'}$, $J_{A'B}$, $J_{BB'} < 2.0$Hz (25).

[k] Approximately 20% solution, 35°C (25).

[l] $J_{AB'} = J_{A'B} = 0.35$, $J_{BB'} = -0.25$.

[m] $\delta_M = 310.256$ (0.01).

[n] 100MHz spectrum; $J_{AB'} = J_{A'B} = 0.3$; $J_{BB'} = \pm 0.3$ (99a).

Coupling Constants, Hz^a						
J_{AM}^e $J_{A'M}$	J_{BM}^e $J_{B'M}$	RMS Error	Max Error^f	Peaks Observed^g	Transitions Calcd.	Transitions Used For Iteration
		Hz.				
3.01	11.1					
		0.120	0.32	22	48	44
3.34 (0.01)	0.16 (0.01)	0.061	0.24	65	128	121
3.2	0					

associated with the more shielded protons (AA′) on the basis of the ^{13}C satellite spectra interpreted by Gagnaire, et al. (29, 30). The magnitudes of $J(H_AX)$ and $J(H_BX)$ in Table 11 differ by no more than 0.4 Hz from those determined by Gagnaire, et al. (30)

The spectra of XXXVI (neat), XLIV (C_6H_6) and XLVII ($CDCl_3$, C_6H_6) were also analyzed. Since the chemical shifts between the methylene protons are about 0.72, 0.87, 0.70 and 0.83 ppm, respectively, analysis on the basis of an AA′KK′X spectrum should give parameters correct to within a few tenths Hz. The lack of spectra with the methyl protons decoupled increases the uncertainty of $J(H_KX)$ and bromide exchange broadens the resonance of XLIV. Approximate values of $J(H_AX)$ and $J(H_KX)$ for these compounds, the more accurate values for those discussed above, and others to be discussed later are given in Table 12.

2. 3,9-Dimethoxy-3,9-diphospha-2,4,8,10-tetraoxaspiro [5.5] undecane (CXVIII)

The ^1H nmr spectrum of CXVIII in benzene has been obtained at 60 and 100 MHz. The 100 MHz resonance of the methylene protons is shown in Figure 5. The spectrum can be divided into four parts, labeled AA′, GG′, MM′ and SS′, each of which corresponds to the resonance of two protons. The methoxyl proton resonance is at 3.20 ppm (J(POCH) = 12.0) and is not shown. The methylene protons and phosphorus nuclei can be labeled as shown below.

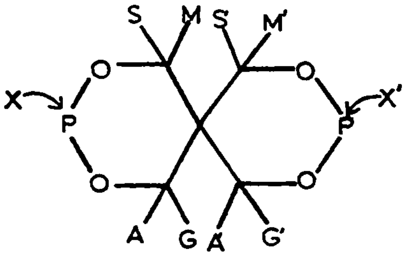


Table 12. Values of J(POCH) for some 1-R-1-phospha-2,6-dioxacyclohexanes

Compound	R	$J(PH_A)^a$	$J(PH_B)^a$	$J(PH_A)+J(PH_B)$	Solvent
XLVI	C_6H_5	10.2,10.0	3,2.85	13.2, 12.85	CS_2[b], C_6H_6
XXIX	OCH_3	10.8	2.8	13.6	CCl_4[b]
XXX A	OCH_3	10.98	2.89	13.87	$CDCl_3$[c]
XXX B	OCH_3	8.40	5.03	13.43	$CDCl_3$[c]
		9.40	3.90	13.30	CS_2[d]
XXXII A	OCH_3		2.1, 2.2±0.2		neat,[e] neat
XXXII B	OCH_3		3.1±0.2		C_6H_6
XXXI A	OCH_3	10.5±0.5	3.1±0.1	13.6±0.6	neat,$CDCl_3$
XXXI B	OCH_3	10.5±0.5	3.5±0.2	14.0±0.7	neat
XXV	$O\underline{t}C_4H_9$	10.7	3.0	13.7	neat
XXIV	OC_6H_5	10.8	2.8	13.6	CCl_4[b]
XLVII	SC_6H_5	9.5±0.2	4.3±0.3	13.8±.5	$CDCl_3$,C_6H_6
XXXVI	F	10.8, 10.9 ±0.3	2.8, 3.0 ±0.5	13.6, 13.9 ±0.8	CCl_4[b], neat
XXXVII A	F	10.5±0.5	3.5±0.2	14.0±0.7	neat
XXXVIII	Cl	10.8, 11.2	6, 5.7	16.8, 16.9	CCl_4[b], neat
XLA	Cl	11.28	5.24	16.52	$CDCl_3$[c]

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[a] $J(PH_A) = J(PH_{A'})$, $J(PH_B) = J(PH_{B'})$. AA′ protons resonate at higher field than BB′ protons.

[b] No uncertainties were given (30).

[c] Approximately 20% solution, 35°C (25).

[d] Approximately 20% solution, -62°C (25).

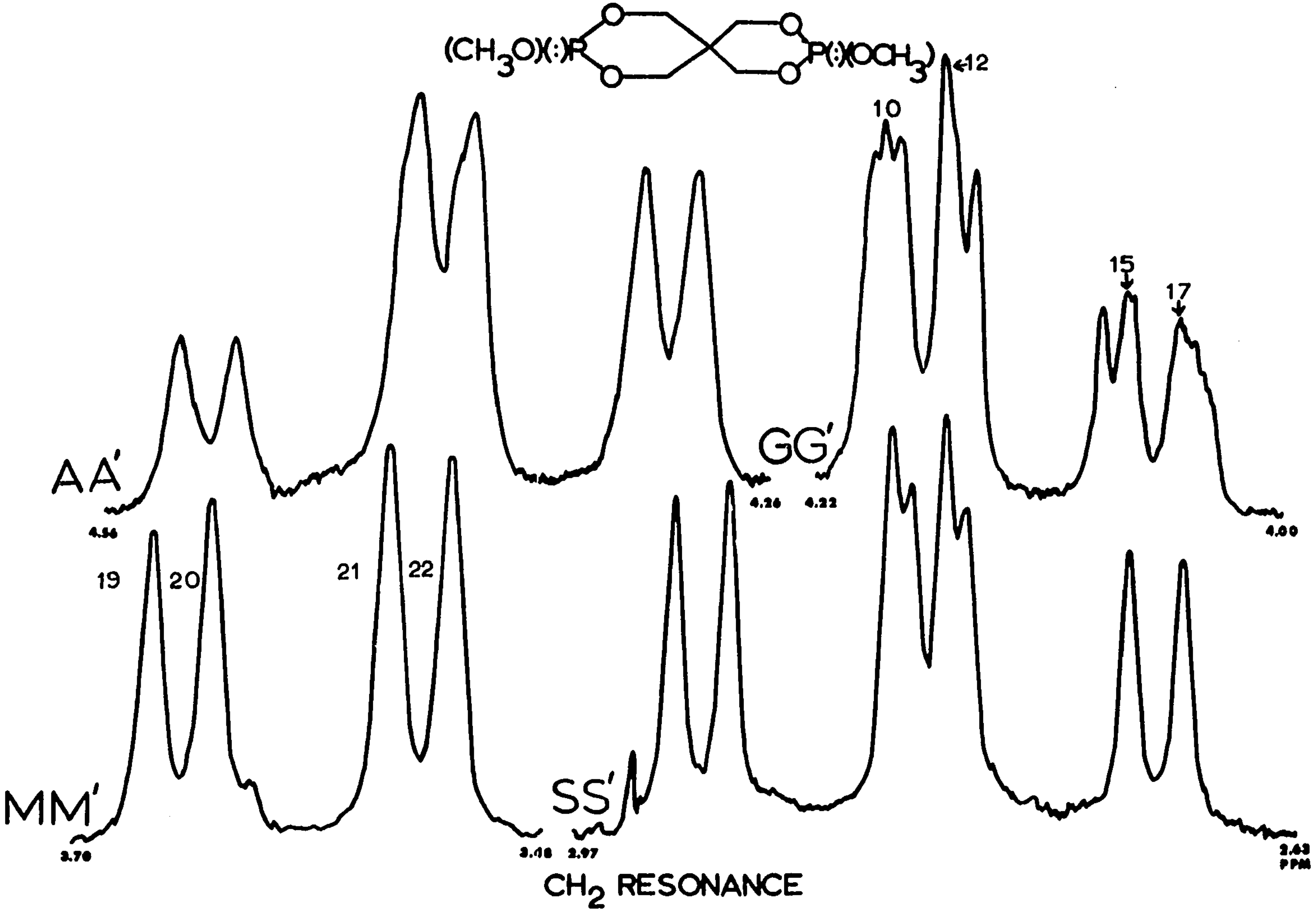
Table 12 (continued)

Compound	R	$J(PH_A)^a$	$J(PH_B)^a$	$J(PH_A)+J(PH_B)$	Solvent
XLI A	Cl		4.8		neat[e]
XXXIX A	Cl	10.5±0.5	5.7±0.2	16.2±0.7	neat, C_6H_6
XLV A	Br	10.5±0.5	6.5±0.5	17.0±1.0	C_6H_6
XLIV	Br	10.5±0.5	6.4±0.5	16.9±1.0	C_6H_6
XXXV	$N(CH_3)_2$	19.6	3.8	23.4	CCl_4[b]

[e] No uncertainties were given (31).

Figure 5. Ring-methlene ^{1}H nmr resonance of 3,9-dimethoxy-3,9-diphospha-2,4,8,10-tetraoxaspiro [5.5] undecane in C_6H_6 at 100 MHz

Each of the four parts of the resonance correponds to two protons. The spectrum amplitude is not the same for all of the parts.


(CH$_3$O)(:)P
P(:)(OCH$_3$)
12
10
15
17
AA'
GG'
4.56
4.26
4.22
4.00
19
20
21
22
MM'
SS'
3.70
3.18
2.97
2.63
PPM
CH$_2$ RESONANCE

In the following analysis, coupling constants and chemical shifts involving only nuclei represented by primed letters, e.g., $J(H_{A'}H_{M'})$, are assumed to be equal to those involving the corresponding unprimed nuclei, e.g., $J(H_AH_M)$, unless explicitly stated otherwise. The smaller splittings within the G group of lines are not presently understood; therefore, data from this resonance were not used to calculate any coupling constants. The intensity perturbations in the spectrum indicate that $J(H_AH_G)$ and $J(H_MH_S)$ are not negligible compared to $\nu(H_AH_G)$ and $\nu(H_MH_S)$, respectively. The splitting in common to groups A, M and S and qualitatively to group G is 11.1 ± 0.1 Hz, which is very similar to the geminal coupling constant found for the 1-R-4,4-dimethyl-1-phospha-2,6-dioxacyclohexanes. Therefore, (H_A, H_G) and (H_M, H_S) are concluded to be geminal pairs of protons. Splittings of 10.3 ± 0.1 Hz and 2.5 ± 0.1 Hz are found in groups A and S. These correspond closely to $J(POCH_A)$ and $J(H_ACCCH_A)$ for the phosphite XXV and are assigned as such. A splitting of 2.8 ± 0.1 Hz occurs in group M but not in group A or S. This is most likely due to coupling to phosphorus because the corresponding $J(POCH_B)$ in XXV is 3.00. This splitting should also occur in group G and does between lines 10 and 12 and lines 15 and 17. If this splitting were due to coupling between H_G and H_M, intensity perturbations would be expected in both G and M resonances because the ratio $\nu(H_GH_M):J(H_GH_M)$ would be about 18.5, less than that for the ethyl protons of ethanol, for which intensity perturbations are observed. The intensity difference between lines 19 and 20 is of opposite sign to that predicted and the difference between lines 21 and 22 is very small but of the correct sign. The perturbations are just as small in the 60 MHz spectrum. Therefore, the 2.8 Hz splitting is concluded to be J(POCH$_G$) = J(POCH$_M$). The couplings thus far discussed account for all the resolved lines in groups A, M and S. Anderson analyzed the spectrum of 3,9-di-t-butyl-2,4,8,10-tetraoxaspiro [5.5] undecane, $(CH_3)_3CCH(OCH_2)_2C(CH_2O)_2CHC(CH_3)_3$, and found an inter-ring coupling of 1.8 Hz between protons analogous to either G and G′ or M and M′ in CXVIII but not both (142). In the absence of this coupling, the A resonance would be a doublet (J(POCH$_A$)) of doublets (J(H$_A$H$_G$)) of doublets (J(H$_A$H$_S$)) and the G resonance would be a doublet (J(POCH$_G$)) of doublets (J(H$_A$H$_G$)). This inter-ring coupling would manifest itself as a tripleting of all the lines in the A and G resonances in a manner like that in Figure 4b. The fine structure observed in the G resonance is not apparent in the A resonance. However, the A lines are broader ($W_{1/2}$ = 1.7 Hz) than the M ($W_{1/2}$ = 1.3 Hz) or S(1.0 Hz) lines, indicating additional long-range coupling by the A and A′ protons. In the absence of a more detailed analysis of this spectrum, an explanation of these additional splittings in the G resonance cannot be given. A summary of the tentative spectral parameters is given below.

δH_A = 4.41 ppm δH_G = 4.11 ppm δH_M = 3.59 ppm δH_S = 2.80 ppm

$J(H_AH_G) = J(H_MH_S) = 11.1\pm0.1$ Hz $J(H_AP) = J(H_SP) = 10.3\pm0.1$ Hz

$J(H_MP) = J(H_GP) = 2.8\pm0.1$ Hz $J(H_AH_S) = 2.5\pm0.1$ Hz

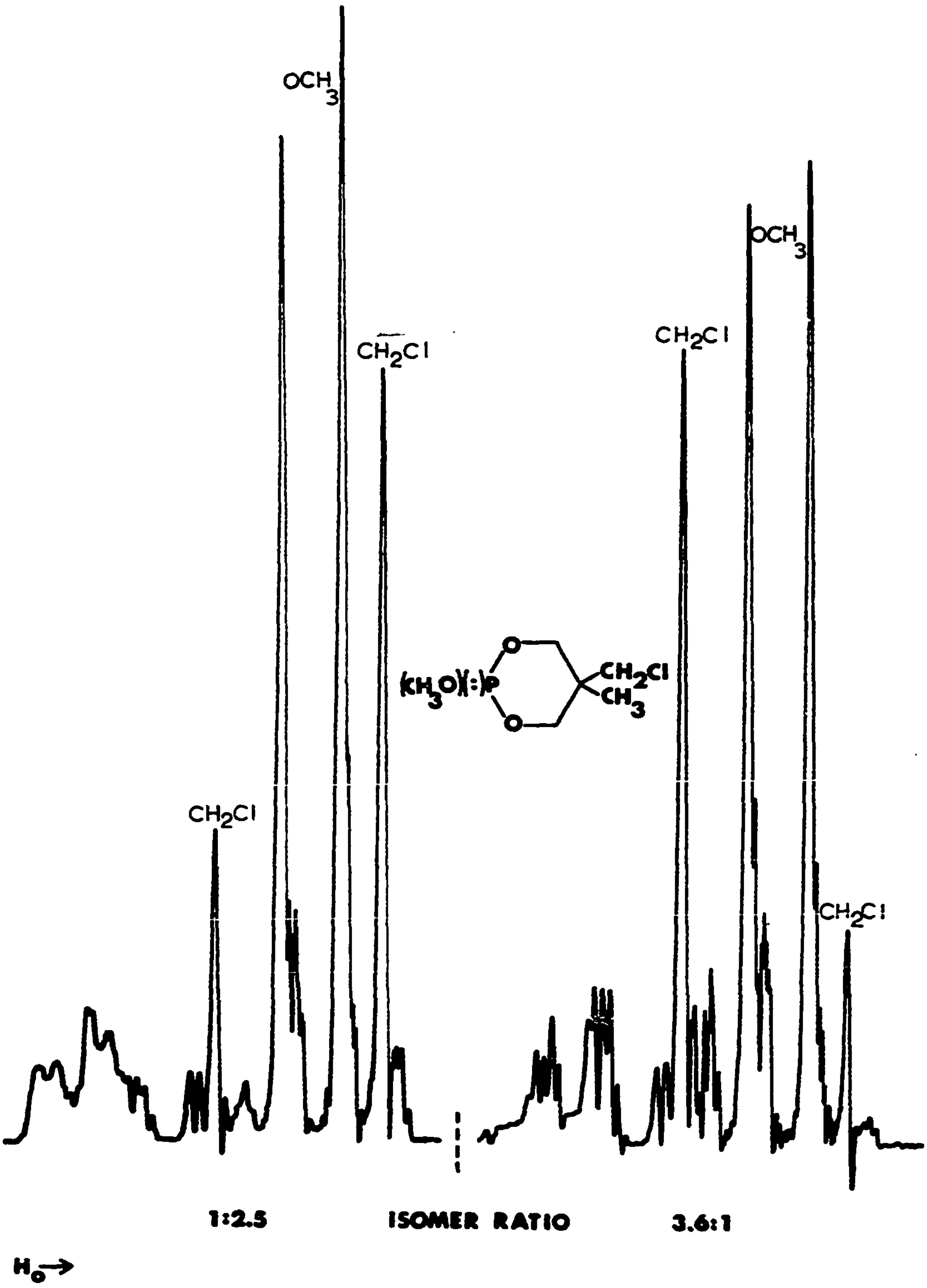
3. 1-R-4-methyl-4-chloromethyl-1-phospha-2,6-dioxacyclohexanes

XXXI A-B, XXXVII A-B, XXXIX A-B and XLV A-B are pairs of geometrical isomers with chloromethyl and methyl substituents at the 4-position in the rings (Table 2). No attempts were made to separate the A and B isomers of any of these pairs. As a result, overlaps of ring methylene resonances exist and usually only the features due to the dominant isomer are evident. The exception is the pair of phosphites XXXI A, B which has been made in varying ratios. The methyl resonances of these phosphites are at 0.761 ppm (XXXI A) and 1.28 ppm (XXXI B), the chloromethyl resonances are at 3.80 ppm (A) and 3.27 ppm (B) and the methylene resonances, by approximate $AA'KK'X$ analysis, are at 4.15 and 3.57 ppm (A) and 4.25 and 3.37 ppm (B). The methylene, chloromethyl and methoxyl resonances of A and B are shown in Figure 6. The left-hand spectrum corresponds to a 3.6:1.0 mixture and the right-hand spectrum to a 1.0:2.5. mixture of A:B. The observable part of the high-field half of the methylene resonance of both A and B consists of sharp triplets (J(POCH) = 10.5 ± 0.5 Hz) as in Figure 4a but the chemical shifts are uncertain (± 1 Hz) because of overlap with the sharp methoxyl doublet at 3.48 ppm ($J(POCH_3)$ = 11.9 Hz). The low-field half of the methylene resonance for B consists of a doublet of doublets of unresolved multiplets (J(POCH) = 3.5 ± 0.2), reminiscent of those in Figure 4a, but that for A consists of sharp lines (J(POCH) = 3.1 ± 0.1 Hz). Expansion of the methyl resonances ($CDCl_3$ solution) exposes a peak with $W_{1/2}$ = 1.02 Hz for A and a triplet ($J(HCCCH_3)$ = 0.7 Hz) with $W_{1/2}$ = 1.80 Hz for B.

The spectral features of the major fluoro isomer XXXVII A are qualitatively like those of XXXI A. The methyl resonances of XXXVII A and B are at 0.82 and 1.33 ppm and the chloromethyl resonances are at 3.79 and 3.26 ppm. The high-field half of the methylene resonance of A is centered at 3.71 ppm (J(POCH) = 10.5 ± 0.5 Hz) and the low-field half at

Figure 6. Partial ^{1}H nmr spectra of mixtures of <u>cis</u> and <u>trans</u>-1-methoxy-4-methyl-4-chloromethyl-1-phospha-2,6-dioxacyclohexane

The left- and right-hand spectra correspond to the methoxyl, chloromethyl and ring methylene resonances for 1:2.5 and 3.6:1 isomer ratios, respectively.


OCH3
CH2Cl
CH2Cl
(CH3O)(:)P
CH2Cl
CH3
CH2Cl
OCH3
CH2Cl
1:2.5
ISOMER RATIO
3.6:1
Ho→

4.17 ppm (J(POCH) = 3.5 ± 0.2 Hz). Estimates of the corresponding centers for B, assuming the coupling constants for A, are 3.52 and 4.32 ppm.

The spectral features of the chloro isomers XXXIX A, B are broadened somewhat by an exchange phenomenon to be discussed later. The methyl resonances of A and B are at 0.87 and 1.33 ppm and the chloromethyl resonances are at 3.76 and 3.29 ppm. The two halves of the methylene resonance of A are centered at 3.84 ppm (J(POCH) = 10-11 Hz) and 4.35 ppm (J(POCH) = 5.5 - 6.0 Hz) but those of the B isomer cannot be located accurately.

The spectral features of the bromo isomers XLV A, B are very much broadened and the two methyl, two chloromethyl, etc. resonances cannot be distinguished. Estimates of J(POCH) for the A isomer of 10.5 ± 0.5 Hz (high-field) and 6.5 ± 0.5 Hz (low-field) can be made from a dilute benzene solution spectrum.

4. 1-R-3,5-dimethyl-1-phospha-2,6-dioxacyclohexanes

Spectra of XXXII A and mixtures of XXXII A and B, derived from meso-2,4-pentanediol, were obtained with and without benzene as a solvent. In the absence of benzene, the methine resonance (R_1, R_4 - Table 2) for XXXII A is a multiplet (0.58 ppm wide) 0.35 ppm downfield from the corresponding resonance for XXXII B (0.58 ppm wide) that is centered at 4.15 ppm. The methoxyl proton chemical shifts at about 3.43 ppm are distinct but differ by less than 0.017 ppm, with that for XXXII B at higher field. These protons exhibit couplings to phosphorus of 11.8 Hz for XXXII A and 10.8 Hz for XXXII B. The multiplet methylene resonances (R_5, R_6 - Table 2) appear at 1.40 - 1.87 ppm for XXXII A and at roughly 1.50 - 2.33 ppm for XXXII B. The methyl resonances appear as a doublet

(J = 6.3 Hz) at 1.13 ppm for XXXII A and 1.22 ppm for XXXII B.

The methylene (R_5, R_6) resonances have not been analyzed but some useful information has been obtained from the methine (R_1, R_4) resonances. The methylene and methine resonances for either isomer are sufficiently separated that the latter represents the X_2 part of an ABX_2 spectrum further complicated by couplings to methyl protons and phosphorus. A first-order AMX_2 spectrum of thirty-two lines is expected for the methine resonance if the chemical shift between the methylene protons is much greater than the geminal coupling constant. This spectrum can be considered a doublet ($J(POCH_X)$ of doublets ($J(H_XCCH_A)$) of doublets ($J(H_XCCH_B)$) of quartets ($J(H_XCCH_3)$). Fortuitously, only eighteen lines appear for XXXII B with intensities indicative of a first-order spectrum exhibiting coupling constants of 11.2, 3.1 and 3.1 Hz in addition to the 6.3 Hz coupling associated with $J(HCCH_3)$. Decoupling of the phosphorus nucleus reduced the number of lines to sixteen and revealed that $J(POCH_X)$ is 3.1 Hz and, thus, the vicinal coupling constants $J(HCCH_2)$ are 11.2 and 3.1 Hz. The intensities of lines in the methine resonance of XXXII A indicate that it is not first order and, from line separations, only approximate magnitudes of $J(HCCH_2)$ of 9.8 and 3.8 Hz can be reported. Decoupling of the phosphorus nucleus revealed a J(POCH) value of 2.2 Hz. No sign information for the above coupling constants has been obtained. Albrand, _et al_. (31) have independently analyzed the spectrum of XXXII A and found $J(POCH_3)$ = 11.7, J(POCH) = 2.1, and $J(HCCH_2)$ = 11.6 and 2.2 Hz for a neat sample. The methine resonance is indeed second order because $\delta(CH_2)$ = 0.120 ppm and J(HCH) = -13.9 Hz or

1.93 times greater than $\delta(CH_2)$ at 60 MHz. Unfortunately, these workers did not analyze the spectrum of XXXII B.

The phosphite XXXIII, derived from d,l-2,4-pentanediol, differs from XXXII A and XXXII B by having chemically nonequivalent methyl groups of protons (R_1, R_3). The doublet resonances of these methyl protons appear at 1.43 ppm ($J(HCCH_3) = 6.8$ Hz) and 1.20 ppm ($J(HCCH_3) = 6.3$ Hz). Only spectra of mixtures of XXXIII and XXXII A and XXXIII, XXXII A and XXXII B have been obtained, but one comparison is worth reporting. The doublet methoxyl resonances of XXXII A, XXXII B and XXXIII appear in this order from low to high field with a range of chemical shifts of 0.020 ppm. Dilution with benzene causes all the doublets to appear at higher field but, whereas those for XXXII A and XXXIII ($J = 12.0$ Hz) are still separated by 0.017 ppm with the doublet of XXXIII at higher field, the doublet for XXXII B now appears 0.043 ppm to lower field of the one for XXXII A.

5. Temperature and concentration dependencies

The spectra of compounds in Table 2 that have been described thus far have been of samples near room temperature and often without solvent. Those compounds whose nmr spectra have been obtained at more than one temperature can be divided into two classes based on the presence or absence of spectral lines which broaden with increased temperature. Those that exhibit such broadening are XXXVIII, XXXIX A, B, XLII, and XLV A, B while those that do not up to about 160° are XXXI A, B, XXXII A, XXXIII, XXXVI, XXXVII A, B and XLI A. Several of the compounds in the former group have also been examined at various concentrations in benzene.

The compounds giving broadened spectral lines contain a phosphorus-chlorine or phosphorus-bromine bond. The methyl resonances of XXXVIII have $W_{1/2}$ = 2.0 Hz (1.23 ppm) and 1.2 Hz (0.788 ppm) and are 0.430 ppm apart at 40°C. With increasing temperature, these peaks broaden and begin to coalesce. At 158°C, the maxima are separated by about 0.30 ppm with very little drop in intensity between them. Gagnaire, et al. (30) did not observe any apparent modification of coupling constants and chemical shifts between -40° and +155°. The discrepancy between the two observations may be due to the presence of a trace of water in the sample exhibiting the line broadening. The isomers XXXIX A and B are present in a 3.9:1 ratio at 40°C but the lines are slightly broader than those of XXXVIII. Dilution of the mixture with benzene caused a sharpening of the lines and a separation of the two halves of the methylene resonances, the two chloromethyl peaks and the two methyl peaks. An increase in temperature from 40° to 148°C caused the two chloromethyl (3.76 and 3.29 ppm at 40°C) and two methyl (0.87 and 1.33 ppm at 40°C) resonances to coalesce to apparent single peaks at 3.59 and 0.99 ppm, respectively. These coalesced peaks are positioned 36 and 26%, respectively, of the separation of the uncoalesced peaks at 40°C from the peaks of the major isomer A. The lines are sharper at 148°C than at intermediate temperatures but not as sharp as at 40°C. The chloro derivatives XLI A and XLII were examined from -30 to 158°C. At -30°C, the methyl resonance of XLI A consists of a sharp doublet and that of XLII consists of two sharp doublets separated by 0.30 ppm. Qualitatively, the doublet of XLI A does not broaden up to 158°C. However, the two doublets of XLII coalesce to one doublet ($J(H_3CCH)$ = 6.3 + 0.2) which is still broad at 158°C. The coalescence temperature for XLII is about 50 ± 10° (60 MHz) or 70 ± 10°C (100 MHz). Dilution of this mixture of XLI A and XLII at 40°C with benzene causes the partially-coalesced doublets of XLII to separate to about 0.40 ppm and sharpen. Addition of tetraphenylarsonium chloride to a dilute benzene solution has no effect on the width of the methyl doublet of XLI A but causes the doublets of XLII to broaden to more than twice their original width. The bromine derivatives XLIV and XLV A, B have broader spectral lines at room temperature than the corresponding chlorine compounds. Moreover, spectra of different samples of a given compound run under the same conditions differed in broadness. The resonances of a mixture of XLV A and B coalesce into four sharp peaks at 1.01(CH_3), 3.58(CH_2Cl), 4.01(OCH_2) and 4.15 ppm(OCH_2) with relative areas 1.5:1.0:1.0:1.0 at 161°C. The high-field halves of the methylene resonances do not coalesce as rapidly as the low-field halves so that the two peaks are of unequal height (1.13:1) at 161°C. Dilution of XLIV or a mixture of XLV A and B with benzene at room temperature causes the broadened and partially-coalesced lines to separate and sharpen. Spectra of these dilute benzene solutions reveal J(POCH) = 6.5±0.3 Hz (low-field) and 10.5 ± 0.5 Hz (high-field) and J(HCH) = 10.7 ± 0.2 Hz for XLIV and XLV A. The sum of the POCH couplings, 17.0 ± 0.8 Hz is the same as twice the separation between the two apparent methylene singlets for the neat XLV A, B mixture at 161°C. It is important to note that spectral lines from isomers A and B coalesce and that the nature of the species giving the spectrum at 161°C is yet to be determined.

The compounds exhibiting no broadening at elevated temperatures are alkoxyl, fluro and chloro derivatives. The one chloro derivative, XLI A has been discussed already. In the case of the fluoro compound XXXVI, the chemical shift between the methylene protons, that between the methyl protons and the splittings dependent on J(POCH) change less than 1 Hz from 40^{o} to 161^{o}. Although the methyl and chloromethyl proton resonances of the fluoro isomers XXXVII A and B do not change more than 1 Hz from 40^{o} to 161^{o}C, the isomer ratio changes from 3.9:1 to about 2.0:1. The methylene resonance of XXXVII A, which masks that of XXXVII B, exhibits changes of less than 1 Hz. The two methoxyl derivatives, XXXII A and XXXIII, were examined as an approximately 1:1 mixture. The two methyl doublet resonances of XXXIII approach one another in $CDCl_3$ from 0.27 ppm at -61.5^{o}C to 0.22 ppm at 40^{o}C and as a neat mixture from 0.23 ppm at 40^{o}C to 0.16 ppm at 156.5^{o}C, but the methyl doublet resonance of neat XXXII A shifts less than 0.017 ppm from 60^{o} to 156.5^{o}C. Obvious changes in line spacings and intensities in the methylene and methine resonances occur throughout this temperature range, but overlap of the resonances of XXXII A and XXXIII prevent attributing the changes to a specific compound. The spectral behavior of the methoxyl isomers XXXI A and B upon changes in temperature can be compared to that of the fluoro isomers XXXVII A and B. In contrast, the isomer ratio decreases less than 5% from 3.6:1 at 40^{o}C to 156.5^{o} although the time of observation was at least as long as that of the fluoro isomers. The two halves of the methylene resonance of XXXI A approach from 0.62 to 0.57 ppm and J(POCH) changes less than 1 Hz. Also, the chloromethyl and methyl resonances of both isomers change less than 0.033

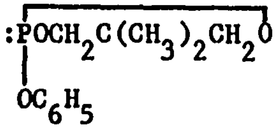
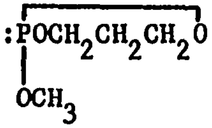
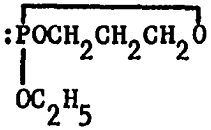
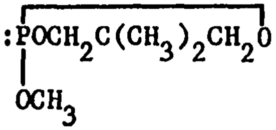
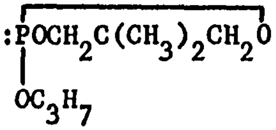
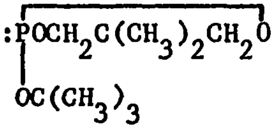
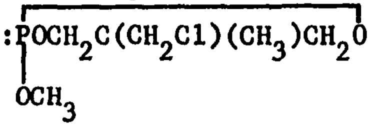
ppm. The isomer ratio in deuteriochloroform was not reproducible. One sample contained a 4.7:1 ratio at -61° and at 40°C three days later. The ratio in another sample at 40°C was 3.3:1 while that of a third, kept in a Dry Ice chest for about a week before being examined at 40°C, was 6.9:1. When a nonequilibrium mixture of ratio 1:1.75 was kept at 70°C, the ratio changed to 2.0:1 after 40 hours and to 3.0:1 after another 27 hours.

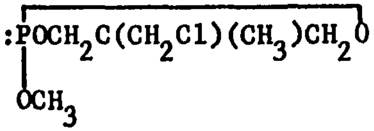
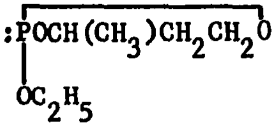
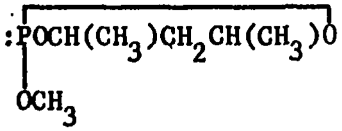
D. ^{31}P NMR Spectra of Trivalent Phosphorus Compounds

Table 13 includes ^{31}P nmr spectral data for CV and a number of the compounds in Table 2. Also, data taken from the literature for these and similar compounds are included for comparison. The A and B isomers were always examined together. Unfortunately, the nature of the fine structure of the resonances of the minor components XXXI B, XXXII A and XXXVII B could not be determined because of a small signal to noise ratio and/or overlap with the resonance of the major component. The broadness of the resonance of the chloro derivative XXXVIII may be due to the quadrupole moment of chlorine.

Several relationships in Table 13 are worth pointing out at this time. Geometrical isomers differ in ^{31}P chemical shift in the three pairs examined. In fact, the ^{31}P shift is almost as sensitive to isomerism as the ^{19}F shift in XXXVII A and B. There is also the substituent effect on the shift that may not be easily distinguishable from the stereochemical effect. The pair of phosphites differing only in methyl substitution at the 4-position, XXXIV and XXIX, and the analogous pair of 1-chloro derivaties have shifts differing by 7-8 ppm in each pair. This

Table 13. ^{31}P spectral parameters of some 1-phospha-2,6-dioxacyclohexanes and bicyclic phosphites

	Compound	Chemical Shift, ppm	Appearance[a]	Splittings, Hz
XXIV	 $:\underset{OC_6H_5}{P}OCH_2C(CH_3)_2CH_2O$	-115.3,[b] -114.8[c]		
XXXIV	 $:\underset{OCH_3}{P}OCH_2CH_2CH_2O$	-131	bd qt	
	 $:\underset{OC_2H_5}{P}OCH_2CH_2CH_2O$	-128,[c] -132±1[c]		
XXIX	 $:\underset{OCH_3}{P}OCH_2C(CH_3)_2CH_2O$	-123, -122.7[b]	bd qt	
	 $:\underset{OC_3H_7}{P}OCH_2C(CH_3)_2CH_2O$	-138[c]		
XXV	 $:\underset{OC(CH_3)_3}{P}OCH_2C(CH_3)_2CH_2O$	-117.5±0.8	bd tpt	10.5±0.5
XXXI A	 $:\underset{OCH_3}{P}OCH_2C(CH_2Cl)(CH_3)CH_2O$	-123.5	1:3:6:3:1 mpt of tpts	11.5 and 3.0±0.5

XXXI B	 $\underset{\text{OCH}_3}{:\text{P}}\overline{\text{OCH}_2\text{C(CH}_2\text{Cl)(CH}_3\text{)CH}_2\text{O}}$	-122.6	
XXVI A	 $\underset{\text{OC}_2\text{H}_5}{:\text{P}}\overline{\text{OCH(CH}_3\text{)CH}_2\text{CH}_2\text{O}}$	-131±1[c]	
XXXII A	 $\underset{\text{OCH}_3}{:\text{P}}\overline{\text{OCH(CH}_3\text{)CH}_2\text{CH(CH}_3\text{)O}}$	-133	bd qt

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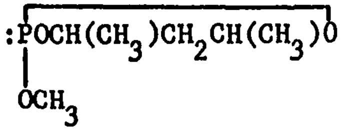
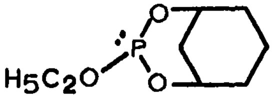
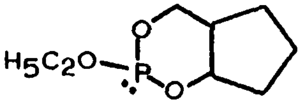
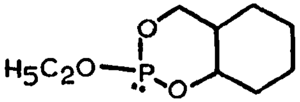
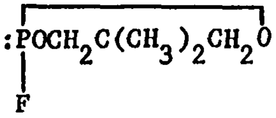
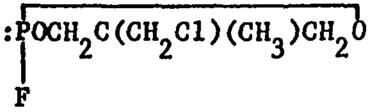
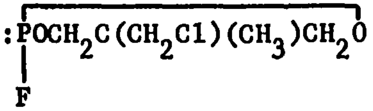
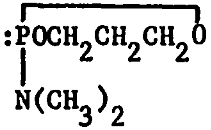
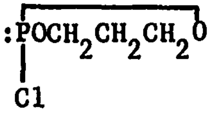
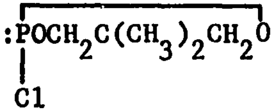
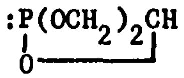
[a] Qt = quartet, bd = broad, tpt = triplet, mpt = multiplet, dbt = doublet, $w_{1/2}$ = width at half height.

[b] Reference 30.

[c] Reference 143.

Table 13 (continued)

Compound		Chemical Shift, ppm	Appearance[a]	Splittings, Hz
XXXII B	 $:\underset{\mathrm{OCH_3}}{\mathrm{P}}\mathrm{OCH(CH_3)CH_2CH(CH_3)O}$	-129	qt of qts	10.5±0.5 and 2.5±0.5
		-124±1[c]		
		-125±1[c]		
		-125±1[c]		
XXXVI[d]	 $:\underset{\mathrm{F}}{\mathrm{P}}\mathrm{OCH_2C(CH_3)_2CH_2O}$	-111.5, -132.9[b]	dbt of tpts of tpts	1180, 10.8, 3.5, all ± 0.5

XXXVII A[e]  $:\underset{\mathrm{F}}{\mathrm{P}}\mathrm{OCH_2C(CH_2Cl)(CH_3)CH_2O}$	-112.8	dbt of tpts of tpts	10.3 ± 0.3, 3.6 ± 0.3
XXXVII B[f]  $:\underset{\mathrm{F}}{\mathrm{P}}\mathrm{OCH_2C(CH_2Cl)(CH_3)CH_2O}$	-112.2	db of tpts of tpts	
 $:\underset{\mathrm{N(CH_3)_2}}{\mathrm{P}}\mathrm{OCH_2CH_2CH_2O}$	-143.0[c]		
 $:\underset{\mathrm{Cl}}{\mathrm{P}}\mathrm{OCH_2CH_2CH_2O}$	-154, -153,[c] -153.9[c]	bd	
XXXVIII:  $:\underset{\mathrm{Cl}}{\mathrm{P}}\mathrm{OCH_2C(CH_3)_2CH_2O}$	-146, -146.5,[b] -146.7[c]	bd, $w_{\frac{1}{2}} = 30 \pm 5$	
$\mathrm{Cl\text{-}P(OCH_2)_2C(CH_2O)_2P\text{-}Cl}$	-148.1[c]		
XCVII(CH$_3$):$\mathrm{P(OCH_2)_3CCH_3}$	-91.5, -91.8[c]		J(POCH)=2
XCII :$\mathrm{P(OCH)_3C_3H_6}$	-137[c]		J(POCH)=6
CV  $:\mathrm{P(OCH_2)_2CH}$ with O below, ring-closed	-105.4 ± 0.1	dbt of tpts of tpts	15.9, 3.6 and 0.7, all ± 0.2

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[d] $\delta\,^{19}F$ = 6.14 ppm relative to internal CFCl$_3$, J(P-F) = 1174Hz.

[e] $\delta\,^{19}F$ = 5.12 ppm, J(P-F) = 1182.8 Hz.

[f] $\delta\,^{19}F$ = 6.05 ppm, J(P-F) = 1180.8 Hz.

kind of substitution is not expected to affect the stereochemistry. Methyl substitution at the 3-and/or 5-position in the 1-alkoxyl derivatives does not always cause a shift to higher field as does substitution at the 4-position. Dependence of the shift on exocyclic substituent at phosphorus does not appear to be related to the substituent electronegativity. Even the shifts of 1-methoxy-, 1-propoxy- and 1-t-butoxy-4,4-dimethyl-1-phospha-2,6-dioxacyclohexane do not correlate with the electron releasing ability of the alkoxyl substituents.

E. Stereochemistry of 1-R-1-phospha-2,6-dioxacyclohexanes

1. Geometrical isomerism

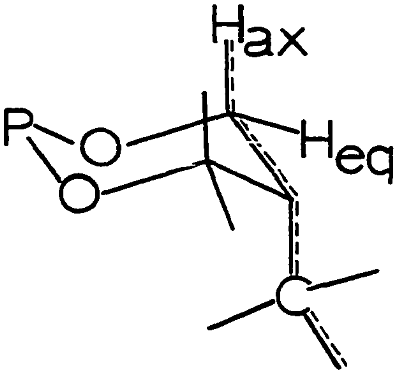
There are two possible geometrically isomeric structures for compounds XXVI-XXVIII, XXX-XXXII, XXXVII, XXXIX-XLI, XLIII and XLV. The ^{1}H nmr resonances of two isomers have been observed at equilibrium for XXVIII (24), XXX (25), XXXI, XXXVII, XXXIX and XLV (dilute benzene); the ratio is about 9:1 for XXX and 3-4:1 for the others. Only one isomer has been found for XXVI (16), XXVII (24), XXXII (24), XL (25), XLI and XLIII (24, 16). With XL being the only exception (25), the generalization can be made that one isomer is very dominant if the isomerism is due to substitution at the 3-and/or 5-positions while both isomers exist in significant percentages if the substitution is at the 4-position.

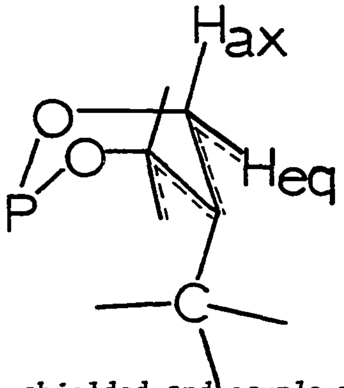
The Denneys (24), Aksnes, et al. (16) and Hargis and Bentrude (25) have concluded that an equilibrium mixture of isomeric six-membered ring phosphites (R = 0 Alk) results when a trialkyl phosphite is transesterified with an appropriately substituted diol. On the other hand, they found that a nonequilibrium mixture is formed when an alcohol and tertiary amine or, alternatively, an alkoxide ion reacts with an appropriately substituted 1-chloro-1-phospha-2,6-dioxacyclohexane (see Review of Literature, pp. 17-19). This is true also for the phosphites XXXI A, B and XXXII A, B. Ratios of XXXI A:B of 1:2.6 and XXXII A:B as great as 1:4 are formed from the chloro derivatives whereas transesterification leads to XXXI A:B = 3.5:1 and essentially all XXXII A. Preparation from the chloro derivatives is thought to involve a Walden inversion at phosphorus and should give an isomer ratio the inverse of that formed by transesterification since the ratio of chloro isomers is very similar to the ratio of phosphite isomers at equilibrium. The fact that complete inversion does not always occur has been attributed to excess strength of the nucleophile (alkoxide ion), excessively high reaction temperatures and/or the presence of nucleophiles after reaction (16, 24). The existence of nonequilibrium isomer mixtures implies that thermal atomic inversion of phosphorus is slow at room temperature. In a mixture of XXXII A and B, the unstable isomer XXXII B does not isomerize in a Dry Ice chest even after a month. A 1:1.75 mixture of XXXI A:B at 70°C does not completely return to the equilibrium value after forty hours and this must be considered a minimum time because isomerization catalysts may have been present. Also, it is not known whether the rate controlling mechanism, in the absence of catalysts, involves a thermal intramolecular inversion or an intermolecular alkoxyl exchange like the halide exchange that will be discussed later.

2. Ring conformations

Each of the compounds in Table 2 might exist in one or more conformations such as those analogous to the chair, boat or skew-boat forms of cyclohexane. Although no solid state or gas phase structural determination has been reported for any 1-R-1-phospha-2,6-dioxacyclohexanes, one of the possible chair conformers has been found by solid-state x-ray diffraction methods: for each of three 1-R-1-oxo-1-phospha-2,6-dioxacyclohexanes, XLVIII - L. In each compound, the phosphorus end of the chair-like ring is flattened 10-20° with respect to a cyclohexane chair. This flattening is probably due to the smaller-than-tetrahedral OPO angle and larger-than-tetrahedral POC angles. The OPO angle would be expected to be even smaller when phosphorus is in the trivalent state and, therefore, the ring flattening should be even more prominent in 1-R-1-phospha-2,6-dioxacyclohexanes. Also, the possibility that the solid-state and solution structures are different must always be considered.

The results of the analysis of the nmr spectra of the 1-R-1-phospha-4,4-dimethyl-2,6-dioxacyclohexanes can be interpreted in terms of possible ring conformations. The fact that Gagnaire, et al. (30) found no variation of J(POCH) from -40 to 155°C for XXIV, XXIX, XXXVI and XXXVIII indicates that in all likelihood one conformer is very dominant or less likely, the ratio of conformers remains constant over this temperature range. If the latter possibility were correct, the conformers would have to interconvert rapidly enough to give a weighted time average spectrum because spectral lines assignable to only one species are observed. As a result of the ^1H-^1H decoupling experiments described earlier, it may be concluded that just one pair of methylene protons, BB$'$, couples appreciably, 0.7 - 0.8 Hz (30), to just one of the methyl groups of protons. There is even greater HCCCH coupling, 2.5 - 2.9 Hz, between the A and A′ protons but very little between the B and B′ pair. These enhanced HCCCH couplings are usually found when the bonds linking the coupled nuclei form a planar zigzag W (144). Such a pathway exists between the equatorial methylene protons and between each of the axial methylene protons and an appropriately positioned axial methyl proton of either a chair or boat conformer,[3] as shown below.





Thus, the equatorial methylene protons are more shielded and couple more strongly to phosphorus than the axial methylene protons. Also, the axial 4-methyl protons are less shielded than the equatorial 4-methyl protons. These long-range coupling results rule out unsymmetrical boats or twist-boats (examples of which are shown below) inasmuch as they would not possess all of the appropriately-positioned protons.

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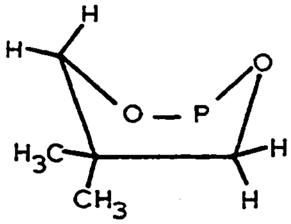
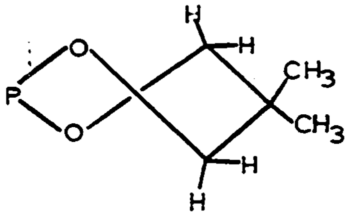
[3] A "boat" or "boat conformer," without preceding adjectives, refers to the form with a plane of symmetry passing through phosphorus and C_4.



unsymmetrical boat



twist-or skew-boat

Also ruled out are comparable quantities of rapidly interconverting chair or boat conformers because the enhanced long-range coupling would then be averaged among all of the methylene and methyl protons according to the ratio of conformers. However, a rapid equilibrium between the chair and boat shown above, which differ only at the phosphorus end of the ring, would allow the same protons to always exist in an environment favorable for enhanced long-range coupling. The usual steric arguments against a boat conformer are not as applicable here as for substituted cyclohexanes if the phosphorus end of the ring is flattened as in the chairs of the sold state pentavalent derivatives. This flattening not only would reduce the bowsprit-flagpole interactions but also would allow the oxygen electron lone-pairs and the methylene protons to be staggered. The ring POCH coupling constants of the 4,4-dimethyl derivatives (Tables 11 and 12) may be used as evidence against a boat conformer (30). If a dihedral angular dependence of J(POCH) similar to that of J(HCCH) exists, as has been suggested (40, 49, 66, 145), the two values of J(POCH) for a boat, with dihedral angles of approximately 60°, should be similar but those for a chair, with dihedral angles of approximately 180° and 60°, should be different. The difference between the values of J(POCH) varies from 4.1 for the bromo derivative XLIV to 15.8

for the dimethylamino derivative XXXV (Table 12).

The 1-R-4-t-butyl-1-phospha-2,6-dioxacyclohexanes investigated by Hargis and Bentrude (25), XXX A, XXX B and XL A, yield additional conformational information. Partial results of the analysis of the ^1H nmr spectra of these compounds in $CDCl_3$ (25) are given in Tables 11 and 12. The vicinal J(HCCH) for XXX A and XL A are in the ranges found for an axial 5-H in 2-substituted-5-t-butyl-1,3-dioxacyclohexanes.[4] However, similar vicinal couplings would also be expected for a boat conformation. The similarity of the ring J(POCH) between XXX A and XXIX or XXV and between XL A and XXXVIII indicates that all are conformationally similar. Evidence against this conclusion is the finding (25) that the cross-ring couplings, J(HCCCH), are less than 2.0 Hz. Both the HCCH and ring POCH couplings for XXX B and their temperature and solvent dependence indicate a conformational equilibrium. Hargis and Bentrude (25) proposed a chair-chair rather than a skewboat-skewboat equilibrium mainly from a comparison of J(HCCH), δH_5 and $\delta C(CH_3)_3$ for XXX B and the 2-substituted-5-t-butyl-1,3-dioxacyclohexanes. They did not consider a chair-boat equilibrium. If the equilibrium is between two chairs and $J(POCH_{ax})$ and $J(POCH_{eq})$ in both conformers are equal to $J(POCH_B)$ and $J(POCH_A)$, respectively, for XXX A, then the conformer ratio at 35° in $CDCl_3$ is approximately 3:1. The vicinal HCCH coupling constants indicate that the t-butyl group is axial in the favored conformer.

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[4] $J(H_{4eq}H_{5eq}) = 1.1\text{-}2.0$, $J(H_{4ax}H_{5eq}) = 3.9\text{-}4.3$, $J(H_{4eq}H_{5ax}) = 4.6\text{-}5.6$ and $J(H_{4ax}H_{5ax}) = 10.6\text{-}12.1$ (21).

The ^1H nmr spectral studies of the 1-R-4-methyl-4-chloromethyl-1-phospha-2,6-dioxacyclohexanes XXXI A and B, XXXVII A, XXXIX A and XLV A indicate a conformational similarity to the analogous 4,4-dimethyl derivatives. The ring POCH coupling constants for XXXI A and XXXVII A do not change from 40° to 160°. An exchange phenomenon, to be discussed later, prevents analysis of the spectra of XXXIX A and XLV A over most of this temperature range. The J(POCH) values listed in Table 12 for these compounds are very similar to those for the corresponding 4,4-dimethyl derivatives. The relatively-narrow 4-methyl resonance for XXXI A and the relative broadness of the same resonance for XXXI B indicates that the A isomer possesses an equatorial and the B isomer an axial 4-methyl group. The splitting of 0.7 Hz in the 4-methyl resonance of XXXI B is the same as that found by Gagnaire, _et al_. (30) for the 4,4-dimethyl compounds and attributed by them to coupling of axial methyl protons with axial methylene protons. The presence of a broadened low-field-half of the methylene resonance for B (Figure 6) is in agreement with this conclusion. On the other hand, the absence of a broadened methylene resonance for XXXI A (Figure 6) is in agreement with the absence of an axial 4-methyl group. The methylene resonances of XXXVII A, XXXIX A (C_6H_6) and XLV A (C_6H_6) are also relatively sharp. Apparently the axial 4-chloromethyl protons in the A isomers are seldom appropriately positioned for enhanced long-range coupling to the axial methylene protons. This would be the case if the chlorine were as far away from the ring as possible. The features of the methylene resonances of XXXVII B, XXXIX B and XLV B are masked by those of the A isomers, but the large chemical shifts between both the A and B methyl and chloromethyl resonances and the similarity of these shifts to those for XXXI A and B are evidence for a conformational similarity of all the B isomers. If the A and B isomers exist as chair conformers rather than as chair-boat equilibria, then the R group at phosphorus must be axial in all of them or equatorial because the isomers of each pair differ in configuration at C-4. The similar isomer ratios of 3-4:1 for the four pairs leads to an axial/equatorial free energy difference for a chloromethyl and methyl group of approximately 0.7 kcal/mole at 40°. The fact that the isomers with an axial chloromethyl group are favored may be due to the fact that the C-Cl bond is longer than the C-H bond. Consequently, steric interactions of the axial chloromethyl group with other atoms in the molecule may be less than those of the axial methyl group.

The ^{1}H and ^{31}P nmr results for the isomeric phosphites derived from <u>meso</u>-2,4-pentanediol, XXXII A and B, strongly suggest that they differ in configuration at phosphorus. The values of J(HCCH) of 11.6 and 2.2 for A (31) and of approximately 11.2 and 3.1 for B imply equatorial 3,5-methyl groups.[5] Also, $\delta(CH_3)$ = 1.14 for XXXII A, 1.23 for XXXII B and 1.20 and 1.43 ppm for the phosphite XXXIII derived from <u>d,l</u>-2,4-pentanediol. These shifts indicate a similar environment for the methyl groups of XXXII A and XXXII B and one of the methyl groups of XXXIII. On steric grounds, equatorial methyl groups would be favored. The ring J(POCH) for XXXII A and B are similar to the J(POCH) assigned to an axial methylene proton in all of the other phosphites in Table 12 except XXX B. Since XXXII A and B are geometrical isomers, the methoxyl

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[5] $J(H_{4ax}H_{5eq})$ = 3.1-3.9 Hz, $J(H_{4ax}H_{5ax})$ = 9.5-10.9 Hz for <u>cis</u>-4,6-dimethyl-1,3-dioxacyclohexanes (21); see also footnote 2, p. 111.

group should be axial in one and equatorial in the other unless one isomer prefers a boat conformation. If both were boat conformers, they would still differ in configuration at phosphorus and the methoxyl disposition could still be called axial and equatorial. The $\delta^{31}P$ values for XXXII A and B differ by 4 ppm whereas those for XXXI A and B or XXXVII A and B, concluded to have the same configuration at phosphorus, differ by less than 1 ppm (Table 13). Also, the contrast in the effect of benzene on the methoxyl chemical shift of XXXII B and that on the corresponding shifts of XXXII A and XXX indicates different environments of the methoxyl group in XXXII A and B. Although the different configurations at phosphorus cause the 3,5-methyl groups to resonate only 0.09 ppm apart, $B < A$, the 3,5-methinyl protons resonate 0.35 ppm apart with $A < B$. The relative magnitudes of the separations are reasonable because the axial methinyl protons are closer than the equatorial methyl protons to the phosphorus electron lone pair and methoxyl group.

The limited information about the phosphite XXXIII indicates that it is not conformationally pure at room temperature. This compound cannot exist in geometrically isomeric forms because the methoxyl group is always cis and trans to a methyl group. The main evidence for a conformational equilibrium is the decrease in the separation of the 3,5-methyl resonances with increasing temperature. This behavior is very similar to that found for the analogous 1-oxo-trans-3,5-dimethyl-1-thia-2,6-dioxacyclohexane by Overberger, et al. (146). These investigators interpreted their data in terms of an equilibrium between two rapidly interconverting chair conformers.

Bodkin and Simpson concluded that XXVI A and XLIII A adopt a chair conformation with the ring methyl equatorial (95). The evidence is only outlined qualitatively but is of the type presented above. The temperature dependence of the ^1H nmr spectrum of XXVI B suggested an equilibrium of rapidly interconverting conformers at room temperature. At -30^{o}, the ring possesses an equatorial methyl substituent (95).

3. Stereochemistry at phosphorus

Four groups of workers have deduced the stereochemistry at phosphorus in 1-R-1-phospha-2,6-dioxacyclohexanes. On the one hand, Gagnaire, et al. (30) concluded that the methoxyl group in XXIX and, because of similar ^1H nmr spectral characteristics, the R group in XXIV, XXXV, XXXVI, XXXVIII and XLVI occupy the equatorial position in a chair conformer. On the other hand, first White, et al. (147), then Bentrude and Hargis (26) and Bodkin and Simpson (95) concluded that, for three different pairs of geometrically isomeric phosphites, the alkoxyl group occupies the axial position of a chair conformation in the more stable isomer. The preference for an axial alkoxyl, equatorial lone-pair stereochemistry is great enough to force a 4-t-butyl group to be axial approximately 75% of the time in XXX B at room temperature (26). Also, the 3-methyl group in the less stable isomer XXVI B apparently does not prefer the equatorial position strongly enough to force the ethoxyl group and phosphorus lone pair of electrons exclusively into an unfavored configuration at room temperature (95). The evidence for the conclusions of Gagnaire, et al., Bentrude and Hargis, and Bodkin and Simpson has been outlined in the Review of Literature. In this section, the deduction of the stereochemistry at phosphorus in several compounds, including XXXI A and B (147) will be presented and discussed in relation to the other methods that have been used.

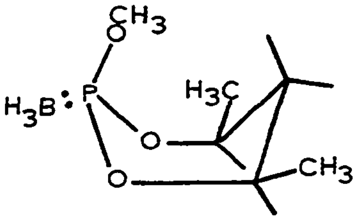
The manner of solving this stereochemical problem can be generalized. A geometrically isomeric 1-R-1-phospha-2,6-dioxacyclohexane is combined with a compound assumed to react with the isomer at phosphorus with either a retention or inversion of configuration. The configuration of the product isomer is then determined and used with the assumed reaction mechanism to deduce the configuration of the reactant isomer. Thus far, the product configurations have been determined in two ways, one from a comparison of experimental and calculated dipole moments (95, 147) and the other from a crystal structure determination by means of x-ray diffraction analysis (26).

Diborane reacts stereospecifically with two mixtures of XXXI A and B, XXXII A, and a mixture of XXXII A and B in ether at -40°C. The stereospecificity of the reactions was deduced from the similarity of the product and reactant isomer ratios as determined from the ^{1}H nmr spectra. Since the reaction involves the formation of a Lewis acid-base adduct, there is no reason why it should proceed with other than a configuration-retention mechanism.

The ^{1}H nmr spectra of mixtures of LXXX and LXXXI, the adducts derived from XXXI A and B, indicate that the stereochemistry at C_4 has not changed radically from that in the phosphites. The adduct isomers are probably not conformationally pure because the two 4-methyl and 4-chloromethyl resonances are separated by 0.39 and 0.35 ppm, respectively, whereas for the phosphites they are separated by 0.53 and 0.57 ppm. An equilibrium between rapidly interconverting conformers could cause this decreased separation for the adducts, but the unknown shielding effects of the substituents at phosphorus could also be responsible except that the affected protons are relatively far from phosphorus. Also, the difference in $W_{1/2}$ of the 4-methyl resonances is only 0.3 - 0.4 Hz whereas it is almost 0.8 Hz for the phosphites, but the coupling between an axial methylene proton and an axial methyl proton may not be the same in both phosphite and adduct. Unfortunately, the methylene resonances of the adducts overlap too extensively with each other and the other resonances to determine the ring J(POCH) values. Nevertheless, the small shifts of the methyl and chloromethyl resonances upon adduct formation plus the other facts cited above strongly suggest that the adduct derived from XXXI A possesses a predominantly axial chloromethyl group and that derived from XXXI B possesses a predominantly equatorial chloromethyl group.

The dipole moments of LXXX and LXXXI were then compared to values calculated by a vector summation of bond moments for the two possible chair conformers of each isomer. In the original calculations (147) the rotating components of the O-C and C-Cl moments were considered to average to zero. Since the experimental moment is a root mean square average of the instantaneous molecular moments, the reported calculated moments are incorrect. An improved method of calculation has been described earlier in this thesis and the corrected values are underlined in Table 7, along with the experimental values. Recall that the methoxyl and chloromethyl groups were assumed to be freely rotating. If this assumption, the bond moments used, and the structural parameters are correct, then the isomer with the greater moment is a mixture of conformers and the other has a predominantly equatorial methoxyl group. The free rotation assumption is very likely incorrect. For instance, an axial methoxyl group would sterically not likely be found positioned over the ring. Also, the chlorine atom of an axial chloromethyl group undoubtedly is not likely to be under the ring. Since the calculated moments are directed more towards the phosphorus than the carbon end of the ring, these restrictions on rotation would cause some of the corrected values in Table 7 to be too great. The uncertainties in the bond moments, especially the P-O moments, have already been discussed. As a result of the above considerations, the stereochemistry at phosphorus in the adduct isomers must unfortunately be considered uncertain for the present.

The phosphites derived from meso-2,4-pentanediol have been concluded to have equatorial 3,5-methyl groups. The BH_3 adducts XCI and XC, derived from XXXII A and B, might be expected to have equatorial 3,5-methyl groups also. This can only be assumed for the present because the ^1H nmr spectra of the adducts have not been analyzed. The experimental moments are surprisingly similar, in contrast to the calculated values (Table 7). A possible reason for this discrepancy, in addition to those considered above, is the existence of XC, derived from the unstable phosphite, in a boat form. This possibility would only be reasonable if the preferred stereochemistry at phosphorus were axial methoxyl, equatorial lone pair. Thus, if XC were a chair conformer with equatorial 3,5-methyl groups, the BH_3 group, sterically like a methyl group, would be forced into the unfavored axial position while the methoxyl group would likewise occupy the unfavored equatorial position. The adoption of the boat form shown below would satisfy both groups at phosphorus. Unfortunately, the stereo-



chemistry at phosphorus in these adducts must also be considered uncertain for the present.

The phosphite XXXII A and a mixture of XXXII A and B also combine stereospecifically with triphenylmethyl chloride in acetonitrile at about 80°. This reaction should proceed by the Michaelis-Arbuzov mechanism, considered to involve a retention of configuration at phosphorus (28, pp. 37-45). The product isomers will be assumed to have equatorial 3,5-methyl groups. The experimental dipole moments differ by 1.03 D whereas the "best" calculated values (underlined in Table 7) differ by over 3 D. Rotation of exocyclic groups cannot alter the molecular moment; therefore, either one or more of the bond moments are incorrect or the ring does not adopt a conformation similar to the chairs assumed. Although the related compound XXI′ (Table 14) adopts a chair conformation with an axial methyl group at phosphorus and equatorial 4-t-butyl group in the solid (27), Bentrude and Hargis (98) have postulated a boat form in equilibrium with a chair in $CDCl_3$ at 35°. If this were also the case for the analogous triphenylmethyl isomer in benzene, the observed moment should be less than the 6.17 D predicted for the chair conformer. Therefore, it is possible to rationalize the observed moments and conclude that the triphenylmethyl group primarily adopts the axial position in the product derived from XXXII B and the equatorial position in the product derived from XXXII A. Since the mechanism of the reaction is that shown on p. 20, the methoxyl group in the more stable phosphite isomer XXXII A is axially disposed.

Bodkin and Simpson (95) used the same method as described above to determine the phosphorus stereochemistry in XXVI A and B. However, instead of preparing borane adducts or 1-oxo-1-triphenylmethyl derivatives, they added sulfur to the phosphites. Their predicted moments of 5.78 and 3.31 D for the thiophosphate isomers in benzene are quite close to the observed values of 5.36 and 3.19 D (Table 7). They employed a $S{=}PO_3$ group moment derived from the moment of the bicyclic thiophosphate $SP(OCH_2)_3CCH_3$, a freely rotating ethoxyl group and tetrahedral angles in their vector summation calculation. Although the applicability of the $S{=}PO_3$ group moment to these isomers is questionable, the "best" calculated moments (underlined in Table 7) differ only 0.17 and 0.42 D from these authors' calculated values.

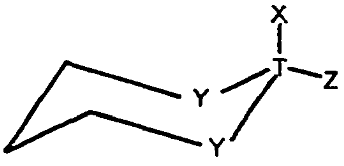
Bentrude and Hargis (26) used the methyl iodide Michaelis-Arbuzov reaction and *t*-butyl hydroperoxide oxidation of XXX A and B as their reference reactions. The configuration of one of the isomers from each reaction was determined from x-ray diffraction analysis. This procedure is much more satisfactory than a dipole moment analysis and the conclusion that the methoxyl group of XXX A is axially disposed in a chair-conformer appears firmly established. There is no reason why the alkoxyl group should not also be axially disposed in the other phosphite A isomers and XXIX and XXXIV.

Evidence has been presented for a conformational equilibrium for the phosphite XXXIII derived from d,l-2,4-pentanediol. This compound is different from the others because either the 3-or 5-methyl group would have to be axial in a chair-conformer. Overberger, et al. (146) have pointed out, in connection with the analogous 1-oxo-trans-3,5-dimethyl-1-thia 2,6-dioxacyclohexane, that repulsion between axial 3- or 5-methyl and S=O groups may reduce the stabilization of the S=O group in the axial position.

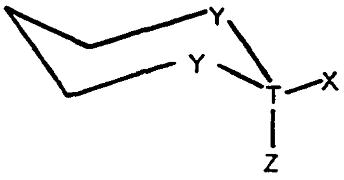
The conclusion of Gagnaire, et al. (30) that the preferred stereochemistry is equatorial R, axial phosphorus lone-pair is based on a steric argument and the dependence of the magnitude of J(POCH) on the POCH dihedral angle and the disposition of the phosphorus lone-pair relative to the coupled nuclei. Similar arguments have been given and the same conclusion deduced by Albrand, et al. (31) (the same group of investigators) in a discussion of the phosphorus stereochemistry in XXXII A and XLI A. In the latter paper (31), the POCCH couplings were the primary evidence. The steric argument has already been shown to be weak and the coupling argument will be analyzed and shown to be inconclusive in Section IV.J.1.

A much more direct method of determining the stereochemistry at phosphorus than those previously described would be an x-ray diffraction analysis of one of the 1-R-1-phospha-2,6-dioxacyclohexanes. Such a study is hindered by the liquid nature of most of these compounds at room temperature. One of the better possibilities would be XXXII A. The 3,5-methyl substituents are likely to be equatorial in both solid and liquid such that the solid-state structure could more confidently be extrapolated to the liquid state. A low-temperature x-ray analysis is currently being carried out on the phosphite XXIX (148). Dipole moments of XXXII A and B (believed to differ in stereochemistry at phosphorus) have been measured but they differ by only 0.6 D. The uncertainties involved in predicting dipole moments and the instability of phosphites towards water preclude making a stereochemical prediction based on these moments.

The adoption of a stereochemistry contrary to that expected on steric grounds is not unknown in heterocyclic chemistry. The axial oxygen, equatorial sulfur electron lone-pair stereochemistry has been concluded to be generally preferred in 1-oxo-1-thia-2,6-dioxacyclohexanes (23). Also, an axial alkoxyl, equatorial hydrogen stereochemistry is preferred in 2-alkoxy-1,3-dioxacyclohexanes (149). These preferences are termed anomeric effects, by which is meant the greater preference of an electron-withdrawing group for the axial position when it is located adjacent to a heteroatom in a ring than when it is located elsewhere (150, p. 375). The paper by Eliel and Giza (149) should be consulted for references to additional examples. Steric and electrostatic factors are thought to be important in determining the position of the generalized equilibrium shown below. Y is a heteroatom, T is carbon or phosphorus in this dis-



A



B

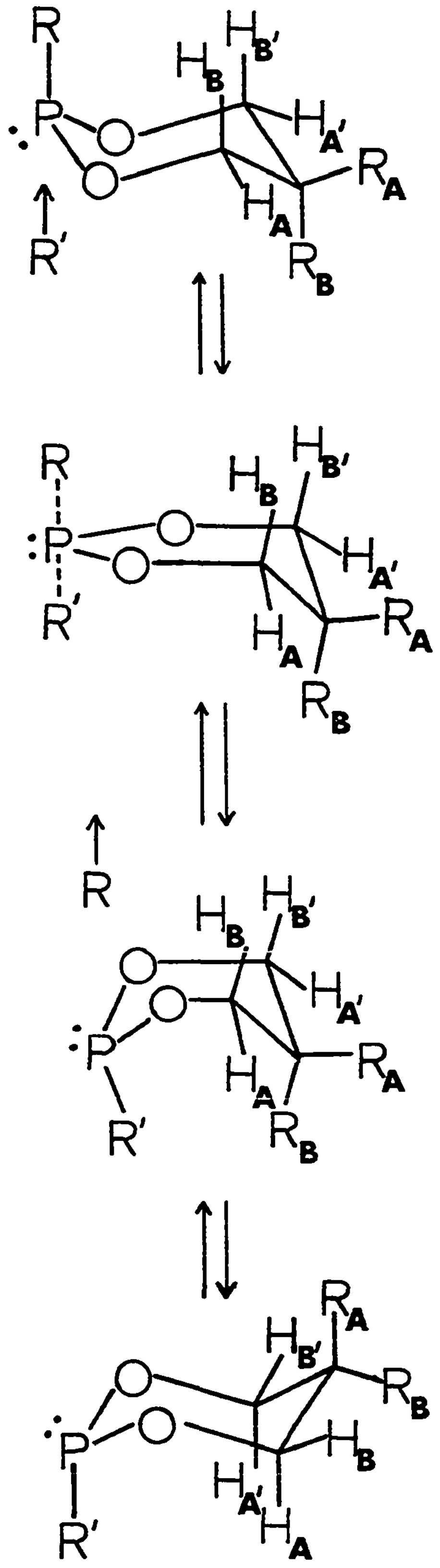
cussion and X and Z are the exocyclic substituents adjacent to the heteroatom of the ring. If X is bulkier than Z, the steric factor will cause conformer B to be favored more in a 1,3-dioxacyclohexane than in a 1-phospha-2,6-dioxacyclohexane because the hetero end of the ring is compressed relative to cyclohexane in the former structure (149) and probably flattened relative to cyclohexane in the latter structure. Compression would increase the interactions of the axial substituent X or Z with other axial substituents but more so for the bulkier X. The electrostatic factor will cause the conformer with its bond dipoles closest to an anti-parallel arrangement, i.e., the conformer having the lower dipole moment, to be favored. If the T-X bond is more polar than the T-Z bond and the moments are directed towards X or Z, then conformer A should be favored because in B the T-X bond moment is approximately parallel to the C-Y moments, which are directed towards Y. If X is methoxyl, there will be an additional OCH_3 moment to consider. Eliel and Giza (149) have reasoned that, electrostatically, A should be favored if Y = oxygen, T = carbon and Z = hydrogen. It is difficult to predict which conformer will be favored when Y = oxygen, T = phosphorus, X = methoxyl and Z = lone pair of electrons because the P-O and phosphorus lone-pair moments are unknown. However, the moment of the more stable isomer XXXII A is smaller than that of the less stable XXXII B in benzene (Table 7). The facts are that the axial methoxyl group is preferred by 0.35 kcal/mole in 2-methoxyl-1,3-dioxacyclohexanes (149) and by at least 1 kcal/mole in 1-alkoxy-1-phospha-2,6-dioxacyclohexanes. The alkoxyl preference in the two classes of compounds cannot be compared because Z is not the same in both, but a comparison can be made of the stereochemical preference of the pair of substituents X and Z. It is quite improbable that the steric factor alone would cause the observed stereochemistry in the phosphorus compounds to be preferred to any extent. Thus, if the electrostatic factor is the only other important factor, it must favor the observed stereochemistry by at least 1 kcal/mole.

4. Interpretation of temperature and concentration dependencies of ^1H nmr spectra

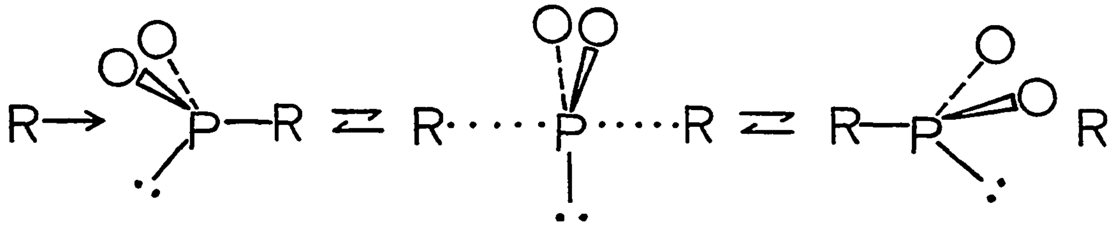
A process that will account for the temperature and concentration dependencies of the ^1H nmr spectra of the 1-R-1-phospha-2,6-dioxacyclohexanes (R = OCH_3, F, Cl, Br) is an intermolecular exchange of the exocyclic R group at phosphorus involving an inversion of the bonds to phosphorus. A mechanism for this process is shown in Figure 7. The R group and phosphorus lone-pair are assumed in this discussion to prefer the axial and equatorial positions, respectively, of a chair conformer. Also, the mechanism is assumed to be the same for all the molecules investigated. In the initial structure in Figure 7, H_A, $H_{A'}$ and R_B are trans to R and H_B, H_B, and R_A are cis to R. In the final chair conformer, the cis, trans relationships of these atoms are reversed. Also, H_A, $H_{A'}$ and R_A are initially in equatorial positions but move to axial positions as a result of the exchange process; H_B, $H_{B'}$ and R_B similarly change from axial to equatorial positions.

The process is believed to be an intermolecular exchange rather than a thermal intramolecular inversion at phosphorus for two reasons. Firstly, dilution with benzene of compounds that exhibit partially coalesced resonances causes the resonances to separate and sharpen. It is now realized that benzene was a poor choice as a diluant because it commonly

Figure 7. A mechanism for intermolecular exchange of the exocyclic R group at phosphorus in 1-R-1-phospha-2,6-dioxacyclohexanes


R
P
O
O
R'
H_B'
H_B
H_A'
H_A
R_A
R_B

causes resonances to shift to higher field to different extents. Consider a case where two 4-methyl groups are exchanging axial, equatorial positions and have the same probability of being in either position. The shape of the two coalescing spectral lines depends on the product of the magnitude of the frequency difference of the lines in the absence of exchange ($|\nu_A - \nu_B|$) and the lifetime (2τ) of a methyl group in either site. Thus, any agent that causes $2\tau|\nu_A - \nu_B|$ to increase will cause the lines to separate and sharpen (138, p. 223). Benzene has been observed to cause $|\nu_A - \nu_B|$ to increase in instances where line broadening has not been noted. Thus, it is not known for certain that dilution with benzene causes 2τ to increase also. Goldwhite and Fontal (15) found that the process causing the two methyl resonances of the five-membered cyclic compound 1-chloro-3,3,4,4-tetramethyl-1-phospha-2,5-dioxacyclopentane to coalesce could be slowed by diluting the compound with benzene, toluene, chloroform and dioxane. These authors determined coalescence temperatures for a neat sample (-23°C) and two toluene solutions and determined peak positions as a function of concentration in benzene. The results for the aromatic solvents are meaningless if these solvents cause $|\nu_A - \nu_B|$ to change with concentration. Dilution with chloroform and dioxane should not cause $|\nu_A - \nu_B|$ to change appreciably; therefore, the rate controlling process seems to be intermolecular. There is no obvious reason why a similar process should not occur for the six-membered cyclic compounds. Secondly, tetraphenylarsonium chloride causes the 3,5-dimethyl resonances of XLII to broaden. This is reasonable if the rate-controlling step of the process involves attack of chlorine on the cyclic molecule. It is not possible, from the available facts, to distinguish between dissociative and nondissociative mechanisms. Examination of molecular models shows that a four-center collision complex is sterically more favorable if the R group is axially rather than equatorially disposed. However, it is impossible to place both attacking atoms in positions to simultaneously undergo the idealized Walden inversion shown below. One possibility



would be attack of an undissociated R on the phosphorus atom of a second molecule, dissociation of the anion R^- of the second molecule and then attack of this R^- on phosphorus of the first molecule. The second R may attack the first phosphorus before it is completely dissociated from the second phosphorus.

The proposed mechanism can readily account for the temperature dependence of the spectra of the two pairs of isomers XXXIX A, B and XLV A, B. In each isomer, R_A and R_B are different, i.e., CH_2Cl and CH_3. For both pairs, an increase of the temperature causes resonances characteristic of two isomers to coalesce. The mechanism shown in Figure 7 allows the phosphorus lone-pair and R group to remain in their favored stereochemistry and also allows the carbon end of each molecule to flip rapidly. Thus, for the isomeric pairs, this process is an isomerization. The ratio of axial to equatorial R_A is determined by the relative preferences of R_A and R_B for the axial and equatorial positions. This ratio is about

1.8-2.8:1 at 148° for $R_A = CH_2Cl$ in XXXIX A and B as determined by the positions of the coalesced chloromethyl and methyl resonances relative to the resonances in the absence of exchange. This ratio is similar to the ratio of fluoro isomers XXXVII A, B at 161° and indicates that the stereochemistry at phosphorus is the same in both chloro and fluoro isomers. Since H_A, H_A', H_B and H_B' do not change their <u>cis</u>, <u>trans</u> roles relative to R_A and R_B, the chemical shifts of H_A and H_A' are not expected to become equal to those of H_B and H_B' at any temperature. The methylene resonance of a mixture of XLV A and B changes from a complex resonance at 40° to two observable lines of different width at 161°. Unfortunately, all that can be concluded is that $[\nu_{AB} + \frac{1}{2}(J_{AX} - J_{BX})]^2/(2J_{AB})$ is becoming small (139). Rapid flipping of the carbon end of the molecule should cause $(J_{AX} - J_{BX})$ to be less than the 4 ± 1 Hz observed for XLV A at 40° (C_6H_6). Since the methylene protons are changing their axial, equatorial roles, ν_{AB} should also be less than when one pair is always axially and the other equatorially positioned. Thus, when coalescence is complete, the coupling constants and chemical shifts of all protons should be averages weighted according to the ratio of time spent by each nucleus in different environments.

The 1-chloro derivative XLI A exhibits no spectral broadening from -30° to 158° and tetraphenylarsonium chloride does not cause the 3,5-dimethyl resonance to broaden. The proposed exchange mechanism can account for this behavior in the following way. Although the stereochemistry at phosphorus is the same in the initial and final structures, the 3,5-methyl groups change from equatorial to axial positions. The latter positions should be sterically very unfavorable and flipping of the carbon end of the ring should be slow relative to the nmr time scale. Even if the flipping rate were great, the weighted average chemical shift of the methyl groups would be practically identical to the shift in non-exchanging XLI A and no broadening would be observed. In other words, the two sites of the methyl groups have very different probabilities of being occupied.

If the proposed mechanism is correct, the chemical shifts of the two exocyclic substituents at each ring carbon atom in XXXVIII, XLIV and other compounds with two identical substituents at these carbons should become equal at a sufficiently-high temperature. Such a temperature has yet to be found. The bromo derivative XLIV exhibits the most broadening at room temperature but has not been examined at higher temperatures. The 1-chloro derivative XLII derived from d,l-2,4-pentanediol should exhibit one 3,5-methyl resonance at high-enough temperatures. The two doublets do coalesce but the peaks of the resulting doublet at 139° still have $W_{1/2} = 3.2 \pm 0.2$ compared to $W_{1/2} = 0.8 \pm 0.1$ for the XLI A in the same sample.

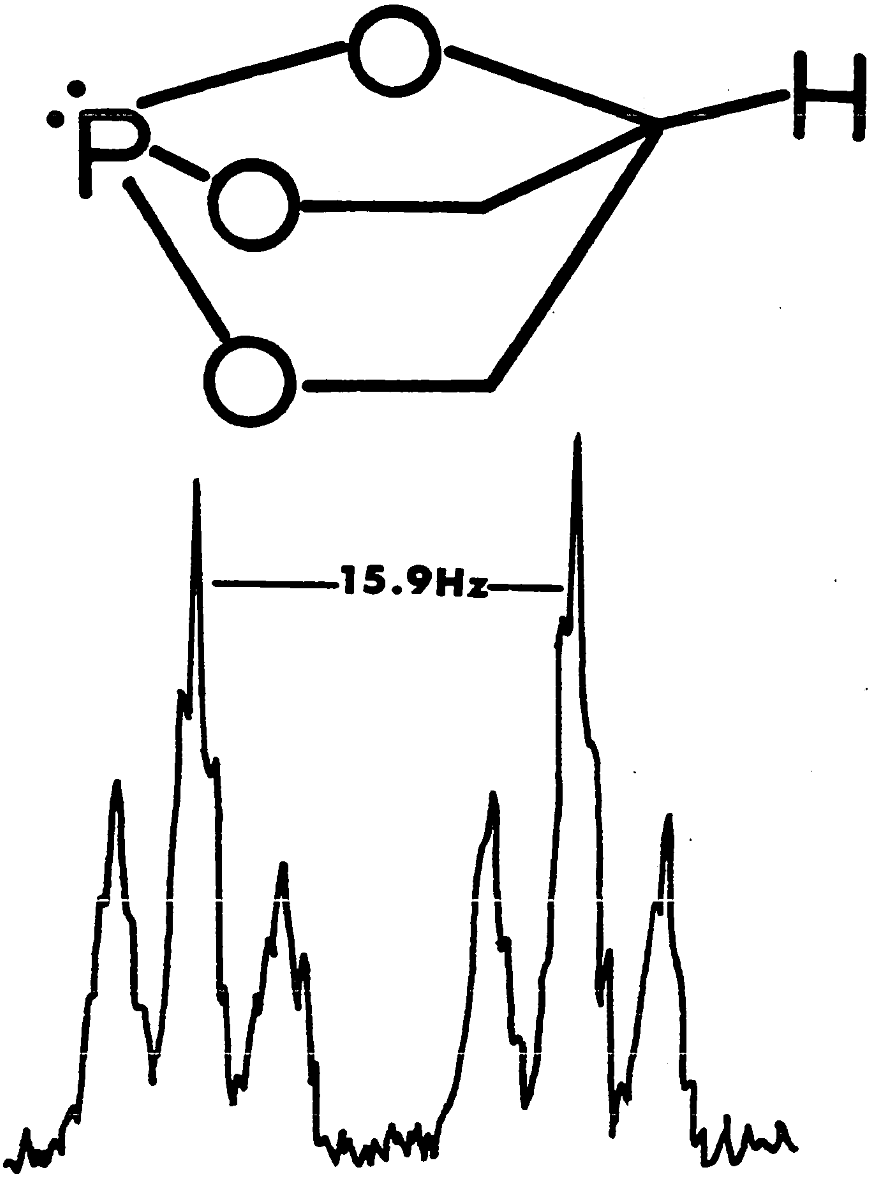
The rate of exchange for the isomeric pairs XXXI A-B, XXXVII A-B, XXXIX A-B and XLV A-B depends on the exocyclic R in the order: $CH_3O < F < Cl < Br$. The order $CH_3O < F$ is based on the fact that the ratio of the fluoro isomers changed appreciably from 40° to 161° whereas the ratio of methoxyl isomers did not during approximately the same length of time. A difference in the rate of intramolecular inversion of the bonds to phosphorus or the presence of an isomerization catalyst in the sample of fluoro isomers could also account for this observation. Nevertheless, the exchange rate for XXXI A, B appears to be quite small. The extent of spectral broadening at a given temperature can be used as an indication of relative exchange rate for a series of compounds if the uncoalesced lines are equally separated in all the compounds. Thus, the 4-methyl resonances in the pairs being discussed are separated by 0.52, 0.51 and 0.46 ppm, respectively, at room temperature. The value for the chloro compound may be small because the lines are slightly broadened at this temperature. The separation for the bromo compound is probably similar to that for the others and, if so, the order Cl < Br follows. Likewise, the separations of the 4,4-dimethyl resonances in XXIX, XXXVI and XXXVIII are 0.49, 0.48 and 0.43 ppm, respectively, at room temperature. If the separation for the chloro and bromo isomers is assumed to be approximately the same, then the exchange rate order is $(CH_3O,F) <$ Cl < Br. The methoxyl and fluoro derivatives cannot be compared because no temperature dependence was observed in this investigation or by Gagnaire, et al. (30).

F. Description and Analysis of ^{31}P and ^1H NMR Spectra of 2,6,7-Trioxa-1-phosphabicyclo [2.2.1] heptane (CV)

The ^1H and ^{31}P nuclei of CV constitute an $AA'BB'MX$ spin system. The nuclei are labeled in Table 11. The complete spectrum is shown in Figure 8. Trial magnitudes of the chemical shifts and other coupling constants, except $J_{AB'}$ $(= J_{A'B})$, $J_{AA'}$ and $J_{BB'}$, were obtained by analyzing the spectrum as an $AA'GG'MX$ type without appreciable J(HCCCH). In this approximation, the X resonance should be a doublet (J_{MX}) of triplets $(J_{AX} = J_{A'X})$ of triplets $(J_{GX} = J_{G'X})$; the M resonance a doublet (J_{MX}) of triplets $(J_{AM} = J_{A'M})$ of triplets $(J_{GM} = J_{G'M})$; the GG' re-

Figure 8. The ^1H and ^{31}P nmr spectra of 2,6,7-trioxa-1-phosphabicyclo [2.2.1] heptane (CV)

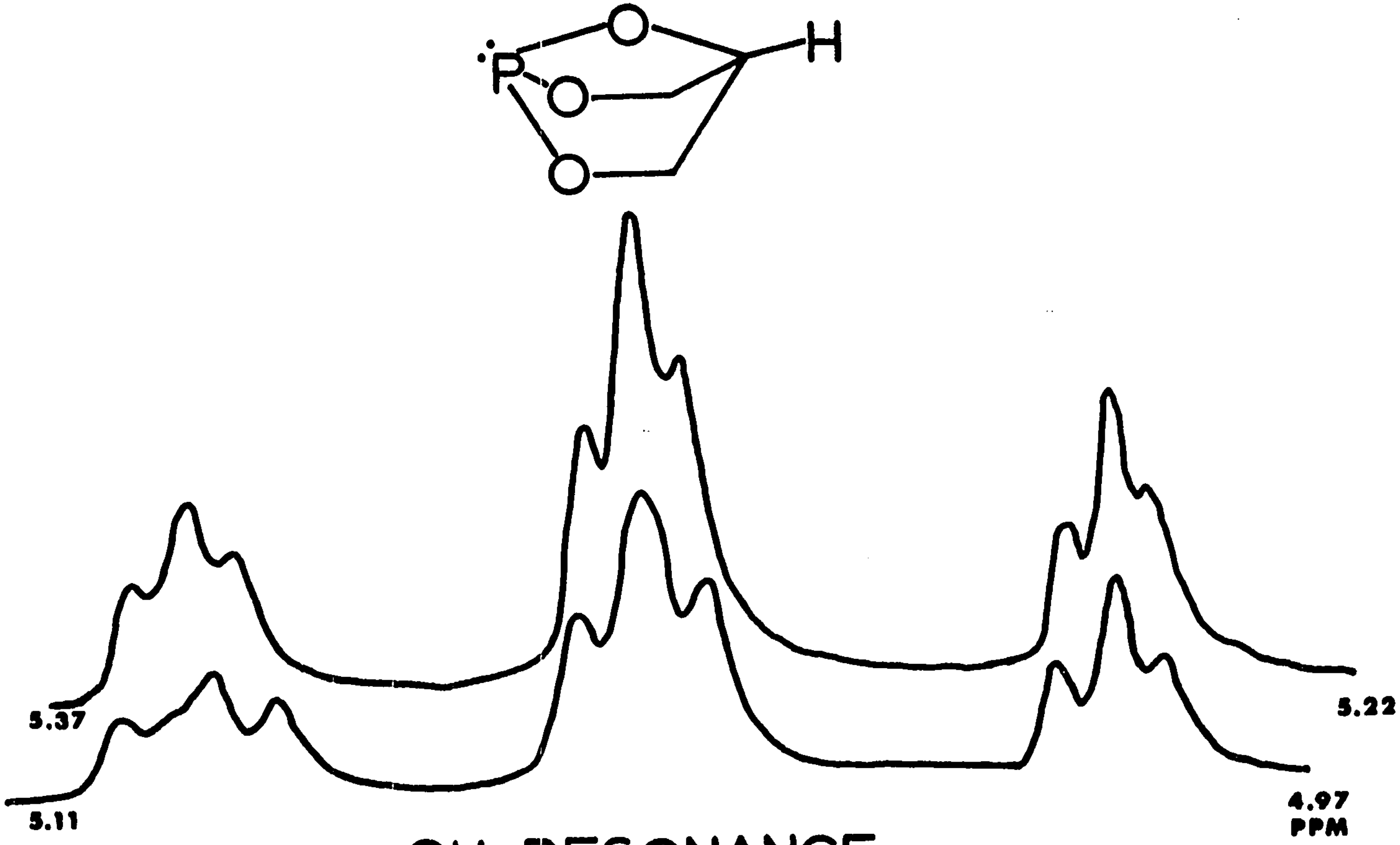
a. The ^{31}P resonance.



P RESONANCE

Figure 8 (continued)

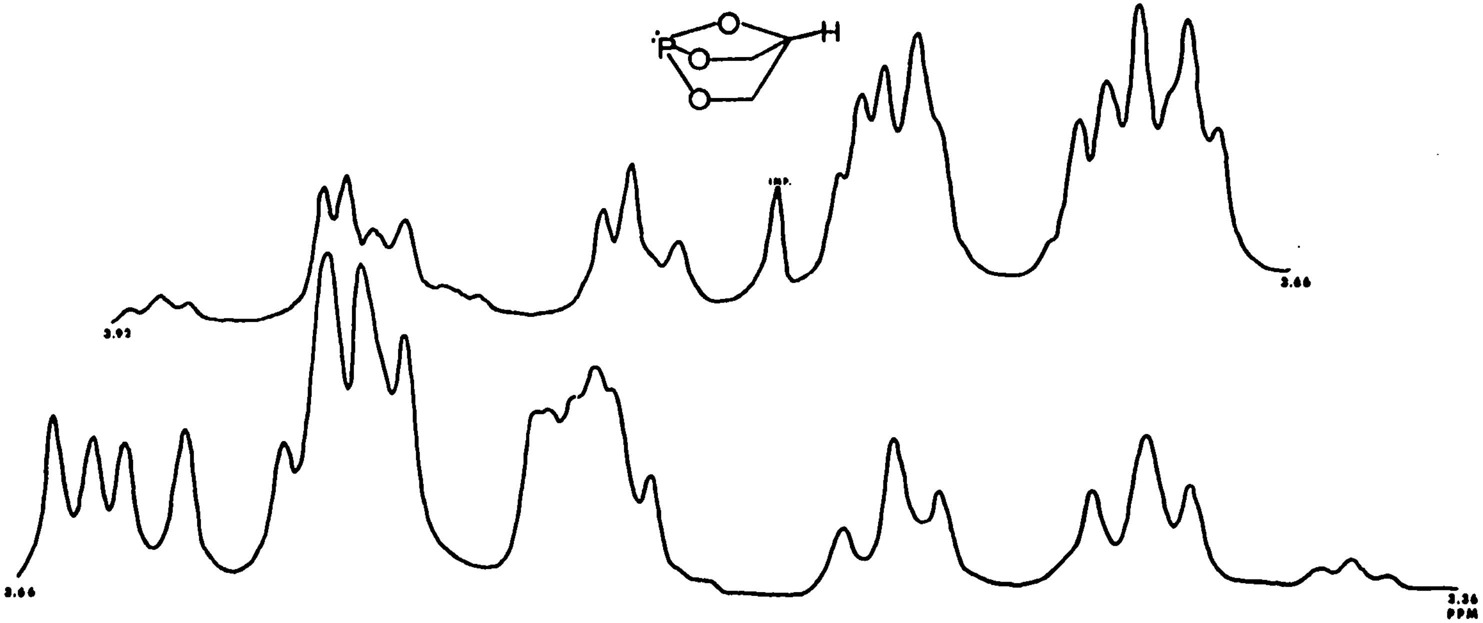
b. The bridgehead ^1H resonance.



CH RESONANCE

Figure 8 (continued)

c. The methylene ^1H resonance. One peak is assigned to an impurity (IMP) because its relative intensity changed by a factor of three when CV was recrystallized.



CH_2 RESONANCE

sonance a doublet (J_{AG} or $J_{A'G'}$) of doublets (J_{GM} or $J_{G'M}$) of doublets (J_{GX} or $J_{G'X}$) and the AA$'$ resonance a doublet (J_{AG} or $J_{A'G'}$) of doublets (J_{AM} or $J_{A'M}$) of doublets (J_{AX} or $J_{A'X}$). The spacing due to J_{MX} is common to the M and X resonances and is 15.88 Hz (M resonance). The other spacings in the X resonance are approximately 3.6 and 0.6 Hz and those in the M resonance are 3.1 and 0.3 Hz. The approximate mirror-plane-symmetry of the AA$'$BB$'$ resonance suggests that one pair of protons is more strongly coupled to X and less strongly coupled to M than the other pair. The magnitude of J_{AB} was estimated as 7.0 Hz. The chemical shifts of the AA$'$ and BB$'$ protons were initially arbitrarily taken as the centers of the high- and low-field halves, respectively, of the AA$'$BB$'$ resonance. After establishing these trial parameters, approximate magnitudes of the J(HCCCH) coupling constants were determined by calculating, with the aid of LAOCN 3 (140), the AA$'$BB$'$ part of the spectrum with various sets of J(HCCCH) values until calculated lines could be associated with the four peaks at the center and the triplet at each end of the resonance. Vicinal J(POCH) (see Section IV.J.1) and J(HCCH) (141, pp. 172-4) couplings were made positive and J(HCH) and J(HCCCH) couplings were made negative (141, pp. 172-4). LAOCN 3 (140) was then used to determine a best set of parameters. The X resonance peak positions were used only in the earlier iterations because they are known with less accuracy and precision than those of the ^1H resonances. Use of the above coupling constant signs led to a root mean square error of calculated <u>versus</u> observed line positions no less than 0.15 Hz. However, when $J_{AA'}$ was made positive, iteration led to a root mean square error of 0.061 Hz. After this change, neither interchange of the chemical shifts of AA$'$ and BB$'$ nor interchange of these shifts and $J_{AA'}$ and $J_{BB'}$ allowed an iteration giving a rms error less than 0.14 Hz. Thus, the smaller J(POCH), larger J(HCCH) and largest J(HCCCH) appear to be associated with the methylene protons (AA$'$) resonating at higher applied magnetic field. The best set of parameters and related information are given in Table 11. No additional reversals of coupling constant signs or interchanges of parameters were attempted to determine their uniqueness.

The final coupling constants and chemical shifts can be tentatively assigned to nuclei as shown in Table 11. The large J(HCCCH) is associated with the exo protons because they are undoubtedly linked by a planar W arrangement of bonds. Examination of a molecular model shows that the HCCH dihedral angles are ca. 80° (endo) and ca. 40° (exo). The smaller J(HCCH) value of 0.16 Hz can be associated with the endo protons and the larger magnitude of 3.34 Hz with the exo protons if J(HCCH) is related to the HCCH dihedral angle as it is in hydrocarbons (151), where J(HCCH) is a maximum for dihedral angles of 0° and 180° and a minimum for an angle of 90°. It is not unreasonable that the exo protons resonate at higher field than the endo protons since the equatorial OCH_2 protons resonate at higher field than the axial OCH_2 protons in all the 1-R-1-phospha-2,6-dioxacyclohexanes studied thus far. The J(POCH) values of 0.29 Hz is associated with the exo protons and that of 3.83 Hz with the endo protons as a consequence of the foregoing assignments.

Robert (99a) examined the ^1H nmr spectrum of a CCl_4 solution of CV at 100 MHz. The small spacings of about 0.3 Hz in the M resonance were not noted. The results of the AA$'$BB$'$MX analysis are given in Table 11. They compare very favorably with those found independently from the 60 MHz spectrum. The coupling constants and chemical shifts were associated with the nuclei in the manner described above. Robert could not determine the relative signs of J(BX) and J(AX).

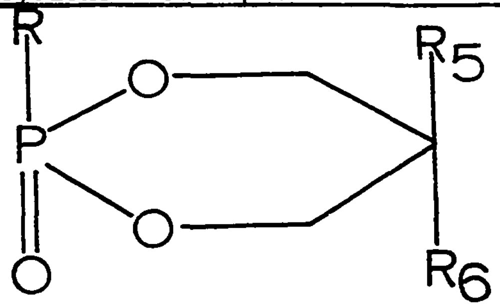
Spectra of CV in acetonitrile and deuteriochloroform appear similar to the neat spectrum. However, dilution with benzene causes the AA′ and BB′ resonances to move upfield and converge, resulting in a limiting resonance of three intense lines and some very weak outer lines, as observed at 500 Hz sweep width with a Varian A 60 spectrometer. The M resonance moves upfield more rapidly than the others and additional lines appear.

G. Stereochemistry of 1-Oxo-1-R-1-phospha-2,6-dioxacyclohexanes

1. ^{1}H nmr spectra

a. Results of analysis   Tables 14 and 15 contain the results of analysis of 77 ^{1}H nmr spectra of 34 1-oxo-1-R-1-phospha-2,6-dioxacyclohexanes. Some of the compounds were examined at more than one concentration or temperature or in more than one solvent. Each of the pairs of spectra III′c-d, III′e-f, XIX′c-d, XIX′e-f, XIX′g-h and XXXIII′c-d represents the highest and lowest temperature spectra that were analyzed at the listed concentration and solvent. The spectral parameters at temperatures between the limits are qualitatively those expected by interpolation. Included in Tables 14 and 15 are pertinent results from the literature (35, 39, 40, 98). All of the 4-halomethyl-4-alkyl derivatives, except XXX′, have the trans-1-R-4-halomethyl configuration because they were prepared from $P(OCH_2)_3CR_5$ by the Michaelis-Arbuzov reaction (42); compound XXX′ has been concluded to have the opposite configuration (42).

Table 14. Results of spectral analysis of some 1-R-1-oxo-1-phospha-2,6-dioxacyclohexanes - part 1



Compound and Spectrum Number	R	R_5	R_6	Ring Methylene Proton Chemical Shifts	
				A	B
I′a	$C(C_6H_5)_3$	CH_3	CH_3	3.45	4.22
b				3.46	4.26
II′a	$C(C_6H_5)_3$	CH_3	CH_2Br	3.42	4.28
III′a	$C(C_6H_5)_3$	CH_3	CH_2Cl	3.00	4.04
b				3.49	4.43
c				3.47	4.41
d				3.45	4.35
e				2.91	3.91
f				2.97	3.93
g				3.37	4.25
IV′ a	$C(C_6H_5)_3$	$\underline{n}$-C_3H_7	CH_2Cl	3.46	4.24
V′ a[d]	$C(CH_3)_2OH$	[CH_2OH,	CH_3]	4.79	4.39

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[a] The protons coupled more strongly to phosphorus are designated A.

[b] C_5H_5N = pyridine and C_6H_7Cl = $\underline{\alpha}$ - chloronapthalene.

[c] The eight- five-and two-line spectra contain no, one and two collapsed AB quartets, respectively. A quartet is considered collapsed if the two central lines cannot be resolved.

[d] Isomer unknown.

Ring J(POCH) Coupling Constants[a]		Solvent[b]	Concentration Molarity	Temperature, °C	Spectrum[c]	Analysis
A	B					
14.6	6.5	$CDCl_3$	1.0	30	8	ABX
14.2	6.5	$CDCl_3$	0.12	40	8	AMX
11.4	9.4	$CDCl_3$	0.46	40	8	ABX
12.7	8.0	C_6H_6	0.17	40	8	AMX
11.2	9.2	C_5H_5N	0.54	40	8	ABX
10.9	9.5	C_5H_5N	0.38	36	8	AMX
11.4	9.1	C_5H_5N	0.38	84	8	AMX
11.5	9.1	C_6H_7Cl	0.16	92	8	AMX
11.7	9.0	C_6H_7Cl	0.16	122	8	AMX
11.0	9.8	$CDCl_3$	0.27	40	8	ABX
11.5	9.5	$CDCl_3$	0.27	40	8	ABX
10.6	9.4	C_5H_5N	0.31	40	8	ABX

Table 14 (continued)

Compound and Spectrum Number	R	R_5	R_6	Ring Methylene Proton Chemical Shifts A	B
VI′ a[e]	$C(CH_3)_3$	CH_3	CH_3	3.70	4.35
VII′a[e]	$CH(CH_3)(C_2H_5)$	CH_3	CH_3	3.77	4.25
VIII′ a	OCH_3	CH_3	CH_3	Average =	4.01
b				Average =	3.92
c				Average =	3.55
IX′ a	$OC(CH_3)_3$	CH_3	CH_3	3.85	4.04
X′ a[i]	OCH_3	H	$C(CH_3)_3$	4.40	4.40
XI′ a[i]	OCH_3	$C(CH_3)_3$	H	4.42	4.25
XII′ a[k]	OC_6H_5	CH_3	CH_3		
XIII′a	NC_5H_{10}[l]	C_2H_5	CH_2Cl	4.00	4.34

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[e] Reference 35.

[f] Approximately 10% (35).

[g] Ambient (35).

[h] Spectra at 60 and 100 MHz were analyzed.

[i] Reference 98.

[j] Approximately 20% (98).

[k] Reference 40.

[l] Piperidino.

Ring J(POCH) Coupling Constants[a]						
A	B	Solvent[b]	Concentration Molarity	Temperature, °C	Spectrum[c]	Analysis
19	2	$CDCl_3$	---[f]	---[g]	8	ABX
15.4	5.2	$CDCl_3$	---[f]	---[g]	8	ABX
Sum	= 23.6	$CDCl_3$	1.9	40	5	ABX
Sum	= 24.0	CCl_4	0.16	40	5	ABX
Sum	= 23.4	C_6H_6	0.54	40	5	ABX
21.0	3.3	$CDCl_3$	1.1	30	8	ABX[h]
Sum	= 23.4	$CDCl_3$	---[j]	35		AA'BB'XY
22.8	1.14	$CDCl_3$	---[j]	35		AA'BB'XY
21	3	$CHCl_3$				
15.6	9.0	$CDCl_3$	1.0	40	8	ABX

Table 14 (continued)

Compound and Spectrum Number	R	R_5	R_6	Ring Methylene Proton Chemical Shifts A	B
XIV′ a[e]	$NHC(CH_3)_3$	CH_3	CH_3	3.85	4.22
XV′ a[e]	$NHC(CH_3)_3$	C_2H_5	C_2H_5	3.90	4.20
XVI′ a[m]	NH(<u>n</u>-C_3H_7)	CH_3	CH_3		
XVII′ a[m]	$N(C_2H_5)_2$	CH_3	CH_3		
XVIII′ a	CH_3	CH_3	CH_3	3.84	4.16
b				3.22	3.92
XIX′ a	CH_3	CH_3	CH_2Br	4.30	4.08
b				4.33	4.00
c[n]				4.37, 4.34	4.18, 4.21
d				4.33	4.04
e				Average =	4.30
f[n]				4.24, 4.28	4.15, 4.10
g				3.74	3.19
h				Difference =	0.57
i				3.91	3.28
XX′ a	CH_3	CH_3	CH_2I	3.22	3.88
b				4.16	4.16
c				Average =	4.20
d				4.28	4.08
e				4.29	4.04
f				4.32	3.96
XXI′ a[i]	CH_3	$C(CH_3)_3$	H	4.43	4.13
b[i]					
XXII′ a[i]	CH_3	H	$C(CH_3)_3$	4.30	4.40
XXIII′ a	C_2H_5	CH_3	CH_2Br	3.22	3.98
b				4.34	3.99

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[m] Reference 39.

[n] The correct set of parameters has not been determined. The entries on the left side of each column and those on the right side constitute the two sets.

Ring J(POCH) Coupling Constants[a]						
A	B	Solvent[b]	Concentration Molarity	Temperature, °C	Spectrum[c]	Analysis
16.3	7.8	$CDCl_3$	---[f]	---[g]	8	ABX
16.5	8.0	$CDCl_3$	---[f]	---[g]	8	ABX
20.8	2.9	C_6D_6				
21.5	2	C_6D_6				
12.8	10.2	$CDCl_3$	2.6	30	8	ABX[h]
15.2	8.0	C_6H_6	0.17	40	8	ABX
16.6	7.1	$CDCl_3$	1.8	40	8	ABX
14.6	8.4	$CDCl_3$	0.68	40	8	ABX
19.5, 23.2	4.3, 0.6	$CDCl_3$	0.76	-52	8	ABX
15.8	7.2	$CDCl_3$	0.76	1	8	ABX
Sum =	24.4	C_5H_5N	1.0	36	5	ABX
22.7, 17.5	0.9, 6.1	C_5H_5N	1.0	84	8	ABX
14.9	8.7	C_6H_7Cl	0.35	75	8	ABX
12.7	10.8	C_6H_7Cl	0.35	164	8	ABX
13.0	10.6	C_6H_6	0.13	40	8	ABX
12	11	C_6H_6	0.12	40	8	AMX
19.8	3.2	CD_3CN	1.2	40	8	ABX[h]
Sum =	23.5	$CDCl_3$	2.3	40	5	ABX
16.5	7.8	$CDCl_3$	1.3	40	8	ABX
14.5	8.7	$CDCl_3$	0.63	40	8	ABX
12.7	10.9	$CDCl_3$	0.13	40	8	ABX
16.9	6.80	$CDCl_3$	---[j]	35		AA′BB′XY
22.7	6.40	$CDCl_3$	---[j]	-54		AA′BB′XY
20.2	4.14	$CDCl_3$	---[j]	35		AA′BB′XY
13	10	C_6H_6	0.088	40	8	AMX
13.0	10.0	$CDCl_3$	0.92	40	8	ABX

Table 14 (continued)

Compound and Spectrum Number		R	R_5	R_6	Ring Methylene Proton Chemical Shifts A	B
XXIV′	a	<u>n</u>-C_3H_7	CH_3	CH_2Br	4.05	3.47
	b				4.34	3.96
	c				4.36	3.93
XXV′	a	<u>n</u>-C_3H_7	CH_3	CH_2I	4.28	4.00
	b				4.04	3.50
XXVI′	a	C_6H_5	CH_3	CH_3	3.48	4.06
	b				3.38	4.07
	c				3.88	4.26
	d				3.73	4.35
	e				3.74	4.36
	f				4.13	3.89
	g				4.14	3.90
	h				4.15	3.91
	i				4.14	3.89
	j				4.14	3.89
XXVII′	a[e]	$CH_2C_6H_5$	CH_3	CH_3	3.70	4.17
XXVIII′	a[e]	$CH_2C_6H_5$	CH_3	CH_2Cl	4.33	3.79
XXIX′	a	$CH_2C_6H_5$	C_2H_5	CH_2Cl	4.16	3.95
	b				4.25	3.82
	c				3.92	3.15
XXX′	a	$CH_2C_6H_5$	CH_2Cl	C_2H_5	3.94	4.30
XXXI′	a	Br	H	CH_2Br	Average =	4.61
XXXII′	a[n]	Br	CH_3	CH_2Br	4.22, 4.32	4.45, 4.36

Ring J(POCH) Coupling Constants[a]		Solvent[b]	Concentration Molarity	Temperature, °C	Spectrum[c]	Analysis
A	B					
11.3	11.3	C_6H_6	0.35	40	8	ABX
12.8	10.2	$CDCl_3$	0.72	40	8	ABX
11.5	11.3	$CDCl_3$	0.22	40	8	ABX
13.0	9.8	$CDCl_3$	0.89	40	8	ABX
11.2	11.2	C_6H_6	0.59	40	8	AMX
13.8	9.3	C_6H_6	0.65	40	8	ABX
15.4	7.0	C_6H_6	0.14	40	8	ABX
12.8	10.8	$CDCl_3$	1.3	40	8	ABX
16.9	6.5	CCl_3F	0.042	40	8	ABX
16.4	6.5	CCl_4	0.14	40		
13.5	9.5	CH_3CN	1.6	40	8	ABX
13.8	9.6	CH_3CN	0.26	40	8	ABX
15.6	8.6	CH_3CN	1.5	-40	8	ABX
13.4	9.8	CH_3CN	1.5	50	8	ABX
12.6	10.4	CH_3CN	1.5	80	8	ABX
14.9	7.8	$CDCl_3$	---[f]	---[g]	8	ABX
12.0	11.0	$CDCl_3$	---[f]	---[g]	8	ABX
15.1	7.3	$CDCl_3$	1.5	40	8	ABX[h]
11.8	10.2	$CDCl_3$	0.40	40	8	ABX
11.2	11.2	C_6H_6	0.09	40	8	AMX
18.8	4.6	$CDCl_3$	0.75	40	8	ABX
Sum =	34.0	$CDCl_3$	0.90	40	5	ABX
18.7,30.3	14.8,3.0	$CDCl_3$	0.79	40	8	ABX

Table 14 (continued)

Compound and Spectrum Number		R	R_5	R_6	Ring Methylene Proton Chemical Shifts A	B
XXXIII′	a	Cl	CH_3	CH_3	Average =	4.27
	b				Average =	4.16
	c				Average =	3.23
	d				Average =	3.40
XXXIV′	a	H	CH_3	CH_3	Average =	3.54
	b				Average =	3.98

Ring J(POCH) Coupling Constants^a		Solvent^b	Concentration Molarity	Temperature, °C	Spectrum^c	Analysis
A	B					
Sum	= 32.2	$CDCl_3$	0.37	-61.5	5	ABX
Sum	= 31.4	$CDCl_3$	0.44	40	5	ABX
Sum	= 30.8	C_6H_7Cl	0.30	40	5	ABX
Sum	= 30.6	C_6H_7Cl	0.30	95	5	ABX
Sum	= 26.8	C_6H_6	1.1	40	5	ABX
Sum	= 26.6	CCl_4	0.070	40	2	ABX

Table 15. Results of spectral analysis of some 1-R-1-oxo-1-phospha-2,6-dioxacyclohexanes - part 2

Compound and Spectrum Number		R	R_5	R_6	Chemical Shifts			Coupling Constants
					R	R_5^a	R_6^a	
I′	a	$C(C_6H_5)_3$	CH_3	CH_3		[0.76	0.96]^b	
	b				7.08-7.63	[0.78	0.98]^c	
II′	a	$C(C_6H_5)_3$	CH_3	CH_2Br	7.15-7.60	0.80	3.48	
III′	a	$C(C_6H_5)_3$	CH_3	CH_2Cl		0.38	2.96	
	b					0.75	3.82	
	c					0.75	3.82	
	d					0.74	3.75	
	e					0.23	3.17	
	f					0.28	3.18	
	g				7.18-7.63	0.76	3.63	
IV′	a	$C(C_6H_5)_3$	n-C_3H_7	CH_2Cl	7.16-7.55	0.67-1.25	3.63	
V′	a^d	$C(CH_3)_2OH$	[CH_2OH,	CH_3]	$\delta CH_3 = 1.74$	3.83	1.16	$J(PCCH_3) = 15.2$
VI′	a^e	$C(CH_3)_3$	CH_3	CH_3	1.27	0.87	1.25	$J(PCCH_3) = 16.8$
VIII′	a	OCH_3	CH_3	CH_3	3.80	0.91	1.26	[$J(POCH_3) = 10.9$]
	b				3.75	0.90	1.24	
	c				3.46	0.28	0.89	
IX′	a	$OC(CH_3)_3$	CH_3	CH_3	1.51	0.88	1.24	
X′	a^f	OCH_3	H	$C(CH_3)_3$		1.83	1.00	$J(HCCH_A)+J(HCCH_B) = 11.8$
XI′	a^f	OCH_3	$C(CH_3)_3$	H		2.10	0.92	$J(HCCH_A) = 4.44$ $J(HCCH_B) = 11.6$

XIII′	a	NC_5H_{10}	C_2H_5	CH_2Cl	2.9-3.4, 1.4-1.7	0.8-1.1, 1.4-1.9	3.52	
XIV′	a[e]	$NHC(CH_3)_3$	CH_3	CH_3		0.98	1.16	
XVI′	a[g]	NH(<u>n</u>-C_3H_7)	CH_3	CH_3		[0.32	0.95][h]	
XVII′	a[g]	$N(C_2H_5)_2$	CH_3	CH_3		[0.28	0.93][h]	
XVIII′	a	CH_3	CH_3	CH_3	1.57	1.06	1.09	$J(PCH_3) = 17.2$
	b				1.15	0.42	0.67	$J(PCH_3) = 17.5$

---

[a] When $R_5 = R_6 = CH_3$, the broader resonance is listed under R_6.

[b] The relative widths of the resonances could not be determined from this spectrum.

[c] The half widths of the two resonances are very similar.

[d] Isomer unknown.

[e] Reference 35.

[f] Reference 98.

[g] Reference 39.

[h] The relative widths of the resonances were not given (39).

Table 15 (continued)

Compound and Spectrum Number	R	R_5	R_6	Chemical Shifts			Coupling Constants
				R	R_5^a	R_6^a	
XIX′ a	CH_3	CH_3	CH_2Br	1.62	1.04	3.63	$J(PCH_3)$ = 16.6-17.1
b				1.59	1.10	3.54	
c				1.70	1.06	3.71	
d							
e				1.70	0.94	3.80	
f				1.59	0.95	3.68	
g				1.07	0.30	2.94	
h							
i				1.08	0.57	2.88	
XX′ a	CH_3	CH_3	CH_2I	1.05	0.56	2.53	$J(PCH_3)$ = 16.9-17.2
b				1.54	0.94	3.50	
c				1.61	1.03	3.46	
d				1.62	1.08	3.42	
e				1.60	1.09	3.37	
f				1.59	1.12	3.30	
XXI′ a^f	CH_3	$C(CH_3)_3$	H		0.95	2.15	$J(HCCH_A)$ = 4.74, $J(HCCH_B)$ =10.1
b^f							$J(HCCH_A)$ = 5.5, $J(HCCH_B)$ =10.8
XXII′ a^f	CH_3	H	$C(CH_3)_3$		2.05	0.97	$J(HCCH_A)$ = 4.47, $J(HCCH_B)$ =10.5
XXIII′ a	C_2H_5	CH_3	CH_2Br		0.64	2.66	
b					1.12	3.50	
XXIV′ a	$\underline{n}$-C_3H_7	CH_3	CH_2Br		0.73	2.99	

	b					1.14	3.49	
	c					1.16	3.45	
XXV′	a	$\underline{n}$-C_3H_7	CH_3	CH_2I		1.10	3.33	
	b					0.73	2.75	
XXVI′	a	C_6H_5	CH_3	CH_3		0.75	0.62	
	b					0.45	0.74	
	c				7.32-8.18	1.07	1.07	
	d				7.17-8.00	0.98	1.26	
	e				7.35-8.08	1.00	1.25	
	f					0.96	1.13	
	g					0.98	1.15	
	h				7.37-8.04	[0.92	1.16][c]	
	i				7.33-7.97	0.97	1.12	
	j					0.99	1.11	
XXVII′	a[e]	$CH_2C_6H_5$	CH_3	CH_3	δCH_2=3.28	0.95	0.81	$J(PCH_2)$=22.1
XXVIII′	a[e]	$CH_2C_6H_5$	CH_3	CH_2Cl	δCH_2=3.33	0.85	3.58	$J(PCH_2)$=21.7
XXIX′	a	$CH_2C_6H_5$	C_2H_5	CH_2Cl	δCH_2=3.27	0.53-1.47	3.60	[$J(PCH_2)$ = 20.6-21.2]
	b				δCH_2=3.29	0.55-1.47	3.57	
	c				δCH_2=2.97	0.15-0.97	2.93	
XXX′	a	$CH_2C_6H_5$	CH_2Cl	C_2H_5	δCH_2=3.25	0.60-1.48	3.11	$J(PCH_2)$=21.9
XXXI′	a	Br	H	CH_2Br		2.1-2.6	3.68	
XXXII′	a	Br	CH_3	CH_2Br		1.01	3.68	
XXXIII′	a	Cl	CH_3	CH_3		1.37	1.00	
	b					0.95	1.34	
	c					-0.23	0.58	
	d					-0.053	0.68	
XXXIV′	a	H	CH_3	CH_3	5.55	0.37	0.94	J(PH) = 666
	b					0.98	1.22	

The configuration of V′is uncertain, even though it was derived from $P(OCH_2)_3CCH_3$, inasmuch as the reaction mechanism is unknown (43). The configurations of X′, XI′, XXI′ and XXII′ have been determined by Bentrude and Hargis (98). The molar concentrations were determined by comparison of the peak heights of spectra to those for a solution of accurately determined concentration. These concentrations may be in error by 10 or 20% but are qualitatively useful.

The methods of analysis of spectra examined by the author are described in Section IV.B. The "Analysis" and "Spectrum" columns of Table 14 indicate the type of spectrum and the approximation used for analysis, respectively. These spectra were obtained over a period of at least five years and most of them before an adequate appreciation of the important features of AMX, ABX, AA′BB′X and other more complicated spectra had been obtained by those who recorded the spectra. For example, the methylene resonance was seldom expanded so that more precise line positions could be obtained. Also, only a few compounds were examined at two external magnetic field strengths, partially because the second field strength was not available for several years. In addition, the 4-methyl resonances were not expanded to determine accurate values of $W_{1/2}$. Thus, better spectra and more rigorous analyses are possible. The magnitude of $J(H_AH_B)$, not included in Table 14, ranges from 10.6 to 12.1 Hz and averages about 11.2 Hz. Sometimes the ring J(POCH) values are close to $J(H_AH_B)$ and thus peaks overlap and cause the couplings to be less accurately determined.

Several deceptively simple spectra were encountered. The outer lines of the one approximately collapsed AB quartet were not visible in spectra

VIII′a-c, XX′c, XXXIII′ a,b,d and XXXIV′a but were visible in spectra XIX′e, XXXI′a and XXXIII′c. In all of these spectra the central lines of the quartet were not resolved and a determination of δ_A, δ_B, J(POCH$_A$) and J(POCH$_B$) was not considered justifiable. Thus, only $\frac{1}{2}(\delta_A + \delta_B)$ and the sum of J(POCH$_A$) and J(POCH$_B$) are reported. Spectrum XXXIV′ b exhibits only two lines for the methylene resonance but the signal to noise ratio is too small to justify analysis for individual chemical shifts and coupling constants.

b. Conclusions A very important feature of the spectral results is the dependence of the ring J(POCH) for some compounds on temperature, solvent or concentration. Dependence on at least one of these conditions has been found for XVIII′, XIX′, XX′, XXI′, XXVI′ and XXIX′. Edmundson (97) has found a temperature dependence for the ring methylene resonance of XIX′ and the other geometrical isomer and has attributed this dependence to conformational mobility; however, he did not report the coupling constants or chemical shifts at any temperature. In contrast, the triphenylmethyl derivative III′ exhibits less than 2 Hz variation in the J(POCH) for seven spectra in different solvents and at different temperatures. The variety of conditions for I′, XXIII′, XXIV′ and XXV′ is limited but changes of the ring J(POCH) are less than 2 Hz. Conditions were varied for VIII′, XXXIII′ and XXXIV′ but deceptively simple spectra have always been observed. The other compounds were not examined at more than one set of conditions.

A second feature of the results is the general constancy of the sum of J(POCH$_A$) and J(POCH$_B$) for the compounds examined under more than one set of conditions even when the individual couplings change; the only exceptions are XXI′ and XXXIII′. Also, this sum can be used to place all of the compounds except XXI′ into just four groups, as shown in Table 16.

Table 16. Sum of ring J(POCH) for 1-oxo-1-R-1-phospha-2,6-dioxacyclohexanes

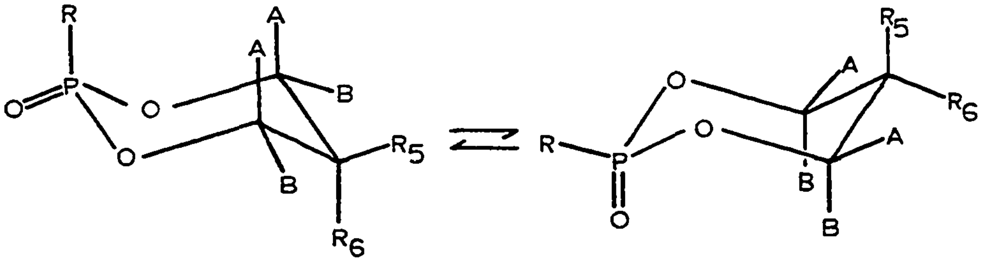
Group	Compounds	No. of Spectra	Mean $J(POCH_A)+J(POCH_B)$	Average Deviation from Mean	Range
1	I′-VII′	14	20.7	0.2	20.0-21.1
2a	VIII′-XVII′	12	23.9	0.3	23.4-24.6
2b	XVIII′-XXX′	42[a]	23.2	0.4	22.0-24.4
3	XXXI′-XXXIII′	6	32.1	1.1	30.6-34.0
4	XXXIV′	2	26.7	0.1	26.6-26.8

[a] Spectrum XXI′ b excluded.

The compounds, number of spectra, average sum, average deviation of the sums from the average and the range of the sums is given for each group. The grouping appears to be a function of R rather than R_5 and/or R_6 but the diversity of R in groups 2a and b is remarkably great. The division into 2a and b was made to separate the electronegative from the electropositive R groups and is not justified on the basis of the coupling constant sum. Group 1 is characterized by R groups with a secondary or tertiary carbon atom bonded to phosphorus. The second group is the largest and doesn't appear to be characterized by any particular factor. The 1-chloro and 1-bromo derivatives constitute group 3 and the single 1-

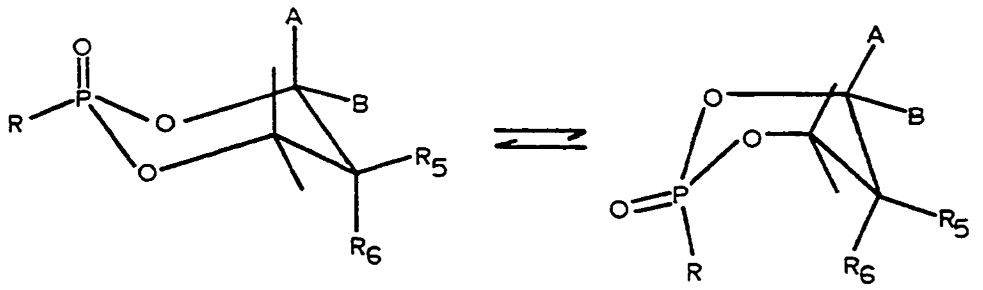
hydro compound XXXIV′ falls into a separate group 4. A similar grouping can be found for the 1-R-1-phospha-2,6-dioxacyclohexanes in Table 12. The derivatives with R = C_6H_5, OCH_3, O-t C_4H_9, OC_6H_5, SC_6H_5 and F have sums between 12.8 and 14.0; those with R = Cl and Br have sums between 16.2 and 17.0 and the dimethylamino derivative is unique with a sum of 23.4. The exceptions to the similarity between the trivalent and pentavalent compounds are the 1-amino compounds, XXXV(P^{III}) and XIII′ - XVII′(P^{V}). The latter fall into main group 2 and thus XXXV would be expected to be in the 12.8-14.0 Hz class. In fact, it has a sum very similar to those of XIII′- XVII′.

The spectral results are generally most consistent with the existence of chair conformers. The variation of spectral parameters with conditions is thus a consequence of a changing ratio of rapidly interconverting conformers. In conformer 1, shown below in equilibrium with conformer 2, the methylene protons labeled A occupy the axial positions but they become equatorially disposed in conformer 2.



1 2

Similarly, the equatorial B protons in conformer 1 become axially disposed in conformer 2. If J(POCH$_{ax}$) and J(POCH$_{eq}$) are independent of the disposition of the exocyclic substituents at phosphorus and C_4, the ratio of conformers is x:1 and the conformers are interconverting rapidly enough to give a weighted time averaged ^{1}H nmr spectrum, then $J(POCH_A) = (\frac{x}{x+1})\ J(POCH_{ax}) + (\frac{1}{x+1})\ J(POCH_{eq})$ and $J(POCH_B) = (\frac{x}{x+1})\ J(POCH_{eq}) + \frac{1}{x+1}\ J(POCH_{ax})$. The sum of $J(POCH_A)$ and $J(POCH_B)$ would always be the sum of $J(POCH_{ax})$ and $J(POCH_{eq})$, independently of x. If $J^1(POCH_{ax}) \neq J^2(POCH_{ax})$, i.e., $J(POCH_{ax})$ is not the same in the two conformers, and $J^1(POCH_{eq}) \neq J^2(POCH_{eq})$, then $J(POCH_A) = (\frac{x}{x+1})\ J^1(POCH_{ax}) + (\frac{1}{x+1})\ J^2(POCH_{eq})$ and $J(POCH_B) = (\frac{x}{x+1})\ J^1(POCH_{eq}) + (\frac{1}{x+1})\ J^2(POCH_{ax})$. This latter possibility would be consistent with a constant sum of $J(POCH_A)$ and $J(POCH_B)$ with changing conformer ratio if $[J^2(POCH_{ax}) - J^1(POCH_{ax})] = [J^1(POCH_{eq}) - J^2(POCH_{eq})]$. For example, the set $J^1(POCH_{ax}) = 2$, $J^1(POCH_{eq}) = 21$, $J^2(POCH_{ax}) = 4$, $J^2(POCH_{eq}) = 19$ cannot be distinguished from the set $J(POCH_{ax}) = 3$, $J(POCH_{eq}) = 20$ if the conformer ratio is unknown. An equilibrium between a chair and a boat conformer, such as that shown below, is unreasonable but cannot be ruled out. If J(POCH) varies with the POCH dihedral angle qualitatively as J(HCCH) varies with the HCCH dihedral angle (Section IV.J.1), then the sum of $J(POCH_A)$ and



$J(POCH_B)$ would be expected to depend on the conformer ratio because the POCH dihedral angles in the chair are approximately 60°(A) and 180°(B) and in the boat are 120° (A and B). Fortuitously, $J(POCH_{120})$ may be $\frac{1}{2}[J(POCH_{60}) + J(POCH_{180})]$. An equation similar to that for the observed coupling constants can be written for the chemical shifts of H_A and H_B, i.e., $\delta H_A = (\frac{x}{x+1})\ \delta^1 H_{ax} + (\frac{1}{x+1})\ \delta^2 H_{eq}$ and $\delta H_B = (\frac{x}{x+1})\ \delta^1 H_{eq} + (\frac{1}{x+1})\ \delta^2 H_{ax}$. None of the conformer chemical shifts $\delta^1 H_{ax}$, $\delta^1 H_{eq}$, $\delta^2 H_{ax}$ and $\delta^2 H_{eq}$ are expected to be equal. Prediction of the dependence of δH_A and δH_B on the conformer ratio is difficult because of 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 shifts on the substituents at phosphorus because of the greater spatial separation of the former from the phosphorus substituents. Thus, the chemical shift difference between two 4-methyl groups ought to decrease as the conformer ratio approaches unity but it probably would not be zero at unity. The spectral results will now be discussed in more detail with the purpose of determining if they can be reasonably interpreted in terms of chair-chair equilibria.

The phosphate XI′ has been assigned a chair conformation with predominantly axial methoxyl and equatorial t-butyl groups in $CDCl_3$ (98). Since the larger J(HCCH) (Table 15) can be assigned as $J(H_{ax}CCH_{ax})$ (see footnote 4, p. 141), $J^1(POCH_{eq}) \approx J(POCH_A) = 1.14$ and $J^1(POCH_{ax}) \approx J(POCH_B) = 22.8$. The t-butoxylphosphate IX′ has values of J(POCH) about 4 Hz closer together than those of XI′ indicating a larger percentage of a second conformer than in a solution of XI′. Two methylene proton resonances of IX′ in $CDCl_3$ at 60 MHz are shown in Figure 9. These are both deceptively simple whereas the resonance at 100 MHz is not. The second resonance was obtained by decoupling the protons giving the broader 4-methyl resonance. It is evident that the methylene protons resonating at low-field are coupled to a 4-methyl group. For reasons discussed in Section IV.E.2, both the coupling methylene protons and the methyl group are concluded to be predominantly axial. If the second resonance is analyzed with the aid of LAOCN 3 (140) as the AA′BB′ part of an AA′BB′X spectrum, assuming that the intense line is not split, then $\delta H_A = 3.87$, $\delta H_B = 4.03$, $J(POCH_A) = \pm 21.63$, $J(POCH_B) = \pm 1.94$, $J(H_ACCCH_{A'}) = 2.67$ and the other J(HCCCH) are less than 0.1.[6] Since the values of J(POCH) are close to those found from analysis of the 100 MHz spectrum, any splitting of the intense line in Figure 9 is probably small. The large four bond coupling suggests that the coupled protons are predominantly equatorial. The comparable values of J(POCH) for XII′, IX′ and XI′ suggest a similar stereochemistry. Unfortunately, the spectra of the other trialkylphosphates, VIII′ and X′, are deceptively simple. Bentrude and Hargis concluded from the sum of $J(HCCH_A)$ and $J(HCCH_B)$ that the 4-_t_-butyl group is equatorial in X′ and, consequently, the methoxyl group is equatorial (98). Since the sum is 4.2 Hz less than the value of 16.0 for the other isomer XI′ (Table 15), an equilibrium between two conformers seems more plausible. If the three spectra for VIII′ are analyzed (ABX) assuming the one AB quartet is completely collapsed, then 21.5, 19.3 and 21.4 Hz are found for $J(POCH_A)$,

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[6] The analysis was performed by Bertrand (99d). The root mean square error for thirteen resolved lines was 0.101 Hz with a maximum deviation of calculated from observed line of 0.231 Hz.

Figure 9. The ring-methylene ^1H nmr resonance of 1-_t_-butoxy-1-oxo-4,4-dimethyl-1-phospha-2,6-dioxacyclohexane in $CDCl_3$

a. The methylene resonance in the absence of decoupling.

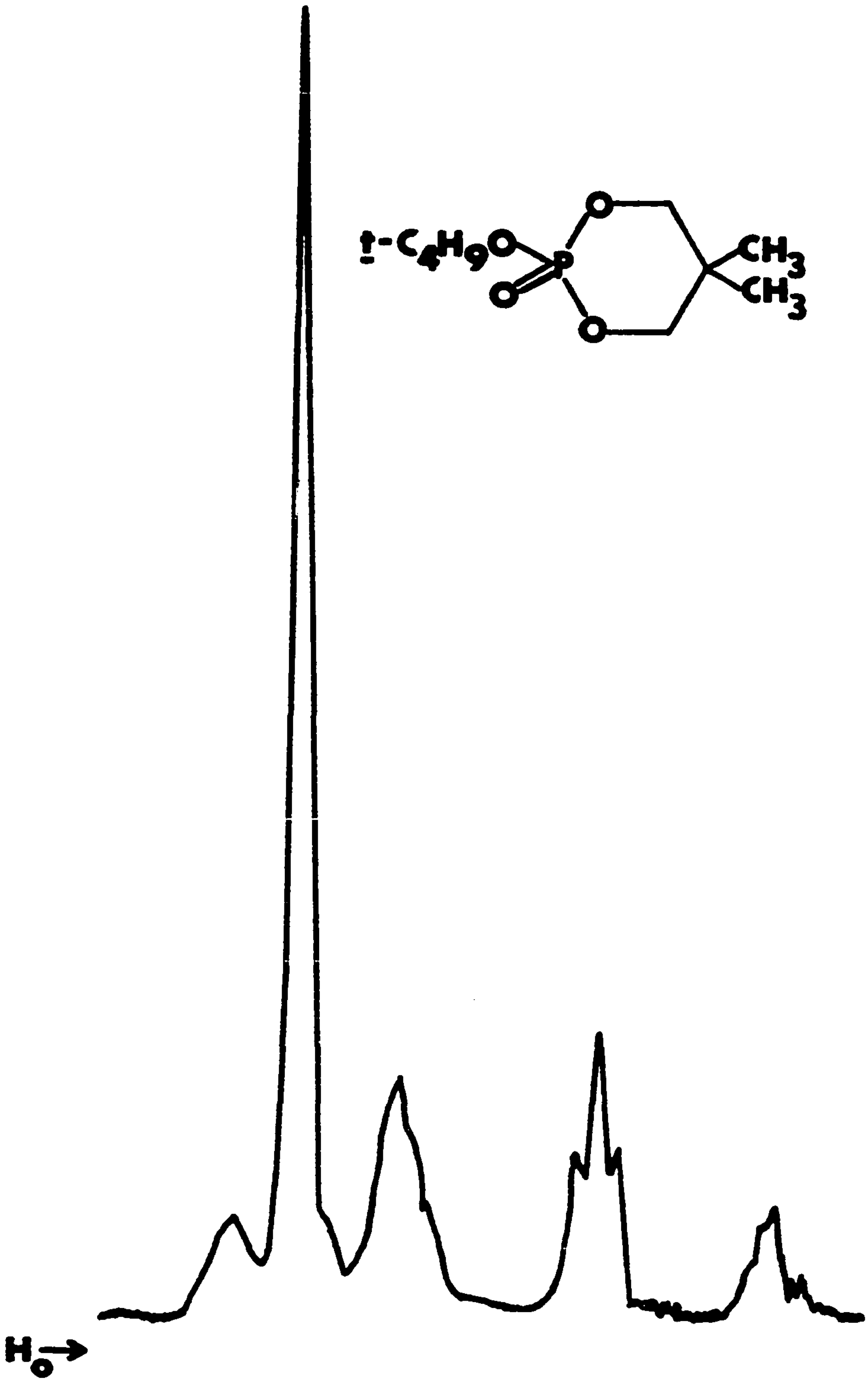
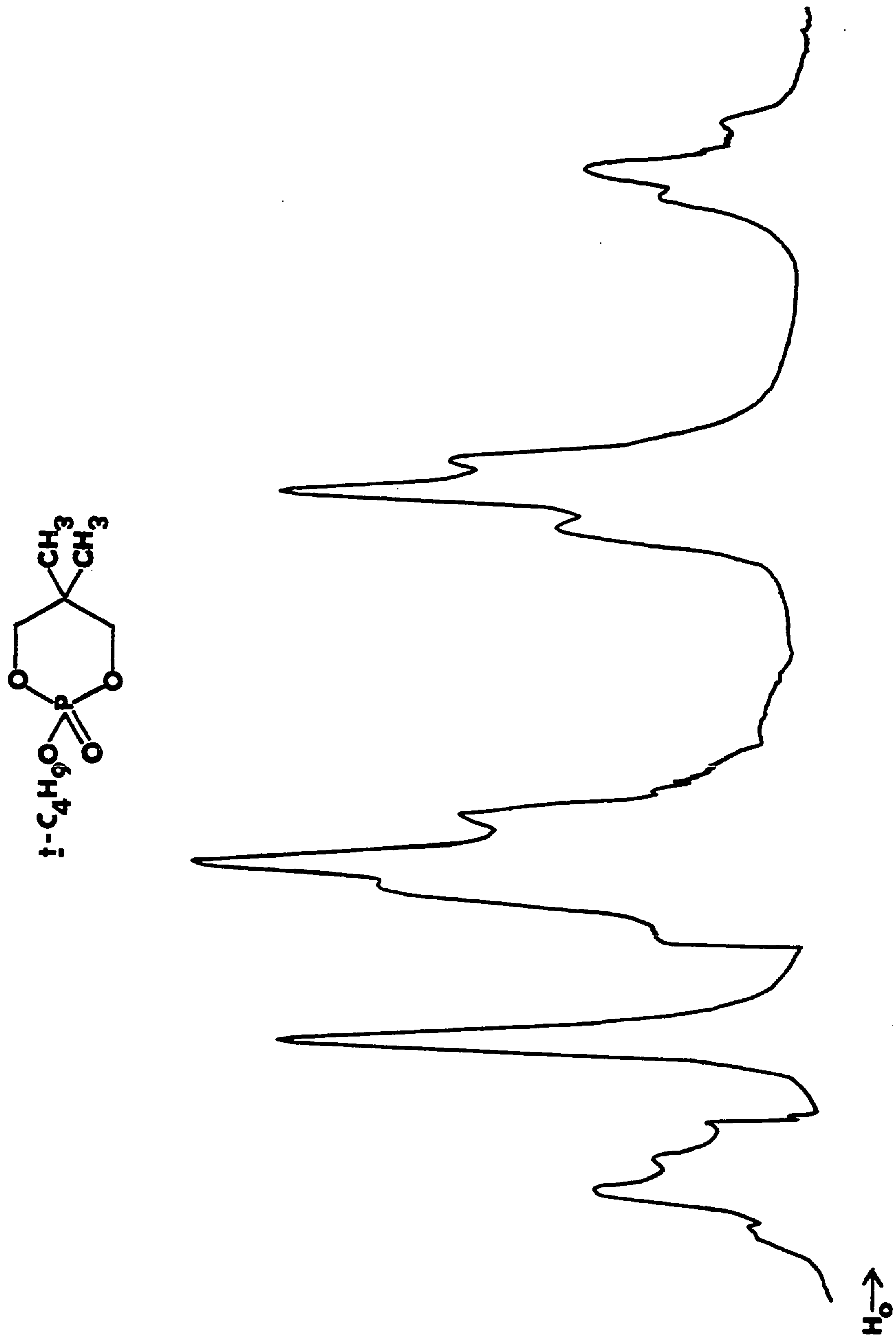

t-C4H9O
P
O
O
O
CH3
CH3
Ho→

Figure 9 (continued)

b. The methylene resonance when the protons giving the broader 4-methyl resonance are decoupled. The intensity of the apparent singlet between the first and third triplets has been greatly reduced.

The spectral amplitudes and sweep widths (Hz/cm) are not the same for parts a and b.


$t\text{-}C_4H_9O$
P
O
O
O
CH_3
CH_3
H_0

respectively, and 2.1, 4.7 and 2.0 Hz for J(POCH$_B$), respectively. Since the error introduced by the assumption should be no more than a few Hertz, the predominance of one conformer for VIII′ is likely. One chair conformer with an axially disposed 1-phenoxyl group has been found for the phosphate L in the solid (33). This fact and the predominance of one conformer for all the phosphates in Table 14, except possibly X′, also suggest that the axial R-equatorial oxygen stereochemistry at phosphorus is preferred.

Less is known about the amino derivatives XIII′ - XVII′ than the phosphates, but the J(POCH) values suggest that the conformer ratios for XIII′- XV′ in $CDCl_3$ are closer to unity than those for XVI′ and XVII′ in C_6D_6. The evidence for the formation of an unstable chair conformer of 1-oxo-1-piperidino-4,4-dimethyl-1-phospha-2,6-dioxacyclohexane (LXXVII b), which slowly isomerizes to the more stable chair conformer (45), was outlined earlier (pp. 30-1). It is possible to deduce from the conclusion that the methoxyl group is axially disposed in the phosphite precursor to LXXVII b (see Section IV.E.3) and the Michaelis-Arbuzov mechanism of the reaction leading to LXXVII b (Equation 10, p. 31) that the piperidino group is equatorial in LXXVII b and axial in the more stable conformer. The fact that ^1H nmr resonances of both conformers were observed (45) indicates a greater energy barrier to ring inversion than for those compounds in Table 14, for example, which exhibit a dependence of spectral parameters on temperature, solvent or concentration readily interpretable in terms of rapidly interconverting conformers.

The conformational free energy differences for 1-alkyl, 1-phenyl and 1-benzyl derivatives are generally less than for the phosphates. A priori, XXII′ would be expected to be a model compound existing as a chair conformer with equatorial 1-methyl and 4-*t*-butyl groups. Bentrude and Hargis (98) have interpreted the ^{1}H nmr specturm (XXII′ a) in terms of such a conformer. Thus, the J(POCH) values of 20.2 and 4.1 Hz can be considered good approximations to $J^2(\mathrm{POCH}_{eq})$ and $J^2(\mathrm{POCH}_{ax})$; these are about 3 Hz smaller and larger, respectively, than those for the phosphate XI′ that has been assigned an equatorial rather than an axial phosphoryl oxygen. The difference between $J(\mathrm{POCH}_A)$ and $J(\mathrm{POCH}_B)$ varies from 9.5 to 1.9 for XIX′, 16.6 to 1 for XX′ and 10.4 to 2.0 for XXVI′ . The larger J(POCH) has been arbitrarily labeled A in Table 14. Actually, the conformer ratio may be ranging from values much greater than unity to values much less than unity. The conformer ratio for the phenyl derivative XXVI′ shows no concentration dependence in CH_3CN in contrast to the behavior in benzene. However, the ratio does increase with decreased temperature (XXVI′h-j). Thus $J(\mathrm{POCH}_A) - J(\mathrm{POCH}_B)$ and $\delta R_6 - \delta R_5$ increase with decreasing temperature while unpredictably, $\delta H_A - \delta H_B$ remains practically constant. Unfortunately, it is not possible to conclude from these spectra which conformer is dominant. Educated guesses of the dominant conformer for other compounds in a few solutions can be made, based on the chemical shift of the 4-methyl group. The resonance of the broader axial 4-methyl group is at lower field than the more narrow equatorial 4-methyl group in 1-R-4,4-dimethyl-1-phospha-2,6-dioxacyclohexanes, VIII′ and IX′, and the pair of isomeric 1-methoxy-4-methyl-4-chloromethyl-1-phospha-2,6-dioxacyclohexanes. In the series of

$CDCl_3$ solutions of XX′(c-f), δ4-$CH_3(R_5)$ decreases as Δ J(POCH) increases. Therefore, the conformer with an equatorial 4-methyl and, consequently, axial 1-methyl group becomes more dominant as the concentration increases. The same conformer is favored as the concentration of XIX′ is increased or its temperature is decreased in $CDCl_3$. The same conclusions result from consideration of the 4-halomethyl rather than the 4-methyl chemical shift. Since the changes of chemical shift are not very great, the above conclusions cannot be considered very certain. An interesting comparison can be made between XVIII′ on the one hand and XIX′ and XX′ on the other hand. Spectra of concentrated $CDCl_3$ solutions are available for each and the conformer ratio appears to be significantly greater for the 4-methyl-4-halomethyl derivatives than for the 4,4-dimethyl derivatives. The conformational preferences of the groups at phosphorus appear to be approximately equal under these conditions but those of the groups at C_4 do not. The axial 4-chloromethyl, equatorial 4-methyl stereochemistry was found to be favored by a 3-4:1 ratio in an equilibrium mixture of XXXI A and B. If this stereochemical preference at C_4 applies to XIX′ and XX′ also, then the favored conformers have an axial 1-methyl group. This is the same conclusion tentatively arrived at above for XIX′ and XX′. The J(POCH) values for XXVII′ indicate different conformational preferences for 1-benzyl and 1-oxo groups. A comparison of the data for XXVII′ and XXVIII′, coupled with the previously determined axial 4-chloromethyl, equatorial 4-methyl preference leads to the conclusion that the preferred stereochemistry at phosphorus is axial oxygen, equatorial benzyl, in agreement with the finding of Edmundson and Mitchell (36). The J(POCH) values are much farther apart for XXX′ than for XXIX′ at a comparable concentration in $CDCl_3$. This is reasonable because in XXX′ the preferred conformations at phosphorus and C_4 cannot exist simultaneously whereas in XXXI′ they can. It is unclear why Edmundson (97) found no temperature dependence for the spectra of $CDCl_3$ solutions of XXVIII′ nor the other geometrical isomer from -30 to +30°, whereas the spectral parameters of the similar XXIX′ in the same solvent are concentration dependent. The 1-methyl derivative XXI′ is unusual among the compounds of Table 14 that were investigated under more than one set of conditions because the sum of J(POCH$_A$) and J(POCH$_B$) increases 5.4 Hz from 35 to -54° for a $CDCl_3$ solution. Bentrude and Hargis (98) interpreted the relatively large change of J(POCH$_A$), the small change of J(POCH$_B$), the small changes of J(HCCH$_A$) and J(HCCH$_B$), and the magnitudes of the couplings in terms of a boat conformer in rapid equilibrium with a chair with equatorial 4-t-butyl and axial 1-methyl groups at 35°. Also, they concluded that the two conformers interconvert by flipping of the phosphorus end of the molecule and that the chair conformer becomes more dominant at -54°. These conclusions are reasonable because a chair conformer is expected to have more widely separated values of J(POCH) than a boat; however, the sum of J(POCH$_A$) and J(POCH$_B$) at 35° is very similar to that for all of the other 1-methyl derivatives in Table 14. If the above interpretation is correct and the J(POCH) for the conformers of the other 1-methyl derivatives are similar to those for the conformers of XXI′, then one is led to the improbable conclusion that the ratio of chair conformers changes but the ratio of boat to total chair conformers does not change with conditions for any of these other derivatives.

Compound XXI′ should be investigated further.

The R groups of the compounds of group 1 (I′ - VII′) are relatively bulky and would be expected to prefer the equatorial position at phosphorus. The J(POCH) values for the 4,4-dimethyl derivatives I′, VI′ and VII′ are further separated than those of the 4-halomethyl-4-alkyl derivatives II′- IV′ in $CDCl_3$. This indicates a greater conformer ratio for the former than for the latter compounds and is reasonable if the axial halomethyl-equatorial alkyl stereochemistry is preferred at C_4. The J(POCH) values of III′ exhibit very little dependence on solvent or temperature and one is tempted to postulate a rigid conformer that is greatly flattened at the phosphorus end of the ring relative to a phosphate conformer, for example. However, VI′ ought to be distorted also, but the J(POCH) values for VI′ are greatly separated and very different from those for III′. In addition, infrared evidence will be presented in Section IV.G.2 for the presence of at least two conformers in solutions of I′ and III′. The fact that the sum of the J(POCH) values for each of I′- VII′ is significantly lower than the sums for the other compounds of Table 14 may be due to a slight additional flattening of the phosphorus end of the rings of the former compounds.

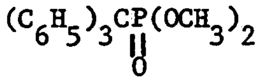
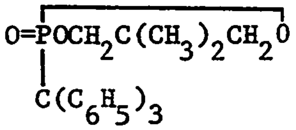
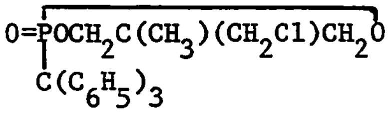
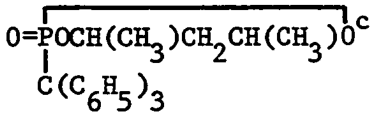
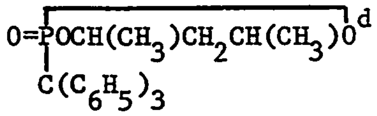
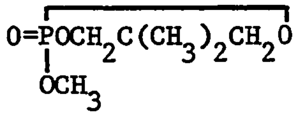
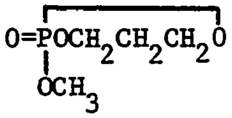
The spectra of the 1-halo and 1-hydro derivatives XXXI′ - XXXIV′ require additional investigation before stereochemical conclusions can be drawn. The spectra are usually deceptively simple at 60 MHz but should be readily analyzable at 100 MHz. If the five-line spectra (ABX approximation) are analyzed assuming a completely collapsed quartet, the J(POCH) values are found to differ by 18.4 (XXXI′a), 26.4 (XXXIII′a), 26.6 (XXXIII′b), 30.8 (XXXIII′c), 31.2 (XXXIII′d) and 18.6 Hz (XXXIV′a). Assumption of a two-line spectrum for XXXIV′b leads to equal couplings of 13.3 Hz. One chair conformer for XXXII′ with axial 4-bromomethyl and 1-bromo substituents has been found in the solid (32). If one conformer also dominates in solution, the more separated pair of J(POCH) values 30.3 and 3.0, is reasonable. The correct pair can be determined by comparison of 60 and 100 MHz spectra.

2. Infrared spectra

If two conformers exist for any of the 1-R-1-oxo-1-phospha-2,6-dioxacyclohexanes, then the phosphoryl stretching band frequencies, ν(P=O) might be different. Two, rather than one weighted time averaged band should appear because the rate of conformer interconversion is expected to be much smaller than the difference in vibrational frequencies. A summary of ν(P=O) assignments for some of these compounds and reference compounds is given in Table 17 and their justifications are given below. The relative band absorbances were determined without correction for band overlaps that often were quite extensive. Also, the ratios of absorbances for bands in a particular spectrum are not necessarily conformer ratios because the band extinction coefficients are unknown.

Two methods were used to locate the phosphoryl stretching bands. The first is the direct method of comparing the number and positions of bands in the 1200 - 1350 cm^{-1} region, where ν(P=O) is expected (73), for the trivalent and pentavalent phosphorus analogs. This method was applied to VIII′, LXXVIII and XXVI′. For example, bands found at 1290 and 1264 cm^{-1} (CCl_4) for XXVI′ were not found in the spectrum of XLVI.

Table 17. Summary of ν(P=0) assignments

	Compound	CCl_4	
		ν(P=0)	Relative Band Absorbance[b]
	 $(C_6H_5)_3C\underset{\underset{O}{\|}}{P}(OCH_3)_2$	1249	
I′	 $O{=}\underset{C(C_6H_5)_3}{P}OCH_2C(CH_3)_2CH_2O$	1264, 1243	1.0, 2.3
III′	 $O{=}\underset{C(C_6H_5)_3}{P}OCH_2C(CH_3)(CH_2Cl)CH_2O$	1264, 1243	1.5, 1.0
CXIX	 $O{=}\underset{C(C_6H_5)_3}{P}OCH(CH_3)CH_2CH(CH_3)O^c$		
CXX	 $O{=}\underset{C(C_6H_5)_3}{P}OCH(CH_3)CH_2CH(CH_3)O^d$		
CIII	$O{=}P(OCH_3)_3$	1290, 1274	1.1, 1.0
VIII′	 $O{=}\underset{OCH_3}{P}OCH_2C(CH_3)_2CH_2O$	1310, 1270	8.7, 1.0
LXXVIII	 $O{=}\underset{OCH_3}{P}OCH_2CH_2CH_2O$	1312, 1279	5.7, 1.0

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[a] The P=0 band is generally broader in this solvent.

[b] The P=0 band often overlaps other bands. The absorbance is only apparent and has not been corrected for band overlaps.

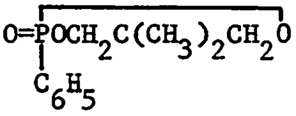
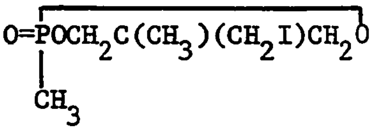
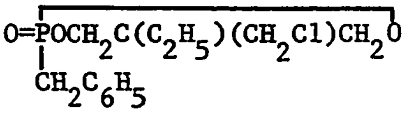
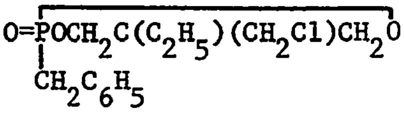
[c] The isomer derived from the more stable phosphite isomer XXXII A. The 3,5-dimethyl groups are trans to the 2-oxo atom.

[d] The isomer derived from the less stable phosphite isomer XXXII B. The 3,5-dimethyl groups are cis to the 2-oxo atom.

[e] The band is slightly asymmetric on the low frequency side and broad.

C_6H_6		$CDCl_3$[a]		Nujol	
ν(P=O)	Relative Band Absorbance[b]	ν(P=O)	Relative Band Absorbance[b]	ν(P=O)	Relative Band Absorbance[b]
1250		1240			
1263,1243	1.0, 1.6	1236,1225	1.0,1.2	1256,1240 1220	1.9,6.1 1.0
1264,1245	1.6, 1.0	1249,1239	1.1,1.0		
1250					
1259					
1292,1274	1.5,1.0	1275			
1310,1269	11,1.0	1295[e]			
1310,1276	9.6,1.0	1297,1288	1,1.1		

Table 17 (continued)

		CCl_4	
	Compound	ν(P=O)	Relative Band Absorbance[b]
XXVI′	 $O{=}\underset{C_6H_5}{P}OCH_2C(CH_3)_2CH_2O$	1290,1264	1.0, 3.4
XX′	 $O{=}\underset{CH_3}{P}OCH_2C(CH_3)(CH_2I)CH_2O$[g]	1258	
XXIX′	 $O{=}\underset{CH_2C_6H_5}{P}OCH_2C(C_2H_5)(CH_2Cl)CH_2O$		
XXX′	 $O{=}\underset{CH_2C_6H_5}{P}OCH_2C(C_2H_5)(CH_2Cl)CH_2O$		

[f] The upper pair of relative absorbances corresponds to a more concentrated solution.

[g] There are many bands in the 1200-1350 cm^{-1} region and these assignments are consequently less certain than those for other compounds.

[h] This band is relatively broad and has a shoulder at *ca.* 1264 cm^{-1}.

[i] There are shoulders at *ca.* 1291 and 1267 cm^{-1}.

C_6H_6		$CDCl_3$[a]		Nujol	
ν(P=O)	Relative Band Absorbance[b]	ν(P=O)	Relative Band Absorbance[b]	ν(P=O)	Relative Band Absorbance[b]
1288,1262	1.0,1.7[f] 1.0,2.0[f]	1272,1260 1236	1.0,1.1 1.2	1272,1265	1.0,1.0
1278,1258	1.0,2.5	1269,1240	1.2,1.0		
1290[h], 1234	2.5,1.0	1280,1236 1230	2.1,1.0 1.0		
1280[i], 1232	2.2,1.0	1274,1230 1225	1.4,1.0 1.0		

The second method is based on the assumption that $CDCl_3$ will deuterium bond to the basic phosphoryl oxygen and cause bands due to phosphoryl stretching to be at lower frequencies in $CDCl_3$ than in solvents such as CCl_4 or C_6H_6. Several studies support this assumption (92, 93, 152-4).

Comparison of the results for the triphenylmethyl derivatives of Table 17 indicates that at least two conformers are present for I′ and III′. Dimethyl triphenylmethylphosphonate exhibits just one band attributable to $\nu(P=0)$; in fact, only one band appears in the range 1200-1350 cm^{-1}. The geometrical isomers, CXIX and CXX, are likely to be conformationally pure and to differ in stereochemistry at phosphorus; CXIX and CXX should have axial and equatorial phosphoryl linkages, respectively (Section IV.E.3). The difference of 9 cm^{-1} in $\nu(P=0)$ for these isomers in C_6H_6 is much less than the 40 cm^{-1} separation found for $\nu(S=0)$ by Lauterbur, et al. (155) for cis- and trans-1-oxo-cis-3,5-dimethyl-1-thia-2,6-dioxacyclohexane. Hellier, et al. (156) have assigned the lower and higher frequency bands for similar sulfites to axial and equatorial sulfinyl linkages, respectively. Forman, et al. (157) have proposed an interaction of the axial sulfinyl oxygen with axial 1,3-hydrogens to account for the preferred axial disposition and for the lower frequency for $\nu(S=0_{ax})$. The decreased difference of axial and equatorial $\nu(P=0)$ compared to $\nu(S=0)$ may be due to the additional flattening of the phosphorus end of the ring for the triphenylmethyl derivatives. Comparison of the CCl_4 or C_6H_6 spectra to the $CDCl_3$ spectra of I′ and III′ leads to the assignment of two bands to phosphoryl stretching for each compound. The separation of the two bands is greater than that for CXIX and CXX and the solvent shift varies from 6-27 cm^{-1}. Three bands appear in a Nujol spectrum of I′. Many organophosphorus compounds exhibit more phosphoryl stretching bands in KBr or Nujol than in CCl_4 or C_6H_6 spectra; the $\nu(P=0)$ are also generally lower in the solid state spectra. The extra bands are usually attributed to intermolecular interactions, a reasonable cause for compounds containing the highly polar phosphoryl bond. If $\nu(P=0_{eq}) > \nu(P=0_{ax})$ for I′ and III′, as suggested by the values for CXIX and CXX, and the extinction coefficients of the bands for each compound are approximately the same, then in CCl_4 and C_6H_6 the conformer with an axial phosphoryl bond is dominant for I′ and that with an equatorial bond is dominant for III′. Conclusions cannot be made for the $CDCl_3$ solutions due to the broadness of the bands and their extensive overlap. The extinction coefficients may not be the same because the ratio of those of the 1250 cm^{-1} band for CXIX and the 1259 cm^{-1} band of CXX in CS_2 is 1.33. A comparison of the conclusions drawn from the nmr and infrared spectral results is difficult because solutions for the former were much more concentrated than those for the latter. Also, conclusions from the infrared results must be considered very qualitative because of the uncertainties discussed above.

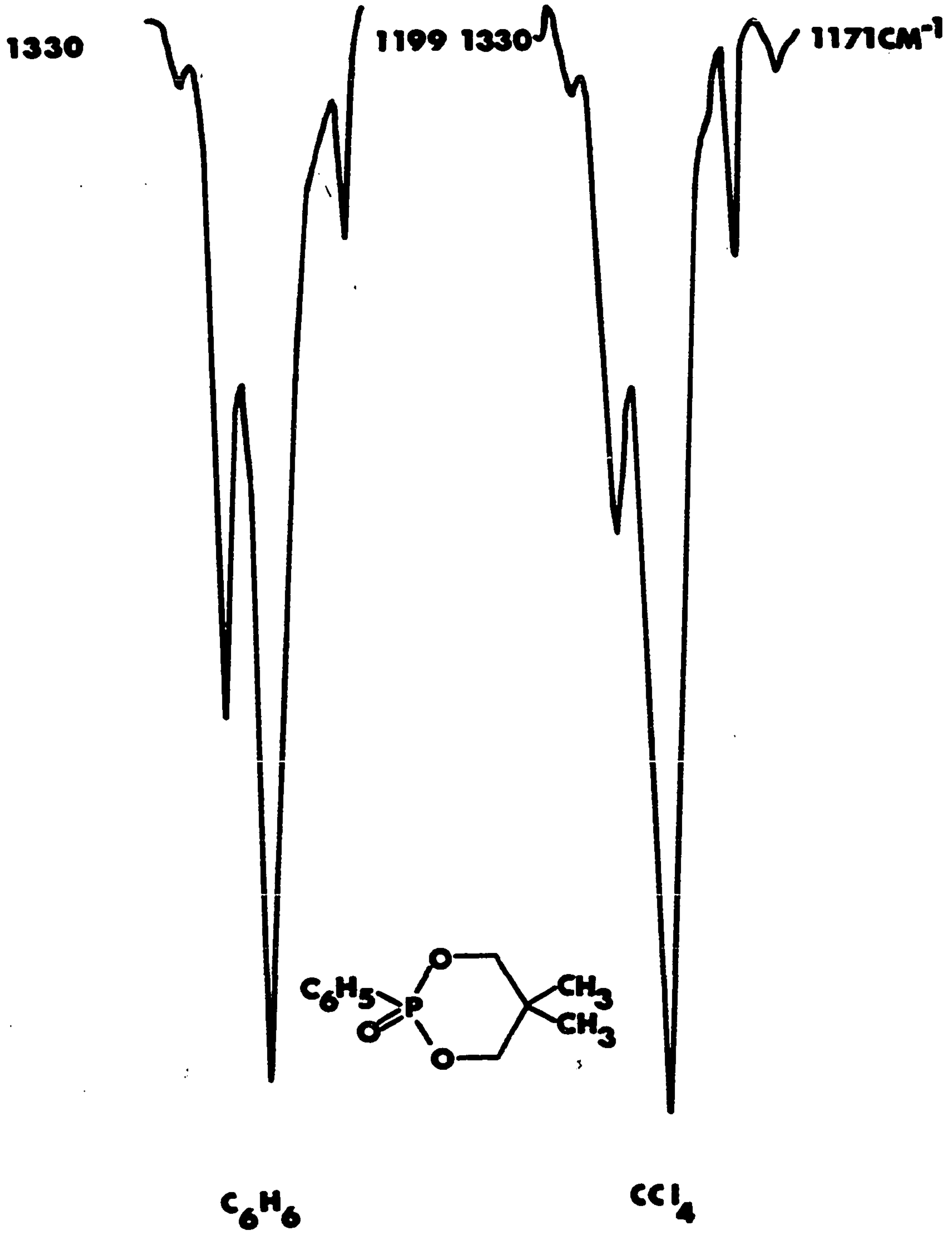
The assignments for the monocyclic trialkyl phosphates suggest that one conformer is very dominant. The two bands for trimethylphosphate have been attributed to rotational isomers, which were discussed earlier (pp. 37-8). The weak lower frequency band listed for VIII′ and LXXVIII in CCl_4 and C_6H_6 may not be due to phosphoryl stretching because a weak band appears at approximately the same position in spectra of the corresponding phosphites. A corresponding band was not observed in the $CDCl_3$ spectra. Kainosho, et al. (38) have assigned bands at 1313 (vs) and

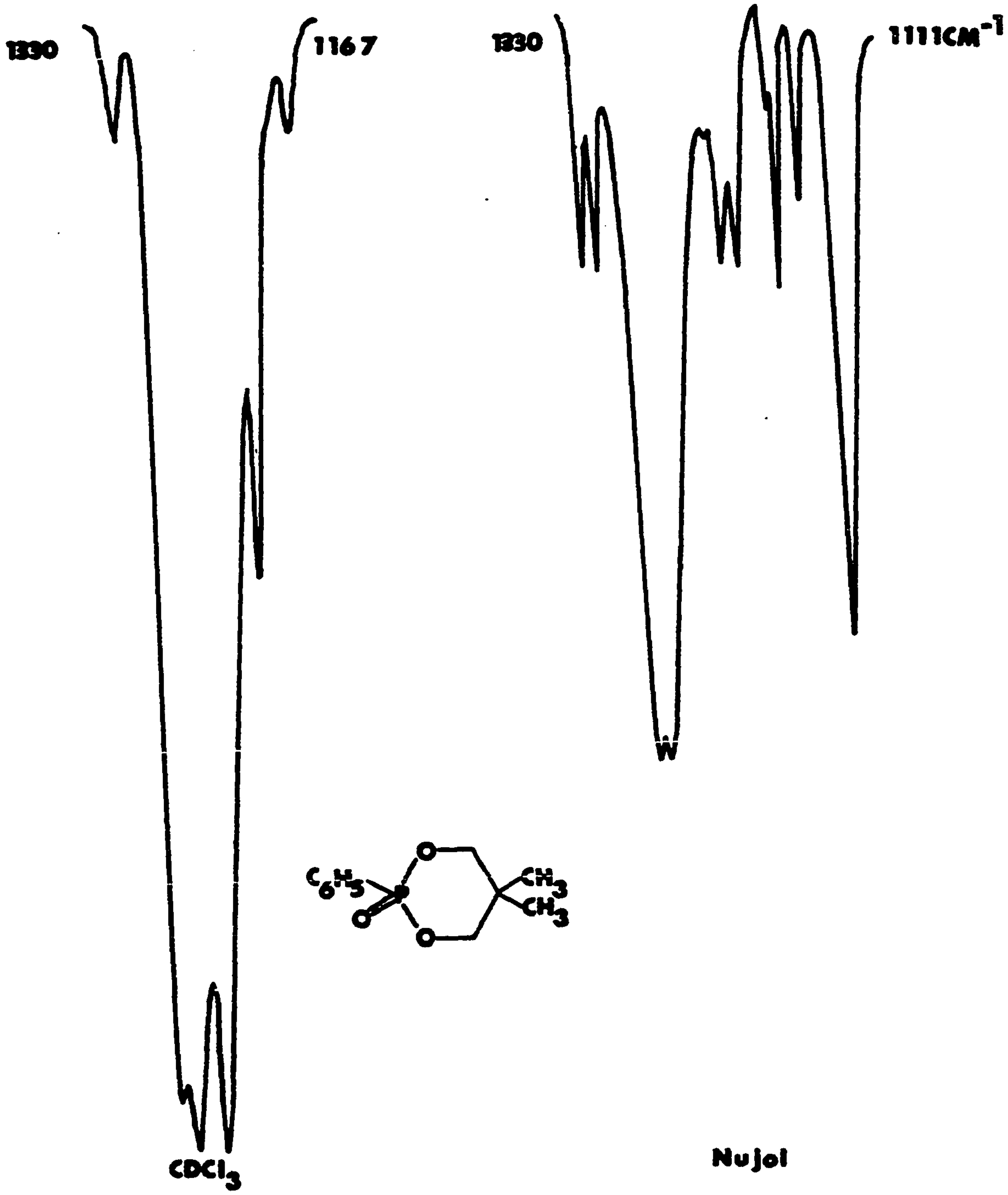
1272 cm^{-1}(w) to phosphoryl stretching for VIII′ in CCl_4 because addition of phenol caused these bands to shift to 1285 and 1234 cm^{-1}, respectively. Although phenol is a stronger acid than $CDCl_3$ and consequently shifts the ν(P=0) further, it exhibits a band in inert solvents at about 1180 cm^{-1} that shifts to higher frequencies in the presence of a phosphoryl oxygen (158). The description of the phenol addition was brief and, therefore, it is not possible to determine if the 1234 cm^{-1} is really a shifted phenol band. The fact that the higher frequency band for the seven phosphates studied shifted 25-32 cm^{-1} from 1308-1322 cm^{-1} to 1277-1294 cm^{-1}, but the lower frequency band shifted 37-70 cm^{-1} from 1267-1298 cm^{-1} to 1227-1234 cm^{-1} (38), makes this possibility worth considering. Nevertheless, the lower-frequency band for VIII′ and LXXVIII is relatively weak and, unless $\nu(P{=}0_{ax})$ and $\nu(P{=}0_{eq})$ are equal, one conformer appears to be very dominant. This is the conclusion drawn from the ^{1}H nmr spectrum of IX′ in $CDCl_3$. The infrared spectrum of LXXVIII in $CDCl_3$ is unusual but reproducible. The doubling of the band may be due to different rotational positions of the 1-methoxyl groups, but this does not easily explain why the doubling is not observed for VIII′.

Spectra of the phosphoryl stretching region of the phenyl derivative XXVI′ in CCl_4, C_6H_6, $CDCl_3$ and Nujol are shown in Figure 10. Two conformers are present, probably in different ratios, in CCl_4 and C_6H_6 solutions. The higher frequency band is doubled in $CDCl_3$ in the same manner as for LXVIII; therefore, the possibility of a third conformer cannot be eliminated. The ^{1}H nmr spectra indicate that for approximately

Figure 10. The infrared phosphoryl stretching region of 1-phenyl-1-oxo-4,4-dimethyl-1-phospha-2,6-dioxacyclohexane in C_6H_6, CCl_4, $CDCl_3$ and Nujol

The solution concentrations are not equal.


1330
1199 1330
1171CM-1
C6H5
P
O
O
O
CH3
CH3
C6H6
CCl4


1330
1167
1330
1111CM^{-1}
W
C_6H_5
CH_3
CH_3
CDCl$_3$
Nujol

0.14 M solutions the conformer ratio is slightly greater in CCl_4 than in C_6H_6. Also, the conformer ratio appears to decrease with increasing concentration in C_6H_6. For all of the compounds investigated at two or more concentrations in $CDCl_3$, the J(POCH) are closer together and the conformer ratio is probably closer to unity at the lowest concentration. If this is also true for XXVI′, then a conformer ratio near unity would be expected in the infrared solution. The infrared and nmr results qualitatively agree in the above respects. In addition, if $\nu(P{=}0_{ax}) < \nu(P{=}0_{eq})$, then the conformer with an axial phosphoryl bond is dominant in CCl_4 and C_6H_6 at low concentrations. The two strong bands at 1272 and 1265 cm^{-1} in the Nujol spectrum probably correspond to the bands at 1272 and 1260 cm^{-1} in the $CDCl_3$ spectrum. Bands at 1313 and 1212 cm^{-1} in the solution spectra are doubled in the Nujol spectrum. The Nujol spectrum compares quite well with the KBr spectrum reported by Siddall and Wilhite (85) except that these authors reported only a single very strong band at 1266 cm^{-1}; this band, as shown in the article, appears broad and asymmetric.

The $\nu(P{=}0)$ assignments for XX′ are very tentative because many bands appear in 1200-1350 cm^{-1} region and extensively overlap. No stereochemical conclusions will be drawn.

Compounds XXIX′ and XXX′ are geometrical isomers, XXIX′ having the <u>trans</u>-1-benzyl-4-chloromethyl configuration. The assignment of the lower-frequency band at approximately 1233 cm^{-1} as $\nu(P{=}0)$ is uncertain because the $CDCl_3$ solvent shift is very small and the difference between the high- and low-frequency bands is considerably greater than that for other compounds in Table 17. The higher frequency band in the C_6H_6 spectrum of both XXIX′ and XXX′ has a shoulder at about 1265 cm^{-1} and that for XXIX′ also has a shoulder at 1291 cm^{-1}. The higher-frequency band in $CDCl_3$ is quite broad and only one maximum is observable. Extrapolation of the nmr spectral results indicates that two conformers are about equally present in dilute C_6H_6 and $CDCl_3$ solutions of XXIX′ and that the ratio may be greater in a dilute $CDCl_3$ solution of XXX′. These results indicate that the lower $\nu(P=O)$ assignment is incorrect and that perhaps one of the shoulders constitutes the second $\nu(P=O)$ absorption.

H. Relationship of Stereochemistry to Dipole Moments of 1-R-1-Y-1-phospha-2,6-dioxacyclohexanes

The dipole moments of a large number of 1-Y-1-R-1-phospha-2,6-dioxacyclohexanes, wherein Y is oxygen, sulfur or BH_3, are given in Table 7. The uncertainties in deducing stereochemistries from dipole moments have been discussed in Section IV.A. Some empirical relationships will be established in this Section and an attempt will be made to relate them to molecular stereochemistries.

The molecular dipole moments calculated by a vector summation of bond moments indicate generally that a conformer with an axial 1-oxo, 1-thio or 1-borino (BH_3) group ought to have a smaller moment than conformers with these groups equatorial. The compounds of each of the following pairs of isomers are thought to differ in stereochemistry mainly at phosphorus: XC - XCI, X′- XI′, CXIX - CXX, XXI′- XXII′ and CXXVI - CXXV. The stereochemistry at phosphorus in the more stable phosphite isomer XXX A has been concluded by Bentrude and Hargis, independently of dipole moment evidence, to be axial methoxyl, equatorial lone-pair (26). It is very likely that this stereochemistry is dominant for XXXII A and XXVI A also. If the mechanisms, discussed earlier, for the formation of the above pairs of compounds from the phosphite isomers are correct, then the second compound of each pair has a predominantly equatorial Y group and the first an axial Y group, in qualitative agreement with the dipole moment calculations (Table 7). The differences between the moments of each pair are not as great as expected, except for the pair CXXV - CXXVI. As discussed previously (Section IV.A.), this is probably partly due to incorrect assumptions used to calculate the moments, but may also be due to the presence of two conformers for some of the compounds.

If the above stereochemical arguments are correct, then the stereochemistry of three additional compounds can be predicted. Firstly, the phosphate LXXVIII has a moment close to that of XI′ and should have an equatorial phosphoryl oxygen. This conclusion is significant because LXXVIII has no exocyclic group(s) at C_3-C_5 that might force an unpreferred stereochemistry at phosphorus. Thus, the preferred stereochemistry is axial methoxyl, equatorial oxygen, in agreement with the solid state structure of L. Secondly, the moment of the triphenylmethyl derivative I′ is smaller than those of CXIX and CXX. This indicates that the phosphoryl oxygen is predominantly axial in I′, in agreement with the findings of Edmundson and Mitchell (36). Thirdly, the moment of the thiophosphate CXXIV is much closer to that of CXXV than to that of CXXVI. The resulting conclusion that the equatorial thiophosphoryl, axial methoxyl stereochemistry is dominant in CXXIV has been predicted by

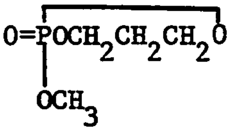
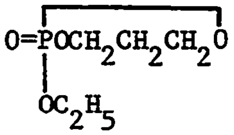
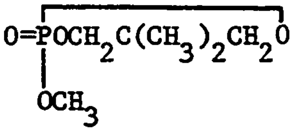
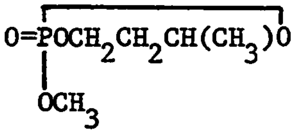
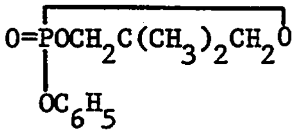
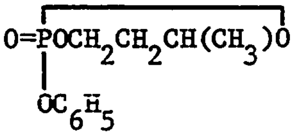
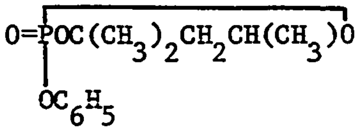
Bentrude and Hargis (98). One additional comparison can be made. The moment of the borane adduct LXXIX is midway between those of XCI and XC. Unfortunately, the 0.39 D difference between the moments of XCI and XC makes a stereochemical prediction unjustifiable.

Prediction of the stereochemistry of compounds possessing a 4-halomethyl group is difficult because the preferred rotational conformation(s) of this group are unknown. Also, no compounds that can be considered with certainty to have a known stereochemistry, except possibly XXXII′ (32), are available for comparison purposes as was the case above. As a result, no predictions will be made.

I. ^{31}P Chemical Shifts of 1-R-1-oxo-1-phospha-2,6-dioxacyclohexanes

The ^{31}P chemical shifts of several 1-R-1-oxo-1-phospha-2,6-dioxacyclohexanes are recorded in Table 18. Most of these have been taken from the literature in order to compare them to those determined in this study. Three empirical relationships are readily apparent. On the one hand, the shifts of VIII′ and LXXVIII are in the same order as those of the trivalent analogs XXXIV and XXIX (Table 13), but the shift difference for the latter pair is about 7 ppm greater than that for the former pair. On the other hand, substitution of a phenoxyl for a methoxyl group in VIII′ causes a 9 ppm upfield shift similar to the 8 ppm shift resulting from the same substitution in the trivalent phosphorus derivative XXIX. Lastly, the similarity of the shifts of V′ and the 1-α-hydroxycyclohexyl derivative is evidence for the structure proposed for V′ by Bertrand (43).

Table 18. ^{31}P spectral data of some 1-R-1-oxo-1-phospha-2,6-dioxacyclohexanes

	Compound	Chemical Shift, ppm
LXXVIII	 $O{=}\underset{OCH_3}{P}OCH_2CH_2CH_2O$	6.02
	 $O{=}\underset{OC_2H_5}{P}OCH_2CH_2CH_2O$	7,[a] 7.7[a] ± 1.0
VIII′	 $O{=}\underset{OCH_3}{P}OCH_2C(CH_3)_2CH_2O$	7.58, 6.8[a]
	 $O{=}\underset{OCH_3}{P}OCH_2CH_2CH(CH_3)O$	7.2 ± 1.0[a]
LIX	 $O{=}\underset{OC_6H_5}{P}OCH_2C(CH_3)_2CH_2O$	126.4,[b] 16[c]
LXXXII, LXXXIII	 $O{=}\underset{OC_6H_5}{P}OCH_2CH_2CH(CH_3)O$	15.1[c,d]
LXXXIV, LXXXV	 $O{=}\underset{OC_6H_5}{P}OC(CH_3)_2CH_2CH(CH_3)O$	(14.2, 16)[c]

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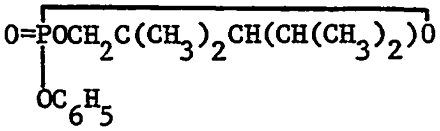
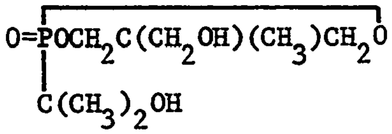
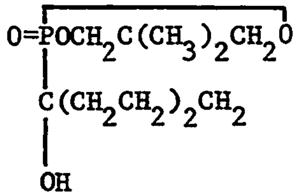
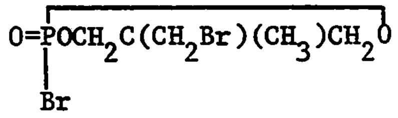
[a] Reference 143.

[b] Upfield from external P_4O_6 (40); 13.4 ppm upfield from H_3PO_4.

[c] Reference 41.

[d] Slightly split (41).

Table 18 (continued)

	Compound	Chemical Shift, ppm
LXXXVI, LXXXVII	 $O{=}POCH_2C(CH_3)_2CH(CH(CH_3)_2)O$, OC_6H_5	$(10.9, 16.5)^c$
V'^{e}	 $O{=}POCH_2C(CH_2OH)(CH_3)CH_2O$, $C(CH_3)_2OH$	-21.5
	 $O{=}POCH_2C(CH_3)_2CH_2O$, $C(CH_2CH_2)_2CH_2$, OH	-21.1^a
XXXII′	 $O{=}POCH_2C(CH_2Br)(CH_3)CH_2O$, Br	14.3 ± .1

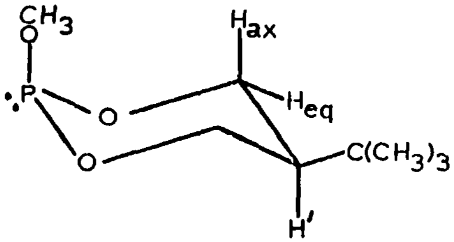
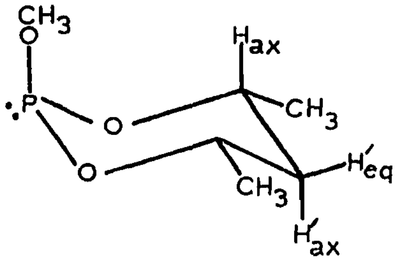
[e] Isomer unknown (43).

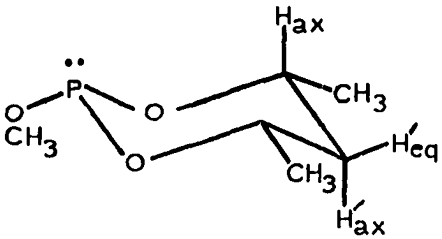
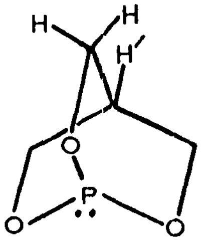
J. Dependencies of J(POCH) and J(POCCH)

1. Stereochemistry

A dependence of J(POCH) on the POCH dihedral angle, qualitatively similar to that of J(HCCH) on the HCCH dihedral angle (151), was employed in earlier discussions and references were given to support this relationship (49, 66, 145). This relationship and the stereochemical dependence of J(POCCH) will now be examined in more detail. Coupling constants and structures of some trivalent and pentavalent phosphorus compounds are given in Tables 19 and 20, respectively. Absolute and relative signs of

Table 19. Dependence of J(POCH) and J(POCCH) on stereochemistry in some trivalent phosphorus compounds

	Compound	J(PH)[a]	Reference	Number of Three Bond Paths[b]	Number of Four Bond Paths[c]
CI	$:P(OCH_3)_3$	+10.0 ± 0.1	159	1	0
	$:P(OCH_2CH_3')_3$	+7.9 (H)	160	1	0
		-0.55 (H′)		0	1
XXXA		11.0 (H_{eq})	25	1(173)	0
		2.9 (H_{ax})		1(67)	0
XXXII A[d]		2.1 (H_{ax})	31	1(67)	0
		11.7 ($POCH_3$)		1	0
		3.6 (H'_{eq})		0	2(53,179)
		0.5 (H'_{ax})		0	2(53,61)

XXXII B		3.1 ± 0.2 (H_{ax})		1(67)	0
		10.8 ($POCH_3$)		1	0
		2.5 ± 0.5 (H'_{ax} or H'_{eq})		0	2
XCVII (H)		1.6 (H)	49	1(120)	0
		7.2 (H′)		0	3(0,180)

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[a] Signs unknown unless explicitly given.

[b] Number of three-bond paths from phosphorus to coupled nucleus. The number in parentheses is the POCH dihedral angle.

[c] Number of four-bond paths from phosphorus to coupled nucleus. The numbers in parentheses are the POCC and OCCH dihedral angles, respectively.

[d] Albrand, et al. (31) concluded that the 1-methoxyl group is equatorial. The signs of J($POCH_{ax}$), J($POCCH'_{eq}$) and J($POCCH'_{ax}$) are the same.

Table 19 (continued)

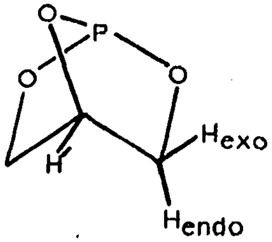
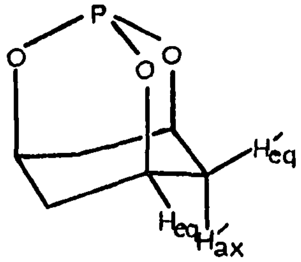
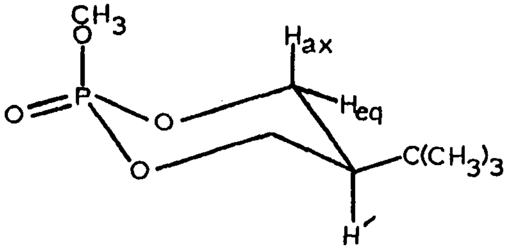
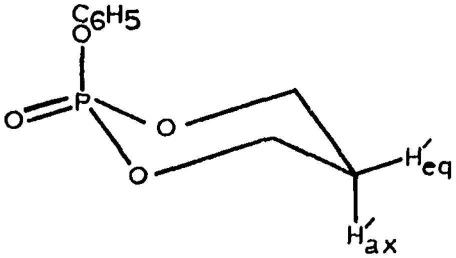
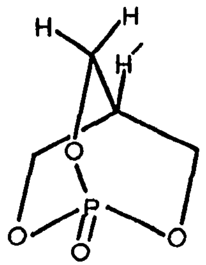
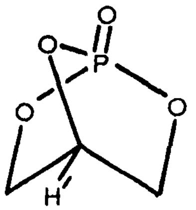
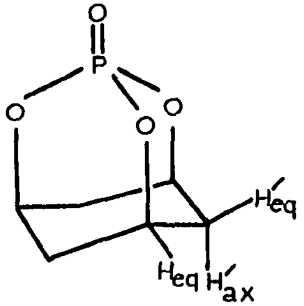
	Compound	J(PH)[a]	Reference	Number of Three Bond Paths[b]	Number of Four Bond Paths[c]
CV		0.29 (H_{exo})		1(120)	1(60,70)
		3.83 (H_{endo})		1(120)	1(60,190)
		15.9 (H')		1(180)	2(0,170)
XCII		6.35 (H_{eq})	116	1(180)	0
		_ca_ 0.5 (H'_{ax})	49	0	2(60,60)
		_ca_ 0 (H'_{eq})	116	0	2(60,180)

Table 20. Dependence of J(POCH) and J(POCCH) on stereochemistry in some pentavalent phosphorus compounds

	Compound	J(PH)[a]	Reference	Number of Three Bond Paths[b]	Number of Four Bond Paths[c]
CIII	$O{=}P(OCH_3)_3$	11.0		1	0
	$O{=}P(OCH_2CH_3')_3$	+8.4 (H) +0.84 (H')	160	1 0	0 1
XI'		22.8 (H_{eq}) 1.1 (H_{ax})	98	1(173) 1(67)	0 0
L		2.6 (H'_{eq}) < 1(H'_{ax})	40	0 0	2(53,179) 2(53, 61)

XCIX(H)		6.5(H)	49	1(120)	0
		6.2(H′)		0	3(0,180)
CVII		24(H′)		1(180)	2(0,170)
XCIV		18.0(H_{eq})	116	1(180)	0
		2.5(H'_{eq})		0	2(60,60)
		2(H'_{ax})	49	0	2(60,180)

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[a] Signs unknown unless explicitly given.

[b] Number of three-bond paths from phosphorus to coupled nucleus. The number in parentheses is the approximate POCH dihedral angle.

[c] Number of four-bond paths from phosphorus to coupled nucleus. The numbers in parentheses are the POCC and OCCH dihedral angles, respectively.

coupling constants are given if known. Gagnaire, et al. (30) have found that the two J(POCH) for XLVI are of the same sign and have concluded similarly for the phosphite XXIX because the coupling constants (10.8 and 2.8 Hz) are similar to those of XLVI (Table 11). Thus, the J(POCH) for XXX A in Table 19 probably have the same sign. Similarly, the J(POCH) values for XI′ in Table 20 probably have the same sign because those for IX′ are similar (21.0 and 3.3 Hz) and the latter do have the same sign (see p. 186). Reasons have been given previously for the conformational purity of the monocyclic compounds included in Tables 19 and 20. The value of 2.5 ± 0.5 Hz for J(POCCH) for XXXII B was obtained from the ^{31}P spectrum. The resonance is a quartet of quartets. The larger quartet splitting is due to J(POCH$_3$) and the small quartet can be considered a triplet of doublets due to J(POCH$_{ax}$) and either J(POCCH$'_{ax}$) or J(POCCH$'_{eq}$). The second J(POCCH′) is probably less than 1 Hz, but the small signal to noise ratio prevents an accurate evaluation.

Interpretation of the coupling constants is often difficult because more than one bond path exists from phosphorus to the coupled nucleus. The number of three- and four-bond paths for each nucleus is given along with the J(PH) value in Tables 19 and 20. Also given are the POCH dihedral angles for the three-bond paths and the POCC and OCCH dihedral angles for the four-bond paths. The dihedral angles for the monocyclic compounds were calculated from ring dihedral angles for L(33) and assumed tetrahedral angles about C$_3$-C$_5$ and are probably more realistic than those calculated from an idealized cyclohexane chair model. The other dihedral angles were determined by examination of molecular models based on Pauling covalent radii (with the exception of the 1.57 A° P-0 bond length) and tetrahedral angles.

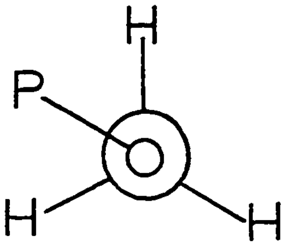
The magnitudes of J(POCH) for trivalent phosphorus are limited to dihedral angles of approximately 67, 120, and 180°. The three couplings for 67° range from 2.1 - 3.1 Hz. The 120° coupling of 1.6 Hz for XCVII(H) is similar, but J(PH_{exo}) and J(PH_{endo}) for CV cannot be compared because both three- and four-bond paths contribute. The J(POCH) for 173 and 180° are 11.0 (XXX A) and 6.35 Hz (XCII), respectively. Gagnaire, et al. (30) have reasoned that the different spatial dispositions of the phosphorus lone-pair relative to the coupled nuclei in XXIX (J($POCH_{eq}$) = 10.8 Hz) and XCII causes the couplings to differ. This argument and a comparison of the steric interactions of a methoxyl group in axial and equatorial positions led them to assign an equatorial methoxyl group in XXIX. Because the bonding and structures of XXIX and XCII are not accurately known, comparison of the coupling constants may not be justified. The fact that J($POCH_{ax}$) in XXXII A and B differ by only 1 Hz (provided the signs are the same) indicates that the phosphorus lone pair disposition is not very important, at least for a dihedral angle of 67°. The arguments given earlier for an axial methoxyl group in the more stable phosphite isomer of several isomer pairs seem more convincing. The J(PH′) for CV cannot be compared to the J(POCH) for 173 and 180° because two four-bond paths also exist for the former coupling.

A useful way to categorize the four-bond J(PH) couplings is in terms of the POCC and OCCH dihedral angles. Couplings for three quite different pairs of angles are available for trivalent phosphorus. If the contributions to J(POCCH) from equivalent paths are equal and additive, then all of the J(POCCH) per path are less than 2.4 Hz. The $J(POCCH'_{eq})$ for XXXII A is approximately 3.6 Hz larger than that for XCII, although the dihedral angles appear to be similar. This difference has been used by Albrand, et al. (31) as evidence for an equatorial methoxyl group in XXXII A. The argument is that the $J(POCCH')$ for the isomer with an axial methoxyl group would be similar to those for XCII because the spatial disposition of the phosphorus lone-pair is similar in the two compounds. However, one of these couplings is about 2.5 Hz for XXXII B, which is believed to have a stereochemistry at phosphorus different than that in XXXII A. Thus, neither XXXII A nor B has four-bond couplings similar to those of XCII. Unless XXXII B is other than a chair conformer, the reasoning of Albrand, et al. (31) loses its validity.

The three J(PH) couplings for the bicyclic phosphite CV are combinations of three and four bond couplings. Prediction of the resultant $J(PH')$ is possible but is probably fortuitous. Thus, $J(PH')$ is the sum of $J(POCH_{180})$ and two $J(POCCH_{0,170})$. If the former is given a value of 11.0 Hz as in XXX A and each of the latter a value of 2.4 (one-third of $J(POCCH')$ for XCVII (H)) the sum is 15.8 Hz versus the observed 15.9 Hz. The $J(POCH_{180})$ for XCII was not used because it does not give the correct sum. Both $J(PH_{exo})$ and $J(PH_{endo})$ include $J(POCH_{120})$ but different J(POCCH). If $J(POCH_{120})$ is 1.6 Hz (as in XCVII (H)) and $J(POCCH_{exo})$ and $J(POCCH_{endo})$ are 0.25 and 1.8 Hz (one-half of $J(POCCH'_{ax})$ and $J(POCCH'_{eq})$, respectively, for XXXII A) then the sums are 1.85 for $J(PH_{exo})$ and 3.4 Hz for $J(PH_{endo})$ versus observed values of 0.29 and 3.83 Hz, respectively. The relative magnitudes are correct but the magnitude of $J(PH_{exo})$ is considerably too large.

The J(POCH) and J(POCCH) values for pentavalent phosphorus can be considered in a similar manner. Unfortunately, fewer couplings are available. In contrast to the J(POCH) values for trivalent phosphorus, couplings for dihedral angles of 67 and 120° are not similar but differ by more than 6 Hz. The J(POCH) values for 173 and 180° are 18.0 (XCIV) and 22.8 Hz (XI′), about as widely separated as the corresponding values for XXX A and XCII (Table 19). As was found for XXXII A (Table 19), $J(POCCH'_{eq})$ is greater than $J(POCCH'_{ax})$ in L. Also, the four-bond couplings for XCIV are similar, as they are in the trivalent analog XCII. The J(PH′) for CVII can be calculated as the sum of 22.8 Hz, from XI′, and 4.1 Hz (two-thirds of 6.2 from XCIX (H)) but the agreement with the observed value of 24 Hz is poor. If the J(POCH) value from XCIV had been used, the agreement would have been excellent.

At least two groups of workers have considered J(POCH) couplings for an acyclic $POCH_3$ group in terms of $J(POCH_{180}) = J_{trans}$ and $J(POCH_{60}) = J_{gauche}$ (40, 66). Hall and Malcolm (40) used the coupling constant magnitudes for XII′ in the equation for $J(average) = \frac{1}{3}(J_{trans} + 2\ J_{gauche})$ and predicted a value of about 9 Hz for the $POCH_3$ group, in good agreement with observed values between 6 and 9. The signs of the couplings for XII′ were concluded to be the same because of the good agreement. Tsuboi, et al. (66) used the J(POCH) value for sodium monomethylphosphate (10.3 Hz) and barium dimethylphosphate (10.5 Hz) and the J_{gauche} of 1.5 Hz for the 3-hydrogen of the assumed chair form of the anion of 1-oxo-1-hydroxy-3-phenyl-1-phospha-2,6-dioxacyclohexane to predict a value of 28 Hz for J_{trans} from the equation given above. The equation was derived (66) by assuming the P-O bond to be trans to one C-H bond and gauche to the other two in each of three equally probable rotational conformers about the C-O bond. One such conformer is shown below in a Newman projection along the O-C bond (66). Interconversion of these conformers was considered sufficiently rapid that one average coupling would be observed. Tsuboi, et al. (66) also interpreted the smaller J(POCH) for mono and diethylphosphate anions, 6.3 and 7.0 Hz, respectively, in terms of unequally probable rotational conformers. Both groups tacitly assumed that the value of J(POCH) is independent of the rotational position of the methoxyl group about the P-O bond. If J(POCH) for trimethyl phosphite (+10.0 Hz) and phosphate (11.0 Hz) are predicted from the above equation for J (average) and J_{trans} and J_{gauche} from XXX A and XI′, then values of 5.6 and 8.3 Hz result, respectively, if all of the couplings are positive, and values of 1.8 and 6.9 result, respectively, if J_{gauche} is negative. In neither case is there agreement between predicted and observed values. The reason for the disagreement is unclear.



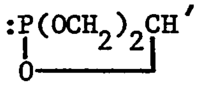
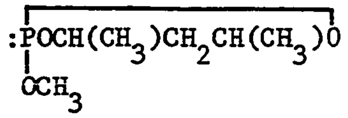
2. Phosphorus oxidation state

The magnitude of J(POCH) increases when phosphorus is oxidized but at least one instance has been found of a decrease in J(POCCH) upon oxidation (49). In the paper by Boros, et al. (49), through-bond and throughspace coupling mechanisms were tentatively proposed to account for this decrease from XCVII (H) to XCIX (H). The purpose of this section is to compare couplings from the literature to new data. These values appear in Tables 19, 20 and 21. The derivatives of a particular $:PRR'R''$ are arranged in Table 21 according to increasing J(POCH) or J(POCCH). The order of the derivatives of CV is seen to be the same as for XCVII (CH_3) and XCII. Also, the magnitude of J(POCCH) for the equatorial 3- and/or 5-methyl group of the monocyclic derivatives depends qualitatively in a similar manner on Y. Substitution of methoxyl for triphenylmethyl in CXX or CXIX causes an increase in J($POCCH_3$). An additional example of decreasing J(POCCH) upon oxidation exists in the pair XXXII A and L, if substitution of phenoxyl for methoxyl has no effect on the coupling.

K. Nature of the Phosphoryl Bond of Trialkylphosphates

The phosphoryl stretching frequencies (ν(P=0)) and phenol shifts of acyclic, monocyclic and bicyclic trialkylphosphates provide information about the nature of their phosphoryl linkages. This linkage is usually considered to result from the sharing of a pair of 3 sp^x hybridized electrons of phosphorus with oxygen in a σ-bond and the sharing of two pairs of electrons of oxygen with the 3d orbitals of phosphorus in π-bonds. The extent of donation in both directions determines the strength of the bond. The ν(P=0) values for compounds of the type 0=PXYZ, wherein X, Y, Z can be the same or different, range from 1087 to 1410 cm^{-1} (73). The primary determinant of ν(P=0) appears to be the inductive effects of X, Y and Z, as indicated by their electronegativities (73). Thus, an increase in the electronegativities of the substituents causes a with-

Table 21. Dependence of J(POCH) and J(POCCH) on the oxidation state of phosphorus

Compound	Y:PRR′R″[a]	Y	J(POCH)	$J(POCCH_3)$	Reference
$XCVII(CH_3)$	$:P(OCH_2)_3CCH_3$		1.8		116
$XCVIII(CH_3)$		BH_3	4.2		116
		CH_3[b]	5.1		161
		S	6		145
$XCIX(CH_3)$		O	7.0		116
XCII	$:P(OCH)_3(CH_2)_3$		6.3		116
XCIII		BH_3	12.5		116
XCV		S	19		145
XCIV		O	20		116
CV	 $:\underset{O}{P}(OCH_2)_2CH'$		15.9 (H′)		
CVI		BH_3	20.0 (H′)		
CVII		O	24 (H′)		
XXXII A	 $:\underset{OCH_3}{P}OCH(CH_3)CH_2CH(CH_3)O$			< 0.3	
XXXII B				< 0.3	
XCI		BH_3		0.85 ± 0.05	
XC		BH_3		0.95 ± 0.05	

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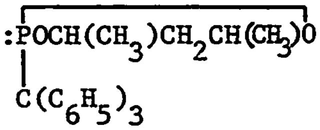
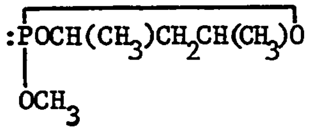
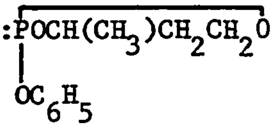
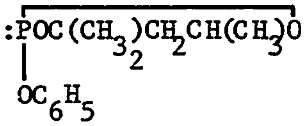
[a] :PRR′R″ is given only for the first compound of a series. Only the Y substituent changes.

[b] The phosphorus containing species is a cation. The anion is BF_4^- (161).

Table 21 (continued)

Compound	Y:PRR′R″[a]	Y	J(POCH)	J($POCCH_3$)	Reference
CXX	 $:\underset{C(C_6H_5)_3}{P}OCH(CH_3)CH_2CH(CH_3)O$	0		1.45 ± 0.05	
CXIX		0		1.75 ± 0.05	
CXXI [c]	 $:\underset{OCH_3}{P}OCH(CH_3)CH_2CH(CH_3)O$	0		2.5	
LXXXIII:	 $\underset{OC_6H_5}{P}OCH(CH_3)CH_2CH_2O$	0		2.0-2.9[d]	40
LXXXIV	 $:\underset{OC_6H_5}{P}OC(CH_3)_2CH_2CH(CH_3)O$	0		2.0-2.9[d]	40

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[c] Isomer unknown.

[d] Coupling to the equatorial methyl group(s). Coupling to the axial methyl group in LXXXIV was unresolved (40).

drawal of electron density from phosphorus that in turn pulls more electron density from the oxygen, resulting in a stiffer phosphoryl bond and a higher stretching frequency (162, p. 299). Wagner has calculated the bond characters of a series of Y_3PO using an internally consistent LCAO-MO method taking into account the π-electrons, the varying polarities of the YP and OP σ-bonds and the changing hybridization of the π-bonding orbital of the central phosphorus atom. The PO π-bond orders were found to correlate well with the ν(P=O), varying from practically zero for

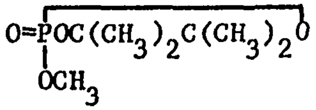
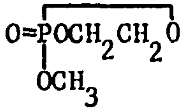
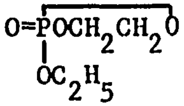
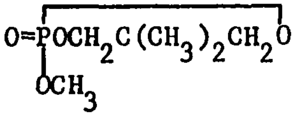
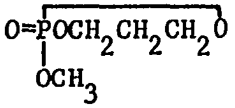
$(CH_3)PO$ to almost two for F_3PO (163). Apparently the σ-bond order remains approximately constant.

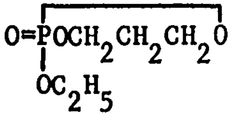
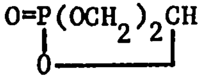
With the above ideas in mind, the ν(P=O) and phenol shifts in Table 22 can be examined. The ν(P=O) values increase in the order acyclic < five-membered monocyclic < six-membered monocyclic < bicyclic, and the phenol shifts decrease in the order acyclic > six-membered monocyclic > five-membered monocyclic > bicyclic. Thus, the phosphoryl π-bond order is greatest for the bicyclic phosphates and least for the acyclic molecules. The phenol shifts generally confirm this conclusion. The phenol shift will be least for the least basic phosphoryl oxygen. Increased phosphoryl π-bonding will decrease electron density on the oxygen and make it less basic. Thus, the bicyclic phosphate XCIX (C_5H_{11}) has a high ν(P=O) and a small phenol shift. Whereas tri-n-butylphosphate is well-known for its good extraction ability of metal ions, XCIX (C_5H_{11}) has been found to be void of such ability (88). Although a decrease in phosphoryl σ-bonding from acyclic to bicyclic phosphates could also account for the decreased phenol shifts, this reason alone would not account for the increase in ν(P=O). No attempt will be made here to explain the differences in bonding in the phosphates. Recent papers should be consulted for pertinent discussions (9, 164, 165).

L. Relative Stability of Trialkylphosphite Boranes

Trialkylphosphites generally form the thermodynamically and hydrolytically stable borane adducts $H_3B{:}P(OR)_3$ (115, 117, 166). Several adducts containing acyclic, monocyclic and bicyclic phosphites were prepared as part of the monocyclic stereochemical studies and in order to

Table 22. Phosphoryl oxygen stretching frequencies and phenol shifts for trialkylphosphates

	Compound	$\nu(P{=}O)$, cm^{-1}	Solvent	Phenol Shift,[a] cm^{-1}
	$O{=}P(O\underline{n}\text{-}C_4H_9)_3$	1260[b]	$CHCl_3$	
	$O{=}P(OC_2H_5)_3$	(1270,1260)[c]	none	345[d]
CIII	$O{=}P(OCH_3)_3$[e]	(1290,1275)[c]	none	304±2
		(1282,1273)[f]	none	315[d]
		(1283,1271)	none	
		(1290,1271)	CCl_4	
II	 $O{=}\underset{OCH_3}{P}OC(CH_3)_2C(CH_3)_2O$	1290[g]	$CHCl_3$	
I	 $O{=}\underset{OCH_3}{P}OCH_2CH_2O$	1302	CCl_4	257±2
		1302[h]	CCl_4	
	 $O{=}\underset{OC_2H_5}{P}OCH_2CH_2O$	1301[i]	CCl_4	270[i]
VIII′	 $O{=}\underset{OCH_3}{P}OCH_2C(CH_3)_2CH_2O$	(1310,1270)[j]	CCl_4	280±2
LXXVIII	 $O{=}\underset{OCH_3}{P}OCH_2CH_2CH_2O$	(1312,1279)[j]	CCl_4	276±2

	 $O=POCH_2CH_2CH_2O$, OC_2H_5	1308[i]	CCl_4	280[i]
XCIX	$(C_5H_{11})O=P(OCH_2)_3CC_5H_{11}$[e]	(1336,1320) (1326,1312)	C_6H_6 CCl_4	230±5
CVII	 $O=P(OCH_2)_2CH$	(1355,1346) 1340[k]	CH_2Cl_2	

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[a] The difference in ν(O-H) for complexed and uncomplexed phenol in carbon tetrachloride.

[b] Reference 88.

[c] Reference 75.

[d] Reference 167.

[e] Values of ν(P=O) in other solvents appear in Table 24.

[f] Reference 77.

[g] Reference 168. A shoulder on the low frequency side of this band appears in the spectrum and may also be assigned as ν(P=O).

[h] Reference 169.

[i] Reference 89.

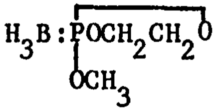
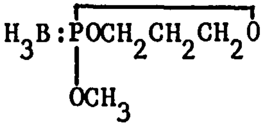
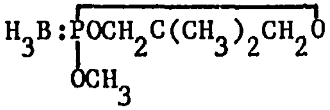
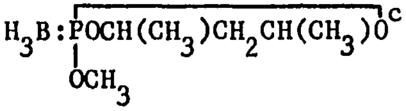
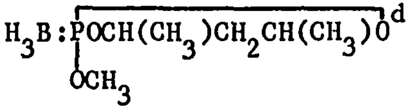
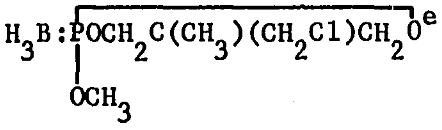
[j] The higher frequency band is very much stronger.

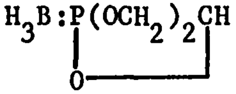
[k] A solvent was not mentioned (55).

determine whether or not any differences in their thermodynamic stabilities could be detected. Infrared bands in the B-H stretching region are listed in Table 23. Assignments of ν(B-H) from the literature for several borane adducts are also included. There is substantial disagreement between the values reported by Heitsch and Verkade (170) for CII and XCVIII (CH_3) and those determined in this study. The use of more polar solvents by Heitsch and Verkade may account for the difference. As noted in Section III.C., the Beckman IR 12 Spectrophotometer was calibrated with a polystyrene film. Three bands were found in the 2200-2500 cm^{-1} region for all of the compounds investigated; however, the lowest frequency band was always relatively weak. If the effective symmetry of the BH_3 group in the adduct is C_{3V}, then one symmetric and one asymmetric stretching vibration should be infrared active and two bands should be observed. The higher frequency band has been attributed to asymmetric B-H stretching (170, 171). The differences in the frequencies of the two bands for BH_3 adducts of NH_3, $N(CH_3)_3$, CO and PF_3 are 53, 58, 55 and 70 cm^{-1}, respectively (170). Since the two higher-frequency bands for the compounds in Table 23 are separated by 40-53 cm^{-1} and the lowest frequency band is separated by at least 140 cm^{-1} from the highest, the two higher frequency bands are attributed to asymmetric and symmetric B-H stretching; the cause of the band in the 2240-2255 cm^{-1} region is unclear.

An increased donation of electron density from phosphorus to boron should cause the hybridization of the boron valence orbitals to change towards sp^3 from sp^2. As a result, the boron orbitals used to bond to the hydrogens will have less s-character. Watanabe and Nagasawa (171) have found an approximately linear correlation between $J(^{11}B\text{-}H)$ and the

Table 23. Bands in ν(B-H) region of infrared for trialkylphosphite boranes

	Compound	Bands[a], 2200-2500 cm^{-1}	Solvent
CII	$H_3B{:}P(OCH_3)_3$	2402(s), 2362(w-m), 2255(w), 2375, 2260	C_6H_6 CH_3Br[b]
CXXII	 $H_3B{:}\overline{\underset{OCH_3}{P}OCH_2CH_2O}$	2410(s), 2363(m), 2242(w)	CCl_4
CXXIII	 $H_3B{:}\overline{\underset{OCH_3}{P}OCH_2CH_2CH_2O}$	2411(s), 2364(m), 2245(w)	CCl_4
LXXIX	 $H_3B{:}\overline{\underset{OCH_3}{P}OCH_2C(CH_3)_2CH_2O}$	2409(s), 2360(m), 2243(w)	CCl_4
XC	 $H_3B{:}\overline{\underset{OCH_3}{P}OCH(CH_3)CH_2CH(CH_3)O}$[c]	2410(s), 2358(m), 2242(w)	CCl_4
XCI	 $H_3B{:}\overline{\underset{OCH_3}{P}OCH(CH_3)CH_2CH(CH_3)O}$[d]	2398(s), 2351(m), 2246(w)	CCl_4
LXXX and LXXXI	 $H_3B{:}\overline{\underset{OCH_3}{P}OCH_2C(CH_3)(CH_2Cl)CH_2O}$[e]	2412(s), 2365(m), 2248(w)	CCl_4

XCVIII(CH_3)	$H_3B{:}P(OCH_2)_3CCH_3$	2415(s), 2366(m), 2250(w)[f]	C_6H_6
		2400, 2355	[$CHCl_3$, CH_2Br_2, CH_3CN, Nujol][b]
XCIII	$H_3B{:}P(OCH)_3(CH_2)_3$	2400, 2350	[$CHCl_3$, CH_2Cl_2 CH_3CN, KBr][b]
CVI	 $H_3B{:}P(OCH_2)_2CH$, O	2433(s), 2380(w-m), 2240(w)[f]	C_6H_6

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[a] The positions of the s(strong) m(medium) and w(weak) bands are precise to within 1, 2, and 5 cm^{-1}, respectively.

[b] Reference 170.

[c] Derived from the more stable phosphite isomer XXXII A.

[d] Derived from the less stable phosphite isomer XXXII B.

[e] A 1:3 mixture of LXXX and LXXXI, derived from XXXI A and B, respectively.

[f] This band is uncertain due to overlap with a benzene band.

weighted root mean square average ν(B-H). Such a correlation is reasonable since both modes are believed to be primarily dependent on the amount of s-character in the B-H bond, i.e., both parameters should decrease as the s-character decreases. The $^{11}BH_3$ proton resonances of many of the compounds in Table 23 are very broad and the values of J(^{11}B-H) are consequently uncertain; values of 96.3± 0.2 for CII and 102 ± 2 for CVI being the most precise. Values of J(^{11}B-H) for CII, XCVIII (CH_3) and XCIII have been reported to be 97.2, 96.0 and 97.6 Hz (170). Thus, there appears to be no correlation between ν(B-H) and J(^{11}B-H) although the small range of the coupling constants and their uncertainties would make any correlation questionable. Since the asymmetric ν(B-H) are known fairly precisely (± 1 cm^{-1}), some qualitative conclusions about the stability of the adducts can be made from a comparison of their values in Table 23. Since an increase in the s-character of C-H bonds causes an increase in ν(C-H), an increase in B-H bond s-character is expected to cause an increase in ν(B-H). In general, ν($B\text{-}H_{asym}$) increases in the order acyclic < monocyclic < bicyclic phosphites and the conclusion is that the acyclic phosphite forms the most thermodynamically stable adduct. The low ν(B-H) for XCI compared to those of the other monocyclic phosphite adducts may well be consonant with the conclusion that it is the only adduct possessing an axial BH_3 group. Compound XCIII also does not fit the above generalization.

Heitsch and Verkade have employed displacement reactions of the type shown below to conclude that XVCII (CH_3) is a weaker base than XCII towards BH_3 (117, 166). Thus, XCVII (CH_3) would not displace trimethyla-

$$\text{Base}^1 + \text{Base}^2\,BH_3 \rightleftharpoons \text{Base}^1\,BH_3 + \text{Base}^2$$

mine from its BH_3 adduct but XCII would do so partially in tetrahydrofuran at room temperature or in the absence of a solvent at elevated temperatures over a period of at least 36 hours, the equilibria being approached from both directions. Reetz found that tri-isopropylphosphite would displace this amine to the extent of 53% in the absence of solvent at 50^o (115). The following pairs of phosphites and phosphite boranes have been equilibrated in benzene: XCVII (CH_3) - CVI, CV - XCVIII (CH_3), XCVII (CH_3) - CII, CI - XCVIII (CH_3) and XXIX - CVI. The ratios of compounds in each solution were determined by integration of ^1H nmr resonances. Both XCVII (CH_3) and XXIX displaced CV from its adduct within a few minutes at room temperature. No change in the spectrum of CV - XCVIII was observed after six hours. The equilibrium constant for the reaction shown below is less than 0.05. Therefore,

$$\underset{\text{XCVII}(CH_3)}{:P(OCH_2)_3CCH_3} + \underset{\text{CII}}{H_3B:P(OCH_3)_3} \rightleftharpoons \underset{\text{XCVIII}(CH_3)}{H_3B:P(OCH_2)_3CCH_3} + \underset{\text{CI}}{P(OCH_3)_3}$$

CI is a stronger base towards BH_3 than XCVII (CH_3). Thus, the following basicity orders can be established: CI > XCVII (CH_3) > CV and XXIX > CV. If triisopropyl and trimethylphosphites have similar basicities and the effect of different reaction media on the equilibrium constant is negligible or constant, then the following order also holds: CI, XCII > XCVII (CH_3) > CV. The $\nu(B\text{-}H_{asym})$ decrease with increasing stability of the adducts as predicted, with the exception of the results for XCIII. Admittedly, the number of compounds is limited. Perhaps the most interesting observation in this study is the instability of CVI and the similarity of its value of $\nu(B\text{-}H_{asym})$ to the value of 2434 cm^{-1} for the unstable borane carbonyl (170).

M. Cause of the Doublet Phosphoryl Stretching Band for Bicyclic Trialkylphosphates

Comparison of Nujol and hexachlorobutadiene (HCBD) mull infrared spectra of XCIX (C_5H_{11}) and the corresponding phosphite XCVII (C_5H_{11}) in the 1250 - 1400 cm^{-1} region reveals bands at 1310(s) and 1325(sh) that are possibly due to phosphoryl stretching. Spectra of XCIX (C_5H_{11}) in many solvents also contain these two bands. In addition, KBr and Nujol/HCBD spectra of other bicyclic phosphates XCIX (R), wherein R is H, CH_3, C_2H_5 and C_3H_7, exhibit comparable bands. Four possible reasons for these two bands will be considered. Firstly, structural isomers, perhaps "twistamers," may have different $\nu(P{=}O)$ values. Secondly, the phosphate molecules may associate with each other, the solvent molecules or a solid diluant, e.g., KBr, possibly through the polar phosphoryl bond. Thirdly, the second band may be due to another fundamental molecular vibration. Fourthly, a combination or overtone band may gain intensity as a result of Fermi resonance with the phosphoryl stretching vibration.

The doublet phosphoryl stretching band for the acyclic trimethylphosphate has been attributed to rotational isomers (see pp. 37-8), but structural isomers for the bicyclic XCIX (R) are unreasonable. Two crystallographically independent molecules of XCIX (CH_3) per unit cell were found by x-ray crystal structure analysis; however, the two molecules were felt to be structurally equivalent (58).

Intermolecular interaction in the solid state is often proposed to account for "extra" infrared bands, but the x-ray study of XCIX (CH_3) revealed no evidence for such an interaction (58). The ^1H nmr absorptions of XCIX (CH_3) and XCIX (C_2H_5) in $CDCl_3$ remain constant upon dilution and molecular weight measurements of XCIX (C_2H_5) over a range of concentrations in C_6H_6 and $CHCl_3$ by vapor pressure osmometry indicate no association (58). Although cryoscopic measurements in benzene led Neunhoeffer and Maiwald (172) to propose dimeric association of XCIX (C_2H_5), Verkade and Reynolds found XCIX (CH_3) to be monomeric in nitrobenzene by the same method (56).

Hildbrand (173) has performed a normal coordinate analysis of XCIX (CH_3) and XCVII (CH_3) based on their solid state infrared and Raman spectra and the known structure of XCIX (CH_3). Only a band at 1308 cm^{-1} (KBr) was assigned as ν(P=O) for XCIX (CH_3). Other bands also appear in the 1300 - 1400 cm^{-1} region at 1300 (OCH deformation), 1358 (CH_3 deformation) and 1378 (CCH_2 deformation), but a strong band at 1329 cm^{-1} was not assigned and was not included in the analysis. Thus, the source of the second band remains unknown. Unfortunately, the KBr spectrum of XCVII (CH_3) exhibits a broad strong band at 1269 cm^{-1} (173) that is not present in $CHCl_3$ or CS_2 spectra (170). This band is very likely due to a phosphoryl stretching band of a hydrolysis product of XCVII (CH_3) because it is relatively much enhanced when a KBr sample of XCVII (CH_3) is reground and repressed. Thus, the normal coordinate analysis of XCVII (CH_3) is highly questionable.

Fermi resonance of a combination or overtone band with the phosphoryl stretching band is the most likely origin of the second band. The sum of the very strong bands for XCIX (CH_3) at 852 and 462 cm^{-1} (KBr), attributed to asymmetric P-O stretching and O=P-O deformation, respectively, by Hildbrand (173) is 1314 cm^{-1}. Since both of these vibrations have E symmetry (C_{3V} molecular symmetry), Fermi resonance of the combination of these fundamental vibrations with the A_1 phosphoryl stretching vibration is possible.

The positions and relative percent transmissions of the two bands for XCIX (C_5H_{11}) in a number of solvents are summarized in Table 24. Similar data for trimethylphosphate (CIII) are included for comparison. The most readily apparent difference between the results for XCIX (C_5H_{11}) and CIII is the much greater solvent dependence of the peak maximum ratio for the former. This behavior for XCIX (C_5H_{11}) is contrary to what would be expected for two fundamental bands, e.g., phosphoryl stretching and a deformation band. Fermi resonance cannot be ruled out because the solvent dependence of the positions and intensities of the vibrational bands contributing to the combination or overtone band in Fermi resonance are unknown.

If the two bands for XCIX (C_5H_{11}) and CIII were due primarily to phosphoryl stretching, then the absorbance of one band of each pair should increase as that of the other decreases, at least qualitatively, when the band absorbance ratio changes. The results in Table 25 reveal such behavior, especially for CIII. This behavior might also be expected if Fermi resonance were operative and the intensities of the fundamental(s) giving rise to the combination or overtone band in re-

Table 24. Frequencies and relative intensities of possible phosphoryl stretching bands for 1-oxo-4-pentyl-2,6,7-trioxa-1-phosphabicyclo [2.2.2] octane and trimethylphosphate in various solvents

	$O{=}P(OCH_3)_3$			$O{=}P(OCH_2)_3CC_5H_{11}$		
Solvent	Frequencies[a]	$\Delta\nu$[b]	Peak Max. Ratio[c]	Frequencies[a]	$\Delta\nu$[b]	Peak Max. Ratio[c]
CCl_4	1290, 1271	19	1.0	1326,1312	14	0.45[d]
CH_3CN	1278, 1266	12	1.6	1329,1320	9	0.68
$CHCl_3$	1276[e]			1332,1319	13	0.95
CH_2Cl_2				1330,1320	10	1.1
C_5H_5N	1284, 1271	13	1.6	1330,1320	10	1.4
C_6H_6	1290, 1273	17	1.3	1336,1320	16	2.4
C_6H_5Br	1288, 1273	15	1.4	1334,1320	14	3.6
$C_6H_5CH_3$	1288, 1271	17	1.2	1338,1315	23	4.1
$C_6H_3(CH_3)_3$	1294, 1277	17	1.1	1340		---[d]

[a] The stronger band of a pair is sharp. The uncertainty in a band position is ∓ 2 cm^{-1}.

[b] The difference between the two band frequencies.

[c] The ratio of percent transmission of the high- to low-frequency band. If the peak maximum ratio differs much from unity, the weaker band is often a shoulder. Percent transmissions were uncorrected for band overlaps.

[d] A vertical scale expansion was employed because the compound solubility was slight.

[e] The band is broader than a single band in other solvents and may contain two overlapping bands.

Table 25. Relationship of sum and ratio of absorbances of possible phosphoryl stretching bands for trimethylphosphate and 1-oxo-4-pentyl-2,6,7-trioxa-1-phosphabicyclo [2.2.2] octane

	$O{=}P(OCH_3)_3$		$O{=}P(OCH_2)_3CC_5H_{11}$	
	CCl_4	C_6H_5Br	CH_3CN	C_6H_5Br
Concentration, M	0.103	0.103	0.0482	0.0482
Frequencies	1290,1271	1288,1272	1328,1320	1335,1322
Absorbance ratio[a]	0.91	0.51	2.0	0.23
Absorbance sum[a]	0.47	0.46	0.49	0.75

[a] Absorbances not corrected for band overlap.

sonance were solvent independent.

An attempt was made to shift the phosphoryl stretching band(s) of XCIX (C_5H_{11}) by adding the acids iodine or phenol to a solution to interact with the basic phosphoryl oxygen. The spectral changes were too small to allow an interpretation, however, presumably because the basicity of XCIX (C_5H_{11}) is relatively weak (Section IV. K.).

In conclusion, Fermi resonance appears to be the most probable cause of the second band of the phosphoryl "doublet" for XCIX (R). Positive evidence for this conclusion would be obtained if substitution of $^{18}O{=}P$ for $^{16}O{=}P$ resulted in a single shifted band and a great loss of intensity of the second band. The shift would be approximately in the range 51-72 cm^{-1}, the limits corresponding to the smallest and largest possible reduced masses, respectively.

V. SUGGESTIONS FOR FUTURE WORK

Several general research areas worthy of investigation will now be considered. Some recommendations of specific experiments were made in Chapter IV and will not be repeated here.

Thermal inversion of the bonds to tricoordinate, trivalent phosphorus in 1-alkoxy-1-phospha-2,6-dioxacyclohexanes appears to have a half-life of many hours at room temperature. The rate of thermal inversion should be less than or equal to the rate of isomerization of such geometrically isomeric phosphites as XXX - XXXII. The inequality will apply if, for instance, an intermolecular alkoxyl exchange similar to halide exchange (see Section IV.E.4.) occurs. Since nonequilibrium mixtures of phosphite isomers can be prepared, the rate of isomerization can be determined from a knowledge of the ratio of isomers as a function of time. The isomer ratios can be found by comparison of areas of ^1H nmr resonances.

A tentative mechanism for intermolecular halide exchange in 1-halo-1-phospha-2,6-dioxacyclohexanes has been proposed. Determination of the free energy, enthalpy and entropy of activation for compounds differing with respect to exocyclic substitution at the carbon atoms of the ring should permit further elucidation of the mechanism. Comparison of these parameters for 1-chloro and 1-bromo analogs should help to clarify the nature of the P-halogen bond.

Geometrically isomeric 1-R-1-phospha-2,6-dioxacyclohexanes (Table 2) undergo a great variety of reactions that do not result in cleavage of the six-membered ring. If the configuration of the product(s) and reactant can be determined, the stereochemical course of the reaction can be deduced. Conversely, if the mechanism of the reaction and the configuration(s) of either the reactant or product cyclic molecule(s) are known, then the unknown configuration(s) can be established. The configurations can be determined by such means as x-ray diffraction and dipole moment analysis. If the latter method is employed, the dipole moments of both isomers of a product or reactant molecule should be determined before the configurations are considered known (see Section IV.H.).

The chemical shifts of the ring-methylene protons of a large number of 1-phospha-2,6-dioxacyclohexanes are reported in this Dissertation but no stereochemical conclusions are drawn from them. If the anisotropies of the bonds and lone-pairs of electrons in these molecules can be determined, then the disposition of exocyclic substituents relative to the ring-methylene protons might be established.

All of the R groups at phosphorus in the 1-R-1-phospha-2,6-dioxacyclohexanes that have been investigated appear to occupy the axial position in a chair conformer unless another exocyclic substituent in the molecule has a greater conformational preference that forces the R group elsewhere. The stereochemistry of compounds in which R is alkyl or aralkyl has not been examined but may provide the first examples of a preferred equatorial R, axial phosphorus lone-pair stereochemistry.

^{1}H nmr and infrared data for some 1-R-1-oxo-1-phospha-2,6-dioxacyclohexanes have been interpreted in terms of equilibria of chair conformers, but further evidence is desirable. Firstly, examination of a solution of one of these compounds at a low temperature may reveal spectra of both conformers rather than a weighted time average spectrum. Secondly, analysis of the ring-methylene proton resonances as the $AA'BB'$ or $AA'KK'$ parts of $AA'BB'X$ or $AA'KK'X$ spectra or analysis of the ^{13}C satellites of these resonances will allow determination of values of J(HCCCH). If two chair conformers are in equilibrium and the conformer ratio approaches unity, then the difference between $J(H_ACCCH_{A'})$ and $J(H_BCCCH_{B'})$ should approach zero. The small magnitudes of these four-bond couplings (< 3 Hz) reduce the attractiveness of this approach to studying conformer equilibria. Thirdly, determination of values of J(POCH) associated with the ring-methylene protons as a function of temperature should permit determination of the couplings for each conformer contributing to the equilibrium and the conformer enthalpy differences. The methyl phosphonate XIX′ (Table 14) exhibits considerable temperature dependence of couplings and ought to be investigated further in this respect.

Trialkylphosphites are not equally basic towards the Lewis acid BH_3 and a few relative basicities have been established. Further equilibrations of phosphites and phosphite boranes (see Section IV.L.) should be carried out and an attempt should be made to correlate the basicities with bonding in the phosphites or some other property. Similarly, an attempt should be made to relate the differences in phosphoryl bonding in trialkylphosphates to the bonding in the rest of the molecule and the molecular stereochemistry.

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