the presence of Cr(V) by magnetic and spectroscopic measurements.

Phase E was identified by comparison of its X-ray powder pattern with those of phase D as the isomorphous compound Sr_2CrO_4Cl. The unknown phase F had the chemical composition of $BaCrO_4$, but X-ray diffraction data and the green color of this phase indicated that this compound is not the familiar pale yellow $BaCrO_4$. The observed color change and shifts of X-ray reflections may suggest the presence of impurities in the crystal lattice or represent a polymorphic transition of $BaCrO_4$.

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Linear Correlation of the Phosphorus–Hydrogen Spin Coupling Constant with Proton Chemical Shifts in a Series of Polycyclic Phosphorus Compounds[1]

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Stable phosphonium salts are reported of the type [R(I)]X and [R(II)]X where I and II are the polycyclic phosphites 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane and 2,8,9-trioxa-1-phosphaadamantane, respectively, wherein R is $(C_6H_5)_3C$ or CH_3CH_2 and X is a perchlorate or tetrafluoroborate anion. Conductivity and n.m.r. spectral studies confirm their salt-like formulation and the caged structure of the phosphonium cation. A linear correlation is observed for the increase in the POCH coupling constant for the protons on the carbon β to the phosphorus atom with the downfield chemical shifts of protons on C_β, C_γ (axial), and C_δ in a series of derivatives of I and II including the salts. The results are discussed in terms of the decrease in s character of the phosphorus σ-bond to the fourth coordinate position on the phosphorus atom and the consequent increase in s character of the P–O links. Some new Arbuzov reactions of I and II are also reported.

Introduction

Although the reactions of trialkyl phosphites with a carbonium ion and a nucleophilic anion involve the Arbuzov reaction, similar reactions with nonnucleophilic anions have been limited to the salts formed from the reaction of trialkyl phosphites and $[(CH_3CH_2)_3O]BF_4$ or $[(C_6H_5)_3C]BF_4$.[2,3] Recently the Arbuzov reactions involving nucleophilic halides and the phosphites II[4,5] and the 4-ethyl analog of I[6] (shown in Figure 1) were described, and evidence was presented for the conformations of the products.

In this paper we report the preparation of stable phosphonium salts of I and II by the reaction of these ligands with triphenylmethyl perchlorate, triphenylmethyl tetrafluoroborate, or triethyloxonium tetrafluoroborate. Arbuzov products similar to those previously discussed[3–5] are also reported for the reactions of I and II with benzyl *p*-toluenesulfonate as well as triphenylmethyl chloride.

The proton chemical shifts and POCH coupling constants of I and II and their adducts formed with a series of Lewis acids were reported recently from our laboratories.[7] In the extension of this study to the H^1 and P^{31} resonances of these ligands in their transition metal complex ions,[8,9] it became of interest to measure the proton chemical shifts in phosphonium salts of I and II wherein phosphorus is tetracovalent as in the metal coordination compounds. In this way the effect of a positive charge on the proton chemical shifts of the base moiety could be ascertained in the absence of influences stemming from the more complex geometries and multiple bonding possibilities of the metal complexes formed with these polycyclic ligands.[9–12]

Experimental[13]

Solvents.—All solvents were reagent grade. Acetonitrile was refluxed over phosphorus pentoxide 3 hr. and distilled at atmospheric pressure. Acetone and methanol were dried over Linde 4-A Molecular Sieve. Pyridine was dried by refluxing over barium oxide for 2 days followed by distillation at atmospheric pressure. The constant-boiling fraction was stored over Linde 4-A Molecular Sieve.

Measurements.—Conductivities were measured on 0.001 *M* solutions at 25° with an Industrial Instruments Inc. Model RC-16B2 conductivity bridge at 1000 c.p.s. Proton n.m.r. spectra were obtained on approximately 10 to 30% by weight solutions at 14,100 gauss on a Varian HR-60 n.m.r. spectrometer. Infrared spectra in the sodium chloride region were obtained in Nujol and hexachlorobutadiene mulls on a Perkin-Elmer Model 21 spectrometer. Melting points were taken in open capillary tubes and are uncorrected. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory. Silver tetrafluoroborate was obtained from Alfa Inorganics, Inc.

Salts of Trialkyl Phosphites.—The tetrafluoroborate salts of

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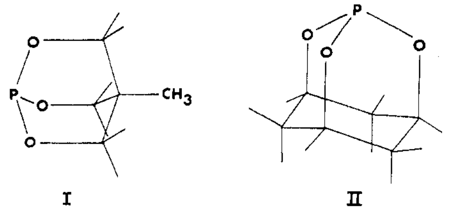

I II

Figure 1.—Structures of 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (I) and 2,8,9-trioxa-1-phosphaadamantane (II).

the cations formulated by Dimroth and Nurrenbach as $[(C_6H_5)_3CP(OCH_3)_3]^+$, $[(C_6H_5)_3CP(OCH_2CH_3)_3]^+$, $[CH_3CH_2P(OCH_3)_3]^+$, and $[CH_3CH_2P(OCH_2CH_3)_3]^+$ were prepared according to the methods described by these authors.[2,3]

4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (I).—The bicyclic phosphite (I) was prepared by a method described elsewhere[14] with the modification that the methyl alcohol was removed by distillation at atmospheric pressure after refluxing the homogeneous reaction mixture for 30 min. The unreacted trimethyl phosphite was then distilled from the mixture at 80° and 0.02 mm. The solid residue yielded 85% of I upon sublimation at 0.02 mm. and 50°.

1-Phospha-2,8,9-trioxaadamantane (II).—The tricyclic phosphite (II) was prepared by a method described previously[3] with the modification that the excess trimethyl phosphite and methanol were removed under vacuum at 80°. The product was obtained in 93% yield upon sublimation of the residue at 0.02 mm. pressure and 75°.

Triphenylmethyl Tetrafluoroborate.—This compound was prepared by the method of Sharp and Sheppard,[15] which involved a metathesis between silver fluoroborate and chlorotriphenylmethane in acetone under an atmosphere of nitrogen.

Triethyloxonium Tetrafluoroborate.—This compound was prepared by the method of Meerwein.[16]

Benzyl *p*-Toluenesulfonate.—This compound, which was prepared by the method of Tipson,[17] involved the reaction of benzyl alcohol with *p*-toluenesulfonyl chloride in pyridine. The product was unstable at room temperature and decomposed slowly even under vacuum. Decomposition was prevented by storing the substance at Dry Ice temperature.

1-Triphenylmethyl-4-methyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane Perchlorate (III).—To a solution of 2.27 g. (8.16 mmoles) of chlorotriphenylmethane in 15 ml. of acetone was added a solution of 1.00 g. (8.16 mmoles) of sodium perchlorate in 10 ml. of acetone. After a period of 5 min. the sodium chloride was filtered off and the supernatant allowed to pass into a solution of 1.21 g. (8.16 mmoles) of I in 10 ml. of acetone. A colorless crystalline material slowly formed over a period of 12 hr. The crystals were filtered and dried under vacuum at room temperature. A total of 3.93 g. (98% yield) of solid was obtained which was recrystallized from boiling acetonitrile.

1-Triphenylmethyl-2,8,9-trioxa-1-phosphaadamantane Perchlorate (IV).—This phosphonium salt was synthesized by the method described in the preceding preparation. A light yellow powder slowly formed over a period of 12 hr. which was filtered and dried under vacuum at room temperature. Upon recrystallization from boiling acetonitrile, 4.10 g. (100% yield) of colorless crystals was obtained.

1-Triphenylmethyl-4-methyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane Tetrafluoroborate (V).—To a solution of 1.43 g. (5.12 mmoles) of chlorotriphenylmethane in 15 ml. of acetone was added a solution of 1.00 g. (5.12 mmoles) of silver tetrafluoroborate in 10 ml. of acetone. After a period of 5 min. the silver chloride was filtered off and the supernatant allowed to pass into a solution of 0.76 g. (5.12 mmoles) of I in 10 ml. of acetone. The colorless crystals that formed were filtered off and dried under vacuum at room temperature. A total of 2.05 g. (84% yield) of solid was collected which was recrystallized from boiling acetone.

1-Triphenylmethyl-2,8,9-trioxa-1-phosphaadamantane Tetrafluoroborate (VI).—This salt was prepared in 80% yield by the method described for the synthesis of the preceding phosphonium salt. The colorless solid was recrystallized from boiling acetone.

1-Ethyl-4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane Tetrafluoroborate (VII).—To a solution of 2.60 g. (13.7 mmoles) of triethyloxonium tetrafluoroborate in 10 ml. of methylene chloride was added 4.06 g. (27.4 mmoles) of I in 10 ml. of methylene chloride. The colorless solution was allowed to stand 3 hr. at room temperature. Cooling to −10° resulted in the formation of colorless crystals which were washed three times with 100-ml. portions of carbon tetrachloride and subjected to vacuum drying at room temperature for 1 hr. A 65% yield was realized.

1-Ethyl-2,8,9-trioxa-1-phosphaadamantane Tetrafluoroborate (VIII).—This salt was prepared in 75% yield by the method described for the preparation of the preceding phosphonium salt.

1-α-Oxo-1-β-benzyl-4-α-*p*-toluenesulfonomethyl-4-β-methyl-1-phospha-2,6-dioxacyclohexane (IX). Method A.—A mixture of 2.62 g. (10.0 mmoles) of benzyl *p*-toluenesulfonate and 1.48 g. (10.0 mmoles) of I was heated in an evacuated sealed tube at 70° for 36 hr. A clear liquid was obtained, which crystallized completely upon standing at room temperature. The product was purified in 23% yield by recrystallizing from boiling methanol.

Method B.—To a solution of 2.62 g. (10.0 mmoles) of benzyl *p*-toluenesulfonate in 50 ml. of toluene was added a solution of 1.48 g. (10.0 mmoles) of I in 50 ml. of toluene. After refluxing for 6 hr. followed by cooling to room temperature, an oil was obtained which partially solidified upon addition of ether. The infrared spectrum of the solid was identical with that of the product obtained using method A.

3-α-Oxo-3-β-benzyl-7-α-*p*-toluenesulfonomethyl-2,4-dioxa-3-phosphabicyclo[3.3.1]nonane (X).—A mixture of 2.62 g. (10.0 mmoles) of benzyl *p*-toluenesulfonate and 1.60 g. (10.0 mmoles) of II was heated in an evacuated sealed tube at 85° for 6 hr. The resulting colorless solid was recrystallized in 21% yield from methanol.

1-α-Oxo-1-β-triphenylmethyl-4-β-methyl-4-α-chloromethyl-1-phospha-2,6-dioxacyclohexane (XI). Method A.—A mixture of 1.48 g. (10.0 mmoles) of I and 2.79 g. (10.0 mmoles) of chlorotriphenylmethane was melted in an evacuated sealed tube at 155° for 16 hr. The solid which formed was recrystallized from boiling acetone. A total of 3.50 g. (82% yield) of colorless crystals was obtained.

Method B.—To a solution of 0.74 g. (5.00 mmoles) of I in 10 ml. of acetonitrile was added a solution of 1.39 g. (5.00 mmoles) of chlorotriphenylmethane in 20 ml. of acetonitrile. A total of 1.80 g. (85% yield) of colorless crystals was collected upon allowing the solution to evaporate slowly. The compound was identical with that prepared by method A by its decomposition point and proton n.m.r. spectrum.

3-α-Oxo-3-β-triphenylmethyl-7-α-chloro-2,4-dioxa-3-phosphabicyclo[3.3.1]nonane (XII). Method A.—This compound was prepared by a procedure analogous to method A described in the preceding preparation. A 43% yield of colorless crystals was collected after recrystallizing the crude product from boiling benzene.

Method B.—This compound was prepared by a procedure analogous to method B in the preceding preparation using acetonitrile as the solvent system. Colorless crystals slowly formed in 92% yield upon standing. The compound was identical with that prepared by method A as shown by its decomposition point and proton n.m.r. spectrum.

Discussion

Structures based on the evidence presented later in this section are summarized in Figure 2. Molar conductances, melting points, and analyses are presented

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[14] C. W. Heitsch and J. G. Verkade, *Inorg. Chem.*, **1**, 392 (1962).

[15] D. W. A. Sharp and N. Sheppard, *J. Chem. Soc.*, 674 (1957).

[16] H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, *J. prakt. Chem.*, **154**, 83 (1939).

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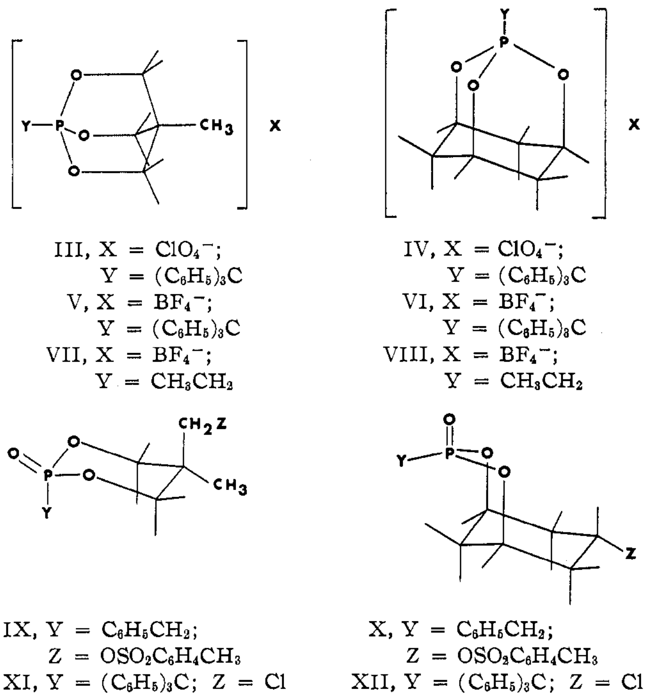

III, $X = ClO_4^-$; $Y = (C_6H_5)_3C$
V, $X = BF_4^-$; $Y = (C_6H_5)_3C$
VII, $X = BF_4^-$; $Y = CH_3CH_2$

IV, $X = ClO_4^-$; $Y = (C_6H_5)_3C$
VI, $X = BF_4^-$; $Y = (C_6H_5)_3C$
VIII, $X = BF_4^-$; $Y = CH_3CH_2$

IX, $Y = C_6H_5CH_2$; $Z = OSO_2C_6H_4CH_3$
XI, $Y = (C_6H_5)_3C$; $Z = Cl$

X, $Y = C_6H_5CH_2$; $Z = OSO_2C_6H_4CH_3$
XII, $Y = (C_6H_5)_3C$; $Z = Cl$

Figure 2.—Structures of compounds III–XII.

TABLE I

MOLAR CONDUCTANCES,[a] MELTING POINTS,[b] AND ANALYSES

Compound	λ, mhos/ cm. mole	M.p., °C.	Calcd., %		Found, %	
			C	H	C	H
III	146	198[c]	58.8	4.94	58.5	5.07
IV	132	183	59.6	4.82	60.5	5.08
V	141	230	60.2	5.08	60.0	5.18
VI	155	190	61.1	4.95	61.8	5.16
VII	131	72	...[e]			
VIII	151	115–117	...[e]			
IX	2.6[d]	171	55.6	5.71	55.6	5.61
X	4.3[d]	168	57.1	5.55	56.8	5.45
XI	0.2	201	67.5	5.64	67.3	5.68
XII	0.3	259	68.5	5.52	68.5	5.39

[a] The molar conductance of $(n\text{-}C_4H_9)_4NNO_3$ in acetonitrile is 158 and that of $(n\text{-}C_4H_9)_4NClO_4$ in methanol is 103. [b] With decomposition. [c] Exploded. [d] In methanol. [e] Air sensitive.

in Table I for the compounds synthesized in this work. Conductances at 25° were obtained in acetonitrile, except where indicated.

Arbuzov Products.—The proton n.m.r. spectra of IX and XI shown in Figure 3 are entirely consistent with the structure proposed by Wadsworth and Emmons for a series of similar compounds. The benzyl methylene in IX occurs as a doublet due to spin–spin splitting ($J_{PCH} = 22$ c.p.s.) by the phosphorus. It is not possible at present to assign the equatorial and axial proton chemical shifts with certainty in these derivatives.[18] Assuming that the transannular coupling between methylene groups is negligible, the six-line spectrum of the methylene hydrogens as split by the phosphorus may be analyzed as an ABX system. The magnitudes of both the POCH couplings and the geminal HCH coupling are all found to be equal (11.6 c.p.s.). The similarity in the n.m.r. spectra of compounds X and XII and the analogous compounds[4,5] in which Z = chloride and Y = benzyl, as well as the comparable steric requirements of these systems, is taken as supporting evidence for the conclusion that they have the same conformation.

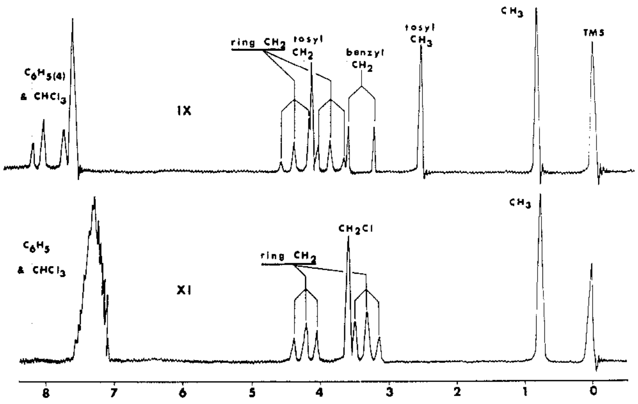

Figure 3.—Proton n.m.r. spectra of IX and XI in deuteriochloroform solution.

The infrared spectra of IX and X are very similar to that reported for the derivative where Z = Cl[3,4] with no significant changes in the P=O (1260 cm.$^{-1}$) and P—O—C (1015 cm.$^{-1}$) frequencies. These values are also found for the P=O and P—O—C frequencies in XI and XII.

Compounds XI and XII were prepared in order to compare their n.m.r. and infrared spectra with those of the triphenylmethyl salts of I and II discussed below. In spite of the low nucleophilic character and excellent ability to function as a leaving group, the *p*-toluenesulfonate anion attacks the cation formed from the triphenylmethyl carbonium ion and I or II to yield IX or X, respectively. These compounds possess no salt-like character as is confirmed by their negligible conductance values shown in Table I.

Phosphonium Salts.—That compounds III, IV, V, VI, VII, and VIII are true salts is supported by the conductivity data in Table I. These compounds are in general stable to heat and moist air and can be prepared in relatively high yields, which is in marked contrast to the instability, low yields, and lower melting points of the previously reported analogous salts of open-chain phosphites.[2,3,19] Although the rigid and symmetrical cations III, IV, V, VI, VII, and VIII contribute to the high lattice energies associated with compounds of polycyclic phosphites,[20] the increased stabilization of the cation in solution can only be attributed to a stronger P–C bond. Apart from changes in hybridization around the phosphorus atom which are undoubtedly minimal upon quaternization of I or II, the main contribution to the increased stability stems from the reduced steric hindrance to coordination of a triphenylmethyl or ethyl carbonium ion as well as the greater polarity of the phosphite moiety.[21]

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[18] See ref. 7 for a discussion of this problem in a series of polycyclic phosphorus compounds of a related structure.

[19] Although these salts do form under the conditions specified by Dimroth and Nurrenbach,[2,3] isomerization has been shown to take place by means of n.m.r. studies. These results will be published in the future.

[20] J. G. Verkade and C. W. Heitsch, *Inorg. Chem.*, **2**, 512 (1963).

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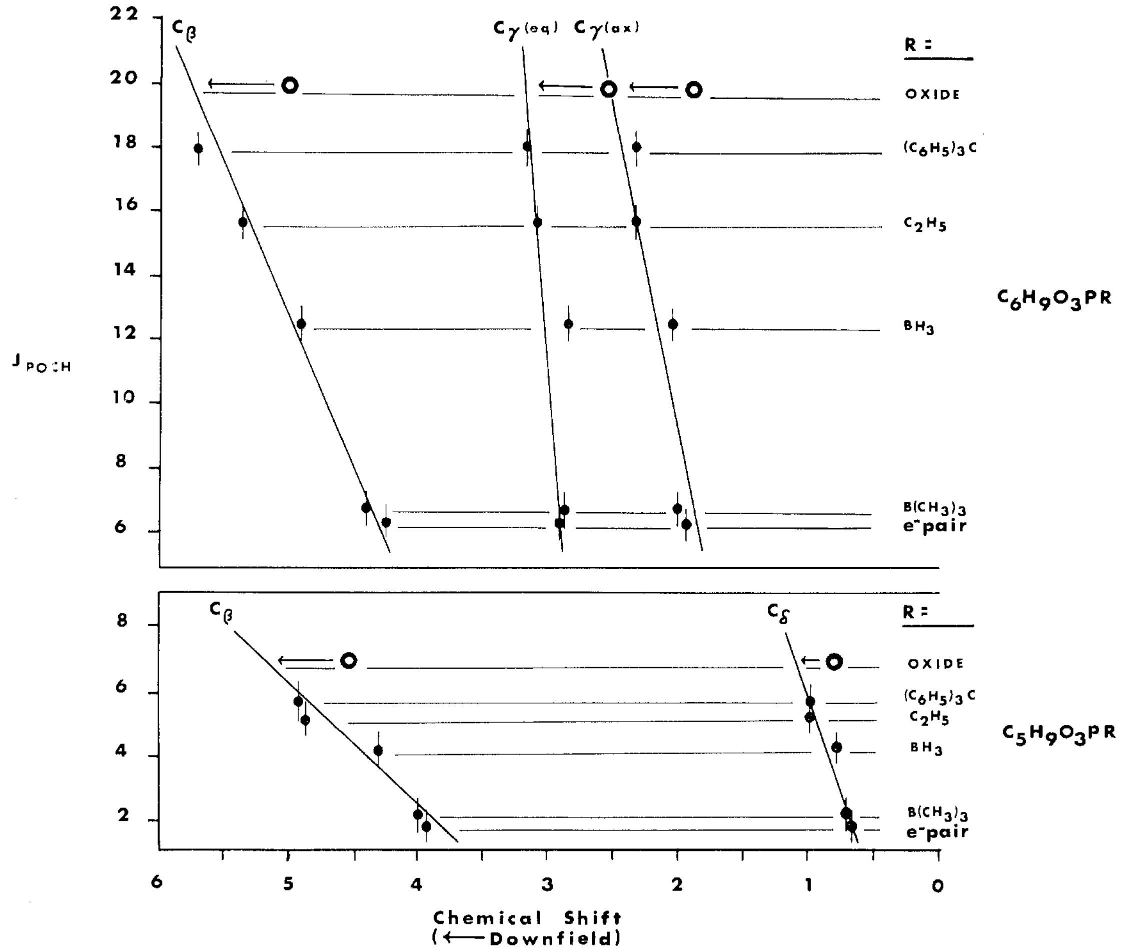

Figure 4.—Spin coupling (c.p.s.) of P to H on C_β carbons (J_{POCH}) *vs.* chemical shift ($-$p.p.m. with respect to tetramethylsilane) of protons in $C_5H_9O_3P$ (I) and $C_6H_9O_3P$ (II) and their $B(CH_3)_3$, BH_3, C_2H_5, $(C_6H_5)_3C$, and oxide derivatives.

N.m.r. Studies.—From Table II it can be seen that there is a variation of the value of J_{POCH} with the chemical shifts of the protons on C_β in I and II and their respective derivatives, in striking contrast to a similar series of compounds of trimethyl and triethyl phosphite. Moreover it is significant that a plot of these parameters for protons on C_β and $C_{\gamma(\text{axial})}$ in II and its derivatives and for protons on C_β and C_δ in I and its compounds is reasonably linear as shown in Figure 4. The large differences in J_{HCOP} values in these two series of compounds have been discussed previously.[7] Whereas the phosphorus–acceptor bond in all of the compounds can be considered to be purely σ in character, it is tentatively concluded that the rise in J_{POCH} stems from an increase in s character of the three P–O bonds as the phosphorus–acceptor bond increases in p character. This rise in s character of the P–O bond is attributable to the increasing electronegativity of the acceptor groups wherein a lone pair of electrons $< B(CH_3)_3 < BH_3 < CH_3CH_2 < (C_6H_5)_3C$. The increase in the electronegativity of these acceptor groups is compatible with the observed downfield trend of the C_β and $C_{\gamma(\text{axial})}$ and C_β and C_δ protons in I and II, respectively, for this series of derivatives, since an increasingly positive charge accumulates on the phosphite moiety. From the constancy of the C^{13}–H coupling constants shown in Table III for an open-chain and a polycyclic phosphite with respect to their corresponding phosphate derivatives, it can be seen that the change in the fraction of s character $(\alpha^2{}_H)^{22}$ of the carbon orbital bonding the methylene hydrogens is negligible upon attachment of an electronegative group such as oxygen to the phosphorus atom.

The deviation of the $C_{\gamma(\text{equatorial})}$ protons in the boron adducts of II can be understood by a consideration of a molecular dipole effect in these compounds. Previously,[7] it was pointed out that the small upfield shift experienced by the $C_{\gamma(\text{equatorial})}$ proton in the increasingly polar boron adducts of II could arise from an increase in moment of the effective dipole along the axis of highest symmetry rather than from a charge effect due to the increasing electron-withdrawing power of the boron moiety.

The interpretation presented above for the results depicted in Figure 4 has been employed by Kaesz, *et al.*,[23] to explain similar trends in a number of trialkylphosphine derivatives. However, no linear correlations of phosphorus–proton coupling constants with the proton chemical shifts in the trialkylphosphines are

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(22) C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).

(23) J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, in press.

TABLE II

PHOSPHITE DERIVATIVE PROTON CHEMICAL SHIFTS (P.P.M. *vs.* $Si(CH_3)_4$)[a,b]

Compound	Cβ	Cγ[c]		Cδ	J_{POCH}, c.p.s.
$(CH_3O)_3P$	3.69				11.35
$(CH_3O)_3PB(CH_3)_3$	3.69				9.60
$(CH_3O)_3PBH_3$	3.70				11.00
$[(CH_3O)_3PCH_2CH_3]BF_4$	...[d]				
$[(CH_3O)_3PC(C_6H_5)_3]BF_4$	3.90				10.85
$(CH_3O)_3P{=}O$	3.46				10.65
$(CH_3CH_2O)_3P$	3.82	1.20			7.50
$[(CH_3CH_2O)_3PCH_2CH_3]BF_4$	4.50	1.42			7.45
$[(CH_3CH_2O)_3PC(C_6H_5)_3]BF_4$	4.33	1.20			6.70
$(CH_3CH_2O)_3P{=}O$	4.05	0.99			6.84
$C_5H_9O_3P$ I	3.93			0.68	1.8
$C_5H_9O_3PB(CH_3)_3$	3.98			0.70	2.2
$C_5H_9O_3PBH_3$	4.30			0.80	4.2
$[C_5H_9O_3PCH_2CH_3]BF_4$ VII	4.86			0.99	5.2
$[C_5H_9O_3PC(C_6H_5)_3]BF_4$ (or ClO_4^-) V (or III)	4.92			0.99	5.8
$C_5H_9O_3P{=}O$	4.48			0.80	7.0
$C_6H_9O_3P$ II	4.24	2.90	1.93		6.3
$C_6H_9O_3PB(CH_3)_3$	4.38	2.87	1.98		6.7
$C_6H_9O_3PBH_3$	4.88	2.85	2.05		12.5
$[C_6H_9O_3PCH_2CH_3]BF_4$ VIII	5.37	3.08	2.33		15.7
$[C_6H_9O_3PC(C_6H_5)_3]BF_4$ (or ClO_4^-) VI (or IV)	5.45	3.18	2.34		18.0
$C_6H_9O_3P{=}O$	5.00	2.56	1.90		20.0

[a] Greek subscripts refer to the position of the proton-bearing carbon atom with respect to phosphorus. [b] The n.m.r. data for the compounds of I and II except for the salts are taken from ref. 7. [c] Where two values are reported, the higher refers to the equatorial and the lower to the axial hydrogen. [d] See ref. 19.

apparent. It is evident that the structural rigidity of the compounds studied in this work precludes any significant conformational changes upon coordination of the phosphite which may be of importance in open-chain phosphines.

TABLE III

C^{13}–H COUPLING CONSTANTS (J)

Compound	J (±1 c.p.s.)	α^2_H, %[a]
$(CH_3O)_3P$	145	29.0
$(CH_3O)_3P{=}O$	148	29.6
$CH_3CH_2C(CH_2O)_3P$	150	30.0
$CH_3CH_2C(CH_2O)_3P{=}O$	154	30.8

[a] The fraction (α^2_H) of s character employed by the carbon in its bond to hydrogen was calculated from $J = 500\alpha^2_H$ (see ref. 22).

Compounds of I and II in which the phosphorus atom can π-bond to the acceptor group consistently fall to the right of the lines in Figure 4 when similarly plotted. The phosphate derivatives of I and II are shown for comparison since an unusually large amount of π-bonding is postulated to occur in these compounds.[24] Similar results for a series of metal carbonyl complexes of I are discussed elsewhere.[9]

No distinct downfield trends are noted in Table II for the protons in trimethyl and triethyl phosphite derivatives with increasing electronegativity of the σ-bonding acceptor group. The anomalous constancy of J_{POCH} in these respective derivatives cannot be interpreted by the simple arguments presented for the derivatives of I and II. It is possible that any change in coupling constant brought about by varying the acceptor group is compensated by a structural change due to the greater flexibility of the open-chain phosphite systems.

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(24) J. G. Verkade, *Inorg. Chem.*, in press.