Preparation and Nuclear Magnetic Resonance Study of Phosphorus Compounds Containing Alkenyl Functional Groups[1]

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The phosphines $PPh_n(CH_2CH_2CH{=}CH_2)_{3-n}$, $n = 2–0$, $PPh_n(CH_2CH_2CH_2CH{=}CH_2)_{3-n}$, $n = 1$ or 2, and $PPh_2CH_2CH{=}CH_2$ have been synthesized and studied by ^1H and ^{31}P magnetic resonance. The n.m.r. spectra of $PPh_2(OCH_2CH{=}CH_2)$, its oxide, $O{=}PPh_2(OCH_2CH{=}CH_2)$, and its Arbuzov rearrangement product, $O{=}PPh_2(CH_2CH{=}CH_2)$, have been investigated by ^{31}P decoupling of the proton spectrum, selective proton decoupling of the ^{31}P spectrum, and comparison with computer-simulated spectra to determine the spin–spin coupling constants. The n.m.r. spectra of the related oxides $O{=}PPh_2CH_2CH_2CH{=}CH_2$, $O{=}P(CH_2CH_2CH{=}CH_2)_3$, and $O{=}P(OCH_2CH{=}CH_2)_3$ are also assigned. The data indicate that $^3J_{PH} > {}^2J_{PH}$ for alkenylphosphines, $^2J_{PH}$ is larger for phosphine oxides than for phosphines, and $^3J_{PH}$ is little changed in comparing phosphorus(III) with phosphorus(V) compounds.

On a synthétisé les phosphines $PPh_n(CH_2CH_2CH{=}CH_2)_{3-n}$, $n = 2–0$, $PPh_n(CH_2CH_2CH_2CH{=}CH_2)_{3-n}$, $n = 1$ ou 2 et $PPh_2CH_2CH{=}CH_2$ et étudié leurs spectres de résonance magnétique du proton et du ^{31}P. Les spectres r.m.n. du $PPh_2(OCH_2CH{=}CH_2)$, de son oxyde $O{=}PPh_2(OCH_2CH{=}CH_2)$ et de son produit de réarrangement d'Arbuzov $O{=}PPh_2(CH_2CH{=}CH_2)$, ont été examiné en découplant le phosphore du spectre du proton, en découplant d'une façon sélective des protons du spectre du ^{31}P et par comparaison avec des spectres simulés par ordinateur pour déterminer les constantes de couplage spin–spin. Les spectres r.m.n. des oxydes $O{=}PPh_2CH_2CH_2CH{=}CH_2$, $O{=}P(CH_2CH_2CH{=}CH_2)_3$ et $O{=}P(OCH_2CH{=}CH_2)_3$ ont aussi été attribués. Les données indiquent que $^3J_{PH} > {}^2J_{PH}$ pour les alkénylphosphines que $^2J_{PH}$ est plus grand pour les oxydes de phosphine que pour les phosphines et que le $^3J_{PH}$ ne subit que peu de changement lorsque l'on compare les composés du phosphore(III) avec les composés du phosphore(V). [Traduit par le journal]

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Introduction

The use of phosphine and phosphite compounds as ligands in low-valent transition metal complexes has increased steadily during the last decade (1). Tertiary phosphorus compounds are able to stabilize electron rich metal atoms since phosphorus participates in σ donation to the metal and may also accept electron density from the metal into energetically favorable d orbitals. In spite of the widespread use of phosphorus compounds as ligands, little n.m.r. data on phosphines containing alkenyl groups is available even though they have been shown to function as chelates with a large number of transition metals (2–8). The determination of the structure of metal–phosphorus complexes is frequently based on the assignment of their ^1H and ^{31}P spectra. In general, a corresponding amount of data concerning the uncomplexed phosphorus ligands has not appeared. We wish to report the ^1H and ^{31}P magnetic resonance spectra of a representative series of phosphine, phosphinite, and phosphite complexes and to present generalizations concerning the chemical shift and coupling data (Fig. 1) for these potential ligands.

Experimental

All reactions were run under an atmosphere of argon using freshly distilled reactants and solvents. Due to the air sensititivity of the phosphorus(III) compounds, all manipulations were carried out under an inert atmosphere. All phosphines were stored under argon and were removed by syringe while under an argon flow.

$PClPh_2$, PCl_2Ph, and PCl_3 were purchased from Aldrich Chemical Co. 4-Bromo-1-butene and 5-bromo-1-butene were purchased from Pierce Chemical Co. The phosphites $P(OCH_2CH{=}CH_2)_3$ and $O{=}P(OCH_2CH{=}CH_2)_3$ were a gift from the Weston Chemical Co.

^{31}P spectra were recorded on a Varian XL-100 spectrometer using 50% by volume solutions in $CHCl_3$. ^1H spectra were obtained on a Varian HR 220 spectrometer using 50% solutions in $CDCl_3$. Phosphorus decoupling power was generated using standard components: an HP-5100B frequency synthesizer, an HP-10515A fre-

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TABLE 1. Preparation of phosphorus(III) compounds

Compound	Alkene	Chlorophosphine	Boiling point (°C)	Yield (%)
$PPh_2(OCH_2CH{=}CH_2)$	$HOCH_2CH{=}CH_2$	$PClPh_2$		92
$PPh_2{-}CH_2CH{=}CH_2$	$ClCH_2CH{=}CH_2$	$PClPh_2$	118–128(0.2 Torr)	80
$PPh_2((CH_2)_2CH{=}CH_2)$	$Br(CH_2)_2CH{=}CH_2$	$PClPh_2$	115 (0.1 Torr)	85
$PPh_2((CH_2)_3CH{=}CH_2)$	$Br(CH_2)_3CH{=}CH_2$	$PClPh_2$	152–154(0.8 Torr)	67
$PPh((CH_2)_2CH{=}CH_2)_2$	$Br(CH_2)_2CH{=}CH_2$	PCl_2Ph	120–122(0.2 Torr)	79
$PPh((CH_2)_3CH{=}CH_2)_2$	$Br(CH_2)_3CH{=}CH_2$	PCl_2Ph	131–133(1.0 Torr)	84
$P((CH_2)_2CH{=}CH_2)_3$	$Br(CH_2)_2CH{=}CH_2$	PCl_3	65– 75(1.0 Torr)	54

quency doubler, an HP-230B tuned amplifier, and an ENI 10 W broad band power amplifier. The additional equipment necessary, a probe matching network, attenuator, and a through-line power SWR meter allowed generation of up to 10 W decoupling power at 89 MHz for the HR 220 probe while observing proton decoupling in the frequency sweep mode.

Theoretical spectra were obtained using a Nicolet n.m.r. spectrum calculation program (NMRCAL) NIC-80/S-7117-D.

Preparation of $P(CH_2CH_2CH{=}CH_2)_3$

All of the PR_3 ligands were prepared by the general method outlined here for $P(CH_2CH_2CH{=}CH_2)_3$. The specific alkene and phosphine chloride used are tabulated in Table 1 along with boiling points and yields.

A Grignard reagent was prepared under argon in a predried reaction vessel by the slow addition of 4-bromo-1-butene (66.0 g, 0.489 mol) in 150 ml of predried ether to magnesium turnings (13.2 g, 0.544 mol) in 300 ml of refluxing ethyl ether. When the formation of the Grignard reagent was complete, phosphorus trichloride (18.7 g, 0.136 mol) in 250 ml of ethyl ether was added dropwise to the solution while maintaining the temperature at 0 °C. Upon completion of the addition, the excess Grignard reagent was hydrolyzed with 50 g of NH_4Cl in 250 ml of water. The organic layer was siphoned into a second flask, dried over Na_2SO_4, and distilled under reduced pressure. All manipulations were carried out under a flow of argon since the phosphine is air sensitive.

All reported oxides were prepared by air oxidation. They were then washed with hexane, dried, and checked for purity by examination of their ^1H and ^{31}P n.m.r. spectra. $O{=}PPh_2(CH_2CH{=}CH_2)$ was also prepared by Arbuzov rearrangement of $PPh_2(OCH_2CH{=}CH_2)$ as described below.

Preparation of $PPh_2(OCH_2CH{=}CH_2)$

This reaction was carried out in a manner similar to that previously reported (9) under a flow of argon in a predried reaction vessel using freshly distilled allyl alcohol and $PClPh_2$. Allyl alcohol (2.8 ml, 0.041 mol), pyridine (3.2 ml, 0.041 mol), and 40 ml of dry ethyl ether were chilled to 0° in an ice bath. $PClPh_2$ (7.1 ml, 0.040 mol) in ether (4 ml) was added over a period of 30 min. The solution was allowed to stir for 20 min and the pyridine hydrochloride, which had precipitated, was then separated by filtration using standard Schlenk technique. The excess reagents and ethyl ether were removed under vacuum. The liquid product cannot be distilled due to extensive Arbuzov rearrangement to $O{=}P(CH_2CH{=}CH_2)$ when heated (10). Purity was checked by ^1H n.m.r. integration and by the absence, in the ^{31}P n.m.r. spectra, of resonances due to species produced by rearrangement or oxidation.

Allowing $PPh_2(OCH_2CH{=}CH_2)$ to come into contact with air for 12 h resulted in its oxidation to $O{=}PPh_2(OCH_2CH{=}CH_2)$ which may also be synthesized by reacting diphenylphosphinic chloride with allyl alcohol in the presence of triethylamine in ether (11).

Results and Discussion

Nuclear Magnetic Resonance Chemical Shifts

A considerable effort has been spent in the interpretation of ^{31}P chemical shifts (12, 13). Changes in the number of substituents and their electronegativities, the degree of π-bonding, and the resultant bond angles about the phosphorus have all been considered. The interrelationships among these parameters and the importance of each have, however, not been established for even the symmetrically substituted phosphines, PR_3. For unsymmetrically substituted compounds the problem is more difficult.

The phosphorus chemical shift values listed in Table 2 can, however, be separated into three groups: PR_3, $\delta = +16$ to $+30.7$ p.p.m.; $O{=}PR_3$, $O{=}P(OR)R_2$, and $O{=}P(OR)_3$, $\delta = -45.9$ to $+1.9$ p.p.m.; and $P(OR)R_2$ and $P(OR)_3$, $\delta = -113$ to -138.8 p.p.m. The large chemical shift difference between groupings is of value for qualitative (12) and semi-quantitative determination of sample purity for these compounds.

Examination of the ^1H n.m.r. spectra of the 13 phosphorus compounds shows three olefinic protons in the region 4.11 to 5.14 τ; methylene protons are observed in the region 7.65 to 8.56 τ for butenyl and pentenyl, *ca.* 7 τ for allyldiphenylphosphine and allyldiphenylphosphine oxide, and *ca.* 5.5–5.7 τ for phosphinites, phosphites, and their oxides.

The phenyl resonance consists of two multiplets, ratio 2:3, consistent with the usual assign-

TABLE 2. Nuclear magnetic resonance data

Compound[a]	^{31}P	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	^3J (H_1–H_3)	^3J (H_2–H_3)	^3J (H_3–H_4)	$^2J_{PH}$	$^3J_{PH}$
$PPh_2OCH_2CH{=}CH_2$[b] (map)	−113.0	4.81	4.99	4.21	5.74			2.53	2.72	17.0	10.3	5.2		9.6
$O{=}PPh_2OCH_2CH{=}CH_2$ (mapo)	−30.9	4.73	4.83	4.13	5.53			2.20	2.63	17.0	10.4	5.6		8.6
$P[OCH_2CH{=}CH_2]_3$[c] (tap)	−138.8	4.76	4.90	4.15	5.72					17.0	10.4	5.2		8.0
$O{=}P[OCH_2CH{=}CH_2]_3$ (tapo)	+1.9	4.69	4.81	4.11	5.50					17.0	10.4	5.6		8.8
$PPh_2CH_2CH{=}CH_2$ (app)	+17.1	5.10	5.14	4.31	7.23			2.60	2.74	17.0	10.3	7.0	≤0.8	6.0
$O{=}PPh_2CH_2CH{=}CH_2$ (appo)	−28.2	4.85	4.85	4.23	6.87			2.20	2.48			7.4	14.4	6.0
$PPh_2(CH_2)_2CH{=}CH_2$ (mbp)	+16.5	5.06	5.11	4.19	7.9	7.9		2.60	2.70	17.0	10.3	5.9		7.5
$O{=}PPh_2(CH_2)_2CH{=}CH_2$ (mbpo)	−30.8	5.03	5.11	4.25	7.65	7.65		2.27	2.61	17.0	10.3	5.4		
$PPh_2(CH_2)_3CH{=}CH_2$ (mpp)	+17.6	5.06	5.13	4.28	7.91	8.51	8.02	2.66	2.86	17.2	10.3	6.6	≤0.8	8.0
$PPh[(CH_2)_2CH{=}CH_2]_2$[d] (dbp)	+25.4	5.00	5.08	4.17	7.92	8.20		2.52	2.68	17.2	10.2	6.6	≤0.8	
$PPh[(CH_2)_3CH{=}CH_2]_2$[e] (dpp)	+26.3	5.10	5.12	4.32	7.95	8.56	8.36	2.58	2.75	17.0	10.4	6.6	≤0.8	8.5
$P[(CH_2)_2CH{=}CH_2]_3$[f] (tbp)	+30.2	4.98	5.06	4.18	7.86	8.53				17.1	10.2	6.0	≤0.8	7.8
$O{=}P[(CH_2)_2CH{=}CH_2]_3$[g] (tbpo)	−45.9	4.90	4.98	4.24	7.57	8.25				17.1	10.3		10.6	

[a] The ^1H n.m.r. spectra of all compounds were analyzed at 16 °C at 220 MHz in 50% (vol.) $CDCl_3$ with TMS as reference at τ 10.0. ^{31}P chemical shifts (± 0.3 p.p.m.) are relative to 85% H_3PO_4. Chemical shifts are for the center of the multiplet. All peak intensities were checked by integration.

[b] Additional coupling constants are: $^4J(P\text{–}H_3) \leq 0.8$ Hz, $^5J(P\text{–}H_1)$ and $^5J(P\text{–}H_2) \leq 1$ Hz.

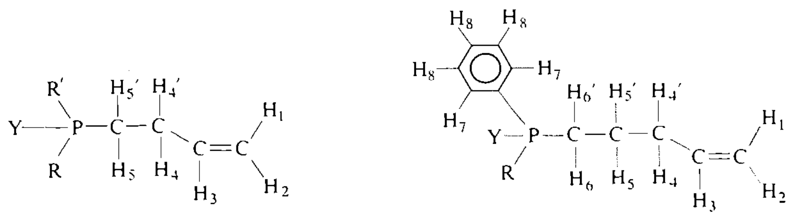
[c] Additional coupling constants are: $^4J(P\text{–}H_3) \leq 0.8$ Hz, $^5J(P\text{–}H_1)$ and $^5J(P\text{–}H_2) \leq 1$ Hz.

[d] Additional coupling constants are: $^3J(H_4\text{–}H_5') = {}^3J(H_4'\text{–}H_5) = 7.0$ Hz, $^3J(H_4'\text{–}H_5') = J(H_4\text{–}H_5) = 8.0$ Hz, $^2J(P\text{–}H_5) = {}^2J(P\text{–}H_5') \leq 0.8$.

[e] Additional coupling constants are: $^3J(H_5\text{–}H_6') = {}^3J(H_5'\text{–}H_6) = 7.0$ Hz, $^3J(H_5'\text{–}H_6') = {}^3J(H_5\text{–}H_6) = 8.0$ Hz, $^2J(P\text{–}H_6) = {}^2J(P\text{–}H_6') \leq 0.8$.

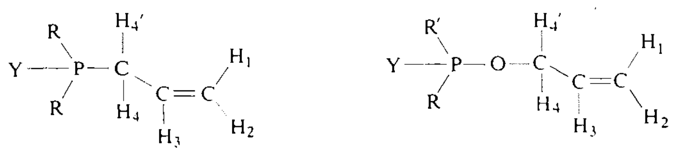
[f] Additional coupling constants are: $^3J(H_4\text{–}H_5') = {}^3J(H_4'\text{–}H_5) = 6.0$ Hz, $^3J(H_4'\text{–}H_5') = {}^3J(H_4\text{–}H_5) = 10.5$ Hz, $^2J(H_4\text{–}H_4') = {}^2J(H_5\text{–}H_5') = 10$ Hz, $^2J(P\text{–}H_5) = {}^2J(P\text{–}H_5') \leq 0.8$ Hz.

[g] Additional coupling constants are: $^3J(H_4\text{–}H_5') = {}^3J(H_4'\text{–}H_5) = 6.0$ Hz, $^3J(H_4'\text{–}H_5') = {}^3J(H_4\text{–}H_5) = 10.5$ Hz, $^2J(H_4\text{–}H_4') = {}^2J(H_5\text{–}H_5') = 10$ Hz, $^2J(P\text{–}H_5) = {}^2J(P\text{–}H_5') = 10.6$ Hz.



mbp Y = Lone pair; R=R'=C_6H_5
mbpo Y = Oxygen; R=R'=C_6H_5
dbp Y = Lone pair; R=C_6H_5; R'=C_4H_7
tbp Y = Lone pair; R=R'=C_4H_7
tbpo Y = Oxygen; R=R'=C_4H_7

mpp Y = Lone pair; R=C_6H_5
dpp Y = Lone pair; R=C_5H_9



app Y = Lone pair; R=C_6H_5
appo Y = Oxygen; R=C_6H_5

map Y = Lone pair; R=R'=C_6H_5
mapo Y = Oxygen; R=R'=C_6H_5
tap Y = Lone pair; R=R'=OC_3H_5
tapo Y = Oxygen; R=R'=OC_3H_5

FIG. 1. Numbering system for the protons of the compounds studied.

ment of two lower field *ortho* protons and three higher field *meta–para* protons. The *ortho* protons in the oxides are shifted to lower fields, 2.20–2.27 τ, than the corresponding phosphorus(III) compounds, 2.52–2.66 τ. This difference in chemical shifts for the *ortho* protons is helpful in the determination of sample purity.

Nuclear Magnetic Resonance Spin–Spin Coupling Constants

The reported variations in the magnitude of P–H couplings are large. In phosphine compounds, PR_3, the observed vicinal coupling constant is larger than the geminal coupling constant $^3J_{PH} > {}^2J_{PH}$; *e.g.* in $P(CH_2CH_3)_3$, $^3J_{PH} = +13.65$ and $^2J_{PH} = +0.5$ (12); and in $P[CH(CH_3)_2]_3$, $^3J_{PH} = +11.73$ and $^2J_{PH} = -2.27$ Hz (14).

The magnitudes of both the geminal and vicinal phosphorus–hydrogen coupling constants have been shown to have angular dependence. The geminal coupling constants in a rigid structure like that for 1-phenyl-3,4-dimethylphosphocyclo-3-pentene vary between +25 Hz for $^2J_{PH}$ at a dihedral angle of 9° from the phosphine lone pair to the geminal hydrogen to −6 Hz for $^2J_{PH}$ where the hydrogen is at a dihedral angle of 111° (15). In compounds where free rotation about the P—C bond is possible $^2J_{PH}$ represents the weighted average of the coupling constants, depending upon the populations of the various conformers. Vicinal coupling constants in cyclic compounds containing the P—O—C linkage have been related to the P—O—C—H dihedral angle with $^3J_{PH}$ reaching a maximum when phosphorus is *trans* to hydrogen and a minimum in the *gauche* position (16). Another study (17) on such cyclic compounds has shown vicinal coupling constants can also be related to the stereochemistry of the phosphorus lone pair. Values as large as 33 Hz have been observed (18). In systems with fast rotation about the O—C bond axis, average $^3J_{PH}$ coupling constants were observed (12), *e.g.* $O{=}P(OCH_2CH_3)_3$, 8.7 Hz and $P(Ph)(OCH_2CH_3)_2$, 6.9 Hz.

The presence of only one methylene group in allyldiphenylphosphinite (map) and tris(allyl)phosphite (tap) permitted the interpretation and assignment of all phosphorus–hydrogen couplings (Table 2). The assignment of the larger coupling in the methylene resonance (Fig. 2) to $^3J_{PH}$ for map was confirmed by ^{31}P partial decoupling of the ^1H n.m.r. spectrum resulting in

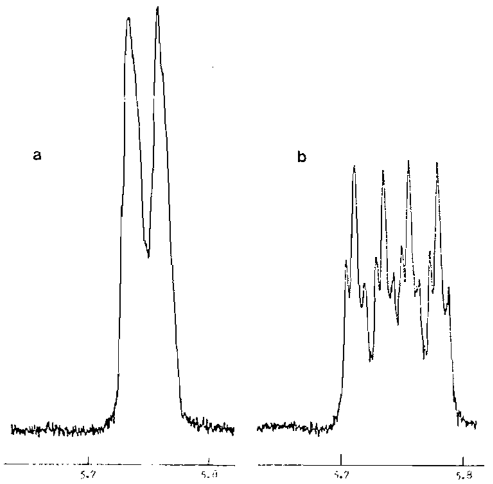


FIG. 2. The 220 MHz ^{1}H n.m.r. spectrum of the methylene region of allyldiphenylphosphinite (map): (*a*) phosphorus decoupled, (*b*) normal.

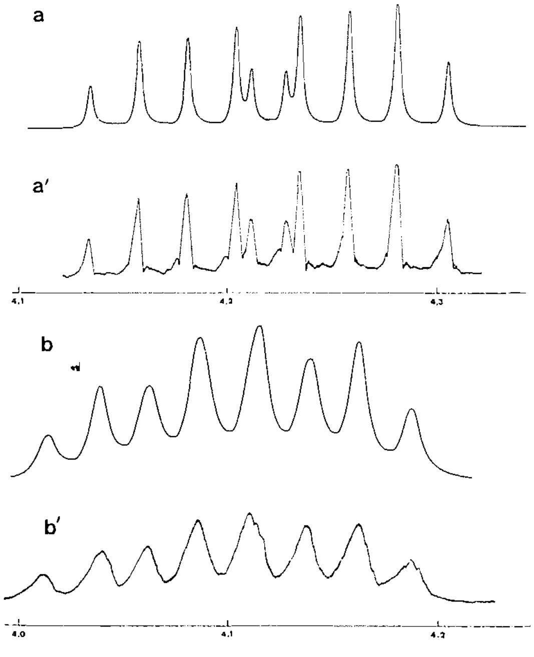


FIG. 3. The 220 MHz ^{1}H n.m.r. spectra of the H_3 olefinic proton in: (*a*) allyldiphenylphosphinite (map), computer simulated, (*a′*) observed; (*b*) triallylphosphate (tapo), computer simulated, (*b′*) observed.

collapse of the quartet of triplets to a pseudo doublet of triplets. The larger remaining coupling in this methylene resonance (Fig. 2*a*) was assigned as vicinal coupling to the olefinic proton, H_3, $^3J(H_3–H_4) = 5.2$ Hz, confirmed by comparison with the computer simulated spectrum (Fig. 3*a*). The vicinal phosphorus–hydrogen coupling for tap was confirmed by observation of the hydrogen coupled ^{31}P resonance at $\delta = -138.8$ in which a septet (single peak $w_{1/2} = 2.2$ Hz) is observed due to coupling to six equivalent methylene protons with $^3J_{PH} = 8.0$ Hz. Additional coupling, $^3J(H_3–H_4) = 5.3$ Hz, was assigned by comparison of the ^{1}H n.m.r. spectrum to the synthesized spectrum (Fig. 3*b*); broadening of the multiplet may be due to additional H–H coupling across phosphorus. The long range phosphorus–hydrogen coupling in map and tap is $^4J(P–H_3) \leqslant 0.8$ Hz, $^5J(P–H_1)$ and $^5J(P–H_2) \leqslant 1$ Hz. Surprisingly, for the oxides of map and tap, $^3J_{PH} = 8.6$ and 8.8 Hz, respectively, varying less than 1 Hz from the corresponding coupling in map and tap.

The assignment of the coupling in the phosphine compounds reported in Table 2 resulted in values of $^2J_{PH} \leqslant 0.8$ Hz and $^3J_{PH} = 6.0$–8.5 Hz. No effort was made to determine the signs of the geminal coupling constants since the values are quite small. The vicinal coupling constants were assumed to be positive. The interpretation of the multiplets for the methylene protons becomes increasingly complicated with increasing numbers of methylene groups due to overlap of the resonances. The assignment of $^2J_{PH} \leqslant 0.8$ and $^3J_{PH} = 6.0$ Hz for the methylene protons in allyldiphenylphosphine (app) is based upon analysis of the ^{1}H n.m.r. spectrum as an A_2BCDX system ($A_2 = H_4, H_4'$; $B = H_2$; $C = H_1$; $D = H_3$; $X = P$) and is confirmed, with assignment of $^3J(H_3,H_4) = 7.0$ Hz, by comparison of the H_3 resonance to the computed spectrum. In the butenyl- and pentenylphosphines the vicinal coupling between H_3 and the adjacent methylene protons, H_4, was obtained from analysis of the H_3 resonance. Phosphorus–hydrogen coupling of similar magnitude to that in app occurs in the other phosphines, for example in tbp $^2J_{PH} \leqslant 0.8$ and $^3J_{PH} = 7.8$ Hz. However, in the oxides of these phosphines the magnitude of the geminal coupling $^2J_{PH}$ is much greater. In allyldiphenylphosphine oxide (appo) $^2J_{PH} = 14.4$ and $^3J_{PH} = 6.0$, and in tributenylphosphine oxide (tbpo) $^2J_{PH} = 10.6$ Hz. This behavior has been previously observed upon complexation of phosphorus(III) compounds to transition metals (19). Thus the large change in $^2J_{PH}$ (from *ca.* 0 to *ca.* 10–14) is valuable in indicating an increase in oxidation state or coordination number of the phosphorus.

The ^{1}H n.m.r. spectra of tributenylphosphine

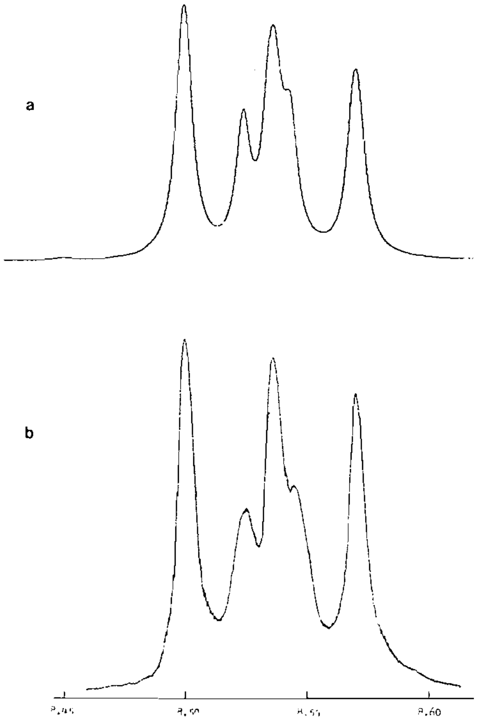


FIG. 4. The 220 MHz ^1H n.m.r. spectra of the methylene protons, H_5, for tributenylphosphine (tbp): (*a*) computer simulated, (*b*) observed.

(tbp) and tributenylphosphine oxide (tbpo) revealed the expected nonequivalence of the methylene protons. These protons appear as part of a pseudo AA'BB'MX pattern (A,A' = H_5,H_5'; B,B' = H_4,H_4'; M = H_3; X = P) since the coupling through the phosphorus and that to H_1 and H_2 is relatively small. For tbp, the spectrum of these methylene protons was computer simulated as a six-spin system using the data in Table 2. Figure 4 compares the calculated and observed spectra of the H_5 protons at 8.53 τ. The H_4 resonance at 7.86 τ was also synthesized with the phosphorus coupling determined by ^{31}P decoupling of the ^1H n.m.r. and by observation of the methylene proton coupling in the ^{31}P n.m.r. spectrum. The ^1H n.m.r. spectrum of tbp did not change between -50 and 50°. The spectrum of tbpo was similar except for the effect of the change of $^2J_{PH}$, from $\leqslant 0.5$ for tbp, to 10.6 Hz for tbpo. The vicinal methylene coupling is 6.0 and 10.5 Hz for both compounds. This data is consistent with rapid rotation about the carbon–carbon bond with a preference for conformer (I), Fig. 5.

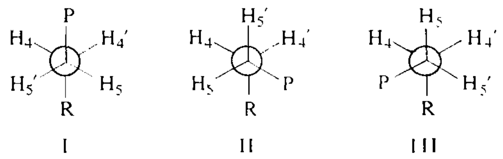


FIG. 5. Possible conformers of PCH_2—CH_2R.

In contrast, the calculated spectra for the H_5 resonances of dibutenylphenylphosphine (dbp) and dipentenylphenylphosphine (dpp) require average vicinal methylene coupling constants of 7 and 8 Hz. These values are also consistent with a rapid rotation about the axis of the two methylene groups but with a nearly equal population of the three conformers.

Vicinal methylene coupling constants could not be determined for butenyldiphenylphosphine (mbp) or pentenyldiphenylphosphine (mpp) due to overlap of resonances.

Practically no variation was observed in the magnitude of the *trans* or *cis* coupling constants for the olefinic protons. The geminal coupling was less than 1.5 Hz.

To conclude, the previously reported behavior showing $^3J_{PH} > {}^2J_{PH}$ for non-cyclized phosphines also occurs in the alkenyl phosphines reported in this work. For the two phosphine oxides in which $^2J_{PH}$ could be determined, appo and tbpo, the magnitude is much larger than in the corresponding phosphine. In the three compounds for which it was possible to obtain $^3J_{PH}$ for *both* the phosphorus(III) and the phosphorus(V) compounds, the change was minimal. Thus, $^2J_{PH}$ in the phosphine oxides studied is greater than $^3J_{PH}$. For all of the compounds only minimal changes in the olefinic coupling constants were observed.

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