

## Carbon-13 Nuclear Magnetic Resonance of Organophosphorus Compounds. V. The Effect of Changes in Phosphorus Oxidation State in Four-Membered Phosphorus Heterocycles

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<sup>13</sup>C chemical shifts and <sup>13</sup>C-<sup>31</sup>P nuclear spin coupling constants have been determined for *cis* and *trans* isomers of 1-X,1-Y 2,2,3,4,4 pentamethylphosphetanes for X = phenyl, methyl, and chloro and Y = lone pair, methyl, and oxide. The data are interpreted in terms of compound isomerism, exocyclic phosphorus substituents, and formal phosphorus oxidation state. Three types of phosphine → phosphonium salt → phosphetane oxide shift behavior are noted for carbons directly bound to the phosphorus. This divergent behavior is rationalized in terms of competing charge-density and π bond-order contributions to the P(III) → P(IV) shifts. Large (presumably negative) <sup>13</sup>C-<sup>31</sup>P one-bond couplings are present in some of the P(III) compounds and are discussed in terms of modern theories of spin coupling. Several strong stereospecific shifts and couplings are noted, some of which involve atoms which do not change their relative orientation within the *cis*-*trans* isomer pairs.

The four-membered phosphorus heterocycles, or phosphetanes, are a class of compounds that command sizable current interest in their bonding, steric interactions, and chemical reactions. We have explored the sensitivity and utility of <sup>13</sup>C chemical shifts and <sup>13</sup>C-<sup>31</sup>P nuclear spin coupling constants in parts II,<sup>2</sup> III,<sup>3</sup> and IV,<sup>4</sup> particularly as a function of methyl substituents bound to the ring atoms. Most of the data thus far have been obtained on phosphetanium salts and phosphetane oxides possessing four-coordinate phosphorus. The data clearly pointed out a greater sensitivity to ring methyl substitution and exocyclic phosphorus substitution than phosphorus "oxidation state." To explore the importance of changes in phosphorus bonding we have now examined some P(III) analogs, and can draw some conclusions concerning the role of phosphorus oxidation state and the corresponding sensitivity of the <sup>13</sup>C nmr parameters.

### Experimental Section

<sup>13</sup>C spectra were obtained on a Varian HA-100 spectrometer operating at 25.14 MHz in a field/frequency locked mode. The instrument was controlled by a Varian 620-i 8K computer which also served for time averaging. A Varian V-3512-1 provided a noise-modulated proton decoupling rf field which eliminated C-H splittings in the <sup>13</sup>C spectra. The V-4335-1 probe accommodated spinning 8-mm tubes and was double-tuned for 25 and 100 MHz. The field/frequency lock signal was derived from the resonance of 60% enriched <sup>13</sup>CH<sub>3</sub>I contained in a sealed 2-mm-o.d. capillary tube supported by teflon collars which could be inserted in the sample tube. Chemical shifts and coupling constants were taken from computer readouts of from usually 10 to 100 spectral accumulations for signal enhancement and accurate peak placement. The line positions were determined to ±0.1 Hz by direct frequency counting of peaks in scans usually 25–50 Hz in width. Scanning rates were normally 1–3 Hz/sec.

Some of the data were taken using a modification of the standard Varian equipment. In these situations the <sup>13</sup>C center band was derived from a 251-MHz signal generated by a Hewlett-Packard 500-MHz synthesizer. This 251-MHz signal, digitally divided by ten and amplified, replaced the crystal-generated rf frequency in the V-4311 rf unit. The analytical frequency sweep was also replaced by a computer-driven Wavetek voltage-controlled oscillator. Using this option, the Varian 620-i computer

generates a digital voltage ramp which, under software control, is keyed to the memory locations. The Wavetek oscillator was stable to ±0.1 Hz over a period of hours.

The oxides were run as saturated solutions (1–2 M) in CHCl<sub>3</sub>. The salts (X = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>) were run as saturated solutions in water; the chloro salts were run in a CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>Cl mixture. The ambient probe temperature was not measured under proton decoupling but was usually significantly higher than room temperature. The chemical shifts of the P(III) compounds are referenced to ~10% internal tetramethylsilane-<sup>13</sup>C (natural abundance) contained in the neat samples.

All the salt and oxide data have been converted to the TMS-<sup>13</sup>C scale by subtracting 20.97 ppm<sup>3</sup> from the shift from the <sup>13</sup>CH<sub>3</sub>I present in the lock capillary. Positive shifts are defined as low-field or deshielded chemical shifts.

Assignments of the P(III) resonances were made on the basis of intensity and peak behavior under low-power off-resonance proton noise decoupling. This technique distinguishes quaternary carbons from those having proton substituents. The assignments of the salts and oxides for X = C<sub>6</sub>H<sub>5</sub> and X = CH<sub>3</sub> have been documented in part III.<sup>3</sup> Assignments for *cis*- and *trans*-1-chloro-1,2,2,3,4,4 hexamethylphosphetanium tetrachloroaluminate were made using the C-3 and C-7 methyl shift and coupling stereospecificities noted for P(IV) salts in part III. The C-7 methyl and PCH<sub>3</sub> carbons were distinguished by the broader PCH<sub>3</sub> resonance. The latter's proton shift is significantly higher than typical proton methyl shifts and thus was not decoupled as efficiently by the noise decoupler. The small available amounts of these materials precluded more definitive off-resonance coherent decoupling experiments.

The preparation of the *cis* and *trans* isomers of 1-phenyl-2,2,3,4,4-pentamethylphosphetane was reported earlier.<sup>5</sup> It should be noted that the isomer assignments in that paper have been reversed as a result of later work.<sup>6</sup>

**Cis and Trans Isomers of 1,2,2,3,4,4-Hexamethylphosphetane.**—The preparation of a predominance of *trans*-1,2,2,3,4,4-hexamethylphosphetane in benzene solution has been described.<sup>5</sup> A 7:3 (*cis*:*trans*) mixture was prepared by treatment of a 7:3 (*trans*:*cis*) mixture of 1-chloro-2,2,3,4,4-pentamethylphosphetane (see below) in ether solution at 30° with methylolithium; the reaction went with inversion of configuration about phosphorus.<sup>7</sup> The pure product was obtained in 35% yield upon aqueous work-up of the reaction mixture and subsequent distillation, bp 36–40° (4.5 mm). The <sup>1</sup>H nmr (neat) of the *trans* isomer (1- and 3-methyl groups) showed peaks (TMS standard) at τ 7.46 (1 H, q, *J*<sub>HCH</sub> = 7.5 Hz), 8.90 (6 H, d, *J*<sub>PCH</sub> = 17.5 Hz), 8.91 (3 H, d, *J*<sub>PCH</sub> = 3 Hz), 9.13 (6 H, d, *J*<sub>PCH</sub> = 7 Hz), and 9.36 (3 H, d, *J*<sub>HCH</sub> = 7.5 Hz). The *cis* isomer showed absorption at τ 7.88 (1 H, dq, *J*<sub>HCH</sub> = 7.5, *J*<sub>PCH</sub> = 2.5 Hz), ~8.95 (6 H, d, *J*<sub>PCH</sub> ≅ 17 Hz), ~9.07 (3 H, d, *J*<sub>PCH</sub> ≅ 3 Hz), 9.05 (6 H, d, *J*<sub>PCH</sub> ≅ 6 Hz), and 9.29 (3 H, dd, *J*<sub>HCH</sub> = 7.5, *J*<sub>PCH</sub> = 1.0 Hz).

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(2) Part II: G. A. Gray and S. E. Cremer, *Tetrahedron Lett.*, 3061 (1971).

(3) Part III: G. A. Gray and S. E. Cremer, *J. Org. Chem.*, **37**, 3458 (1972).

(4) Part IV: G. A. Gray and S. E. Cremer, *Chem. Commun.*, 367 (1972).

(5) S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, **32**, 4066 (1967).

(6) S. E. Cremer, *Chem. Commun.*, 616 (1969).

(7) D. J. H. Smith and S. Trippett, *ibid.*, 855 (1969); J. R. Corfield, R. K. Oram, D. J. H. Smith, and S. Trippett, *J. Chem. Soc., Perkin Trans. 1*, 713 (1972).

**Preparation of a Cis and Trans Mixture of the 1-Chloro-1,2,2,3,4,4-hexamethylphosphetanium Tetrachloroaluminate Salts.**—The isomeric mixture of salts was prepared by treatment of 2,4,4-trimethyl-2-pentene with methylphosphonous dichloride-aluminum chloride in methylene chloride by a previously described procedure;<sup>9</sup> the intermediate tetrachloroaluminate salts were isolated prior to the quench with water. The solvent was evaporated and the product was recrystallized from dry acetonitrile (minimum) and dry diethyl ether. All work-up procedures were carried out in a glove box under nitrogen and strictly anhydrous conditions. The isomeric salts had mp 225–250° dec.

*Anal.* Calcd for C<sub>6</sub>H<sub>15</sub>AlCl<sub>4</sub>P: C, 29.82; H, 5.28; Cl, 48.91; P, 8.55. Found: C, 29.67; H, 5.57; Cl, 48.72; P, 8.33.

**1-Chloro-2,2,3,4,4-pentamethylphosphetane 1-Sulfide.**—To 57 g (0.29 mol) of freshly recrystallized acid chloride<sup>8</sup> in a 500-ml flask equipped with an air condenser and drying tube was added 25 g (0.11 mol) of phosphorus pentasulfide. The mixture was rapidly heated to 150–155° and maintained at that temperature for 6 hr. The air condenser was replaced by a Dry Ice condenser with a vacuum take-off. The solid product sublimed on the cold finger when aspirator vacuum was applied; the mixture was maintained at 150–170°. The product was periodically removed and the process was continued until no further sublimate was collected. The combined material was recrystallized from about 50 ml of petroleum ether (bp 30–60°); the solution was cooled in a refrigerator and then filtered to give 32 g of an isomer mixture of thioacid chlorides, mp 113–120°. An additional 6.5 g was obtained by concentration of the mother liquors. The nmr spectrum (benzene) of the major isomer showed peaks at  $\tau$  8.85 (6 H, d,  $J_{\text{PCH}} = 24.8$  Hz), 8.89 (6 H, d,  $J_{\text{PCH}} \cong 23$  Hz), 9.43 (3 H, dd,  $J_{\text{HCH}} = 7$ ,  $J_{\text{PCH}} = 1.2$  Hz) and that of the minor isomer at  $\tau$  8.78 (6 H, d,  $J_{\text{PCH}} = 24.9$  Hz), 8.91 (6 H, d,  $J_{\text{PCH}} \cong 23$  Hz), 9.36 (3 H, dd,  $J_{\text{HCH}} = 7$ ,  $J_{\text{PCH}} \cong 1$  Hz). The ring hydrogen for the isomers overlapped at  $\tau$  7.8–8.35 (1 H, m). The isomer ratio was ca. 2:1.

*Anal.* Calcd for C<sub>5</sub>H<sub>10</sub>ClPS: C, 45.60; H, 7.65. Found: C, 45.94; H, 7.25.

**1-Chloro-2,2,3,4,4-pentamethylphosphetane.**—A mixture of 28 g (0.13 mol) of the phosphetane sulfide and 53 g (0.2 mol) of triphenylphosphine was heated at 230° in a flask equipped with a distillation head and nitrogen capillary bleed (extended below the surface of the liquid). A rapid stream of nitrogen was passed directly into the hot mixture. The nitrogen flow gradually carried over the product into a cold receiver; the distillation head was heated with a heat gun to accelerate product collection. The distillate was redistilled through a 12-in. Vigreux column to give a colorless liquid, bp 36–38° (0.1 mm) [lit.<sup>7</sup> bp 87° (20 mm)], in 90% yield. The nmr (neat) showed an isomer ratio of 2:1 (trans:cis). The trans isomer gave peaks at  $\tau$  7.20 (1 H, dq,  $J_{\text{HCH}} = 7.5$ ,  $J_{\text{PCH}} = 1.5$  Hz), 8.78 (6 H, d,  $J_{\text{PCH}} = 21$  Hz), 8.86 (6 H, d,  $J_{\text{PCH}} = 7.5$  Hz), 9.23 (3 H, d,  $J_{\text{HCH}} = 7.5$  Hz). The cis isomer showed  $\tau$  7.81 (1 H, dq,  $J_{\text{HCH}} \cong 7$ ,  $J_{\text{PCH}} \cong 2.5$  Hz), 8.80 (6 H, d,  $J_{\text{PCH}} \cong 21$  Hz), 8.83 (6 H, d,  $J_{\text{PCH}} = 6$  Hz), 9.12 (3 H, dd,  $J_{\text{HCH}} \cong 7$ ,  $J_{\text{PCH}} \cong 1$  Hz).

*Anal.* Calcd for C<sub>5</sub>H<sub>10</sub>ClP: C, 53.80; H, 9.03. Found: C, 53.91; H, 9.07.

## Results

There are three actual variables: cis-trans isomerism, exocyclic phosphorus substituent X, and phosphorus oxidation state. There are four stereospecificities evident in the data (Tables I and II) but they are highly dependent on phosphorus oxidation state. In the P(III) phosphines the C-2/C-4 shifts are uniformly higher for the cis isomer by 2–4 ppm. The other two types of phosphorus-bound carbon show mixed behavior in this regard. The dependence on isomerism is greatly attenuated in going to the salts or oxides for all directly bonded carbons. The C-3 shift is sensitive to isomerism, especially for the oxides, while the  $\alpha$  methyls on C-2 and C-4 show stereospecific shifts in the P(III) compounds. A pronounced stereospecific effect is evident in the ortho (C-13) carbon shift in the

P(III) isomers for X = phenyl. Effects such as these in one-bond couplings to exocyclic phosphorus substituents and three-bond couplings to C-7 in the salts and oxides were discussed in parts II<sup>2</sup> and III.<sup>3</sup> Although there are definite isomer-dependent one-bond couplings in the P(III) compounds, no pattern is yet evident. However, the  $\alpha$ -methyl two-bond couplings, essentially insensitive to isomerism in the salts and oxides, clearly reflect their cis-trans nature with respect to the exocyclic phosphorus substituent in the P(III) compounds.<sup>4</sup> It is assumed that the signs of the one- and two-bond couplings, and probably the three-bond couplings, reverse in the transition P(III)  $\rightarrow$  P(IV) or "P(V)", as pointed out by McFarlane.<sup>9</sup> The stereospecificities are not simply related to the number of bonds between the coupled nuclei, since the coupling for C-3 does not show isomer dependence. The C-7 couplings are sensitive to isomer in the P(III) compounds, especially where carbon is present as the exocyclic atom bound to phosphorus.

The data, in general, roughly support additivity of substituent effects, although there are several serious reversals. While the P(III) C-2/C-4 shifts for X = Cl and X = C<sub>6</sub>H<sub>5</sub> are very close, they diverge by 10 ppm for the oxides. Chemical shift substituent effects seem more additive for salt  $\rightarrow$  oxides. The chloro substituent seems to give the greatest deviations from additivity, while the shifts for the phenyl and methyl substituents generally follow one another. Even within these cases there are, however, instances of deviation of several parts per million.

The C-2/C-4 coupling oxidation state trends do not follow one another very closely, especially for the cis isomer. However, there is good uniformity in the trends for the  $\alpha$  methyls. Serious reversals are present in the C-7 coupling trends.

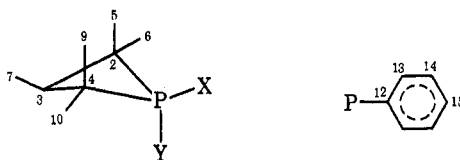
The most interesting changes are those for P(III)  $\rightarrow$  P(IV). The P(III)  $\rightarrow$  P(IV) values range from 17 ppm for C-2/C-4, through –2 ppm for PCH<sub>3</sub>, to –19 ppm for C-12. The  $\alpha$  methyls trans to the lone pair show minimal variation in shift with phosphorus oxidation state, probably reflecting attenuated inductive effects, while the  $\alpha$  methyls cis to the lone pair show an increased shift. Nowhere does a change in phosphorus oxidation state result in such a meteoric change than in the directly bonded couplings of C-2/C-4, PCH<sub>3</sub>, and C-12. In contrast to the variety of trends in their shifts, no disparity occurs here for the coupling trends, but there is a spread in sensitivity for the average of P(III)  $\rightarrow$  P(IV) with 51 Hz for C-2/C-4, 68 Hz for PCH<sub>3</sub>, and 93 Hz for C-12.

## Discussion

**Chemical Shifts.**—<sup>13</sup>C chemical shifts have been treated theoretically by a number of approaches,<sup>10–17</sup>

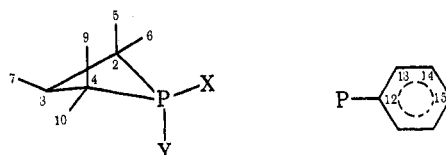
(8) J. J. McBride, Jr., E. Jungermann, J. V. Killheffer, and R. J. Clutter, *J. Org. Chem.*, **27**, 1833 (1962).

(9) W. McFarlane, *Proc. Roy. Soc., Ser. A*, **306**, 185 (1968).  
 (10) T. Yonezawa, I. Morishima, and H. Kato, *Bull. Chem. Soc. Jap.*, **36**, 1389 (1966).  
 (11) B. V. Cheney and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 5319 (1967).  
 (12) J. E. Bloor and D. L. Breen, *ibid.*, **89**, 6835 (1967).  
 (13) T. Tokuhira, N. K. Wilson, and G. Fraenkel, *ibid.*, **90**, 3622 (1968).  
 (14) W. Adam, A. Grimison, and G. Rodriguez, *J. Chem. Phys.*, **50**, 645 (1969).  
 (15) T. Tokuhira and G. Fraenkel, *J. Amer. Chem. Soc.*, **91**, 5005 (1969).  
 (16) H. Spiessicke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961).  
 (17) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).

TABLE I  
<sup>13</sup>C CHEMICAL SHIFTS<sup>a</sup>

Registry no.	Y	X	C-2/C-4	C-12	PCH <sub>3</sub>	C-3	C-5/C-9	C-6/C-10	C-7	C-13 <sup>d</sup>	C-14 <sup>d</sup>	C-15
16083-95-7	C <sub>6</sub> H <sub>5</sub>		30.22	137.71		54.02	26.24	26.52	9.96	135.11	127.57	128.16
35621-97-7	CH <sub>3</sub>		26.37		6.74	51.43	25.06	25.00	9.31			
25145-24-8	Cl		31.65			51.55	22.04	25.48	9.36			
22434-51-1		C <sub>6</sub> H <sub>5</sub>	34.52	140.09		49.70	20.92	32.71	8.12	129.50	127.64	126.15
35622-00-5		CH <sub>3</sub>	28.61		5.23	51.13	19.16	32.46	8.65			
25145-23-7		Cl	35.10			48.04	19.53	30.00	8.94			
35616-93-4	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub> <sup>b</sup>	41.41	119.15	5.93	53.49	20.57	25.43	9.69	135.01	131.28	135.79
35616-94-5	CH <sub>3</sub>	CH <sub>3</sub> <sup>b</sup>	38.07		<sup>c</sup>	51.42	18.96	24.43	8.75			
35616-95-6	Cl	CH <sub>3</sub>	48.25		10.11	52.89	19.54	25.49	13.45			
35616-96-7	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> <sup>b</sup>	42.11	120.68	6.90	50.43	20.17	24.94	8.08	133.81	131.55	135.65
35616-97-8	CH <sub>3</sub>	Cl	48.38		9.72	50.55	19.82	24.54	11.74			
16083-91-3	C <sub>6</sub> H <sub>5</sub>	O <sup>b</sup>	46.68	129.94		44.88	18.90	24.00	7.33	133.32	128.85	132.33
33530-51-7	CH <sub>3</sub>	O <sup>b</sup>	45.41		9.79	42.61	17.28	24.71	7.31			
26674-18-0	Cl	O <sup>b</sup>	57.35			42.79	18.27	26.09	7.37			
20047-46-5	O	C <sub>6</sub> H <sub>5</sub> <sup>b</sup>	46.45	131.88		48.03	20.41	24.81	8.69	132.65	129.12	132.37
28672-43-7	O	CH <sub>3</sub> <sup>b</sup>	44.05		11.47	46.89	19.83	24.66	9.71			
25145-33-9	O	Cl <sup>b</sup>	57.05			46.20	20.74	24.50	9.38			

<sup>a</sup> In parts per million relative to TMS-<sup>13</sup>C. Shifts are accurate to  $\pm 0.01$  ppm when comparing carbons in the same molecule. Solvent, concentration, and bulk susceptibility changes from sample to sample will reduce accuracy of comparison to probably  $\pm 0.2$  ppm. A positive shift represents a higher frequency (downfield) shift or deshielding of the carbon atoms. <sup>b</sup> Data from ref 3. Data for the phosphatanes [P(III) compounds] are internally referenced while the salts and oxides are referenced originally to the <sup>13</sup>CH<sub>3</sub>I in the lock capillary and have been corrected to the TMS-<sup>13</sup>C scale by subtracting 20.97 ppm.<sup>3</sup> <sup>c</sup> Y methyl shift 4.15 ppm, X methyl shift 4.94 ppm. <sup>d</sup> Assignments for P(III) C-13 and C-14 made on the basis of the large differences in <sup>13</sup>C-<sup>31</sup>P couplings (Table II). See F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 4940 (1969).

TABLE II  
<sup>13</sup>C-<sup>31</sup>P NUCLEAR SPIN COUPLING CONSTANTS<sup>a</sup>

Y	X	C-2/C-4	C-12	PCH <sub>3</sub>	C-3	C-5/C-9	C-6/C-10	C-7	C-13	C-14	C-15
C <sub>6</sub> H <sub>5</sub>		-5.9	-41.3		2.7	31.8	2.5	0.0	20.2	6.6	1.1
CH <sub>3</sub>		-7.7		-33.7	3.3	30.5	2.1	0.0			
Cl		-7.8			2.1	37.1	0.0	2.4			
	C <sub>6</sub> H <sub>5</sub>	-2.6	-42.8		5.9	4.9	27.8	13.5	13.1	2.9	1.8
	CH <sub>3</sub>	-6.5		-37.9	2.9	4.3	26.9	8.9			
	Cl	-11.1			7.8	2.5	33.5	1.8			
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub> <sup>b</sup>	45.2	54.9	31.1	10.2	2.1	3.7	17.6	8.5	11.7	0.0
CH <sub>3</sub>	CH <sub>3</sub> <sup>b</sup>	45.2		<sup>c</sup>	11.2	2.5	3.7	18.1			
Cl	CH <sub>3</sub>	35.5		20.1	6.3	0.0	6.6	12.0			
CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> <sup>b</sup>	45.3	48.9	35.9	10.5	3.1	3.4	22.2	8.5	11.3	0.0
CH <sub>3</sub>	Cl	48.1		19.7	9.8	5.8	3.0	17.9			
C <sub>6</sub> H <sub>5</sub>	O <sup>b</sup>	58.7	59.5		6.2	4.6	3.5	23.1	9.0	9.7	2.9
CH <sub>3</sub>	O <sup>b</sup>	59.4		40.9	6.3	4.6	3.6	23.0			
Cl	O <sup>b</sup>	56.8			1.6	3.8	6.8	30.1			
O	C <sub>6</sub> H <sub>5</sub> <sup>b</sup>	58.4	54.5		11.2	1.3	4.6	16.9	8.8	10.1	2.7
O	CH <sub>3</sub> <sup>b</sup>	59.4		36.9	10.0	2.2	4.4	12.6			
O	Cl <sup>b</sup>	55.4			1.8	5.4	5.3	20.5			

<sup>a</sup> To  $\pm 0.1$  Hz. Signs are assigned based on McFarlane's determination of signs in representative compounds.<sup>9</sup> <sup>b</sup> Data from ref 3. <sup>c</sup> Y methyl 34.7 Hz, X methyl 29.1 Hz.

TABLE III  
<sup>13</sup>C SHIFT AS A FUNCTION OF NEIGHBOR ATOM OXIDATION STATE<sup>a</sup>

	P(III) → P(IV) Values, ppm				δ (PCH <sub>3</sub> ), ppm	Ref
	C <sub>α</sub>	C <sub>β</sub>	C <sub>γ</sub>	C <sub>δ</sub>		
(Me) <sub>3</sub> P → (Me) <sub>4</sub> P <sup>+</sup>	-5.1				20.7 → 15.6	b
(Et) <sub>3</sub> P → (Et) <sub>4</sub> P <sup>+</sup>	-7.0	-3.7				b
(n-Bu) <sub>3</sub> P → (n-Bu) <sub>4</sub> P <sup>+</sup>	-6.3	-5.2	-3.9	-0.9		c
(n-Bu) <sub>3</sub> P → (n-Bu) <sub>3</sub> PCH <sub>3</sub> <sup>+</sup>	-4.6	-5.2	-4.1	-0.7	→ 5.0	c
(Ph) <sub>3</sub> P → (Ph) <sub>3</sub> PCH <sub>3</sub> <sup>+</sup>	-18.8	-1.3	1.0	5.6	→ 9.4	c, d
(Me) <sub>2</sub> PhP → (Me) <sub>2</sub> PhPH <sup>+</sup>	-8.4 (methyl)				21.1 → 12.7	b
(Me) <sub>3</sub> N → (Me) <sub>4</sub> N <sup>+</sup>	9.2				47.2 → 56.4	e
Py → Py H <sup>+</sup>	-7.8					f
	P(IV) → "P(V)" Values, ppm					
(Me) <sub>4</sub> P <sup>+</sup> → (Me) <sub>5</sub> PO	3.3				15.6 → 18.6	b, g
(Et) <sub>4</sub> P <sup>+</sup> → (Et) <sub>5</sub> PO	4.2	6.0				b, g

<sup>a</sup> Me = methyl, Et = ethyl, n-Bu = n-butyl, Ph = phenyl, Py = pyridine. All shifts have been placed on the TMS-<sup>13</sup>C scale by using the shift of 128.4 ppm for benzene and 198.5 ppm for the carbonyl carbon of acetic acid. <sup>b</sup> Reference 9. <sup>c</sup> Reference 22. <sup>d</sup> H. J. Jakobsen and O. Manscher, *Acta Chem. Scand.*, **25**, 680 (1971). <sup>e</sup> H. Spiesscke and W. G. Schneider, *J. Chem. Phys.*, **33**, 1888 (1960). <sup>f</sup> Reference 25. <sup>g</sup> Reference 3.

starting from Ramsey's formulation<sup>18</sup> and employing approximations thereto. Recently, Mason<sup>19</sup> has questioned the usual assumption that the diamagnetic contribution, σ<sub>d</sub>, to the <sup>13</sup>C chemical shift varies negligibly when carbon substituents are changed. Based on a predictive relationship for σ<sub>d</sub> formulated by Flygare and Goodisman,<sup>20</sup> Mason corrected the observed shifts for variations in σ<sub>d</sub> and analyzed the resulting σ<sub>p</sub>'s in terms of variations in the average excitation energy. Ditchfield, *et al.*,<sup>21</sup> using *ab initio* techniques, have calculated σ<sub>d</sub> and σ<sub>p</sub> contributions to <sup>13</sup>C shifts. However, the primary burden for changes in shielding was placed on changes in carbon orbital size through inductive charge withdrawal.

The phosphetane shifts can be analyzed in terms of the above ideas. No change in substitution occurs for any of the carbons in going from phosphine to salt or oxide. Therefore, any change in σ<sub>d</sub> for phosphorus-bonded carbon should be negligible, since substituent Z/r values are essentially unchanged.<sup>20</sup> The observed changes in phosphorus-bonded carbon shifts should reflect only changes in σ<sub>p</sub>. The same holds in the other carbons, of course, since they are more than one bond away.

All of the phosphorus-bonded carbons behave similarly in the salts and oxides. However, when P(III) → P(IV) is considered, opposite sensitivities are apparent. Relevant data on other compounds are presented in Table III. The acyclic data serve as "normal" benchmarks for oxidation state dependence. The only cyclic compounds on which pertinent data have been accumulated are phosphacyclopentane<sup>22</sup> and 1-phenylphosphacyclopentane 1-oxide,<sup>3</sup> a phosphine-oxide pair if replacement of a hydrogen by phenyl is ignored. The C-2/C-4 change of -1.2 ppm in this pair is very far removed from the large positive values in the phosphetanes. Clearly, the C-2/C-4 shifts are sensitive to electronic effects in a different way from the exocyclic phosphorus-bound carbons, even though this electronic effect is propagated through phosphorus.

Since this electronic influence is thus anisotropic, it cannot be described by a simple change of effective electronegativity of phosphorus resulting from change in the Y group, and no arguments based on simple inductive charge density polarization can accommodate opposing effects at atoms *geminal* to the inductive center. If *no* double-bond character is present in C-2/C-4 bonds to phosphorus, then the large positive P(III) → P(IV) values for C-2/C-4 could result from inductive charge withdrawal by Y *via* the phosphorus, and all the phosphorus-bonded carbons should experience at least a polarization of the same direction, if not the same magnitude. Then, the large negative P(III) → P(IV) value for C-12 could result from offsetting this *positive* charge density contribution by a still larger *negative* contribution *via* loss of double-bond character<sup>17</sup> present in the P(III) compound. Since normal alk<sub>2</sub>PCH<sub>3</sub> → alk<sub>3</sub>PCH<sub>3</sub> + P(III) → P(IV) values for PCH<sub>3</sub> are in the region of -5 to -9 ppm, the smaller P(III) → P(IV) value for PCH<sub>3</sub> in the phosphetanes could simply imply that the effect of the cyclic nature of the other phosphorus substituents is to place more charge density on the exocyclic PCH<sub>3</sub> than in acyclic counterparts. This has some experimental backing in that the exocyclic PCH<sub>3</sub> have chemical shifts which are smaller than those in P(CH<sub>3</sub>)<sub>3</sub> by ~14-15 ppm. Based on steric contributions to <sup>13</sup>C shifts alone,<sup>23</sup> the carbons in P(CH<sub>3</sub>)<sub>3</sub> should have a smaller shift since their steric interactions should be significantly larger. Thus, in going to the P(IV) compounds the charge density variation is greater for the exocyclic PCH<sub>3</sub> than for P(CH<sub>3</sub>)<sub>3</sub>, and a corresponding positive P(III) → P(IV) contribution is made to the total shift. Loss of partial double-bond character in P(III) → P(IV) would then have to make a contribution of similar magnitude but opposite in sign<sup>17</sup> to achieve a small net P(III) → P(IV) value. This large contribution from partial double-bond character in the P(III) compounds with exocyclic phosphorus-bound phenyl may indicate a more planar arrangement around the phosphorus than in the oxides or salts. Unfortunately, there have been no X-ray studies of P(III) phosphetanes.

The N(III) → N(IV) value for (CH<sub>3</sub>)<sub>3</sub>N is positive

(18) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950); **83**, 540 (1951); **86**, 243 (1952).

(19) J. Mason, *J. Chem. Soc. A*, 1038 (1971).

(20) W. H. Flygare and J. Goodisman, *J. Chem. Phys.*, **49**, 3122 (1968).

(21) R. Ditchfield, D. P. Miller, and J. A. Pople, *J. Chem. Phys.*, **54**, 4186 (1971).

(22) F. J. Weigert, Thesis, California Institute of Technology, 1968.

(23) D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 6612 (1967); D. M. Grant and B. V. Cheney, *ibid.*, **89**, 5315 (1967).

while the analogous value for  $P(CH_3)_3$  is negative. Again a reversal is noted for the  $\alpha$  carbon in pyridinium ion. The former is to be expected on charge density grounds but the latter was explained<sup>24</sup> by invoking variations in  $\Delta E$ . In these cases the shift of one type of carbon was rationalized by a change in one parameter, but it is difficult to explain the three types of sensitivity observed here for directly bonded carbons by variation of one parameter.

The other phosphetane ring carbon, C-3, has a shift which is most sensitive for oxide  $\rightarrow$  salt and about 2-3 times as sensitive in the trans isomer as in the cis isomer. The  $\alpha$ -methyl shifts could be explained on the basis of steric interaction with the exocyclic phosphorus substituent cis to the  $\alpha$  methyl, which is not present in the P(III) compound. This steric crowding is present in all the compounds except for the  $\alpha$  methyls C-5/C-9 in trans isomers and C-6/C-10 in cis isomers. On this basis the steric contribution to the shifts of the  $\alpha$  methyls in the other cases would be  $\sim -6$  ppm.<sup>25</sup> C-7 is apparently not sensitive to phosphorus oxidation state, except for the P(IV) chloro compound. No explanation is apparent for the deviation.

**<sup>13</sup>C-<sup>31</sup>P Coupling Constants.**—There has been much activity in the last decade expended toward the understanding and prediction of nuclear spin couplings. Fairly little work, in comparison, has been directed toward nuclei other than protons, and most of this has been centered on couplings of protons to other nuclei. A detailed coverage of previous theories and calculations was given in part I.<sup>26</sup> In particular, considerable attention was paid to the relatively little work that has been done investigating <sup>13</sup>C-<sup>31</sup>P couplings. The only available theoretical treatments of <sup>13</sup>C-<sup>31</sup>P couplings have been by Cowley and White,<sup>27</sup> who calculated <sup>13</sup>C-<sup>31</sup>P couplings in  $CH_3PH_2$ ,  $CF_3PH_2$ , and  $CH_3PH_3^+$  by a parametrized LCAO-SCF-MO theory in the Pople-Santry<sup>28</sup> approximation; Jameson and Gutowsky,<sup>29,30</sup> who developed a qualitative model of spin coupling based on the Fermi contact and "core electron polarization" contributions to spin coupling; and Gray (part I),<sup>27</sup> who used the finite perturbation-INDO-SCF-MO theory of Pople, McIver, and Ostlund<sup>31</sup> for <sup>13</sup>C-<sup>31</sup>P couplings in a series of phosphonates  $(C_2H_5O)_2P(O)CH_2X$ . Here the relationship between "s character" and <sup>13</sup>C-<sup>31</sup>P couplings was examined and it was found that the coupling followed the calculated bond order but varied about twice as fast. The site of variable substitution was on the phosphonate carbon as opposed to the phosphorus itself as in the phosphetanes. The relationship between one-bond cou-

plings and the  $C_{2s}-P_{3s}$  bond order in this different kind of bonding situation is as yet unexplored. However, analogous treatments of spin coupling involving carbon<sup>31,32</sup> offer good promise that changes in coupling involving carbon, especially for carbons not undergoing substitution, reflect to some degree the changes in valence s orbital bond order between the directly bonded atoms, provided that the Fermi contact mechanism is dominant.

The C-2/C-4 couplings to P(III) are small and probably negative. However, the exocyclic P(III) substituents, whether methyl or phenyl, have a coupling of relatively large magnitude. Large negative one-bond <sup>13</sup>C-<sup>31</sup>P couplings have been found recently for  $(t-Bu)_2PF$  ( $-34.6$  Hz)<sup>33</sup> and  $CH_3PCl_2$  ( $-45$  Hz).<sup>34</sup> It is reasonable to assume that the exocyclic carbon couplings are negative, as all <sup>13</sup>C-<sup>31</sup>P(III) directly bonded couplings have been found to date. If contributions from "core-polarization" are always small<sup>28,29</sup> then a surprisingly sizable Fermi contact contribution of negative sign must be present.

Although the C-2/C-4 and  $PCH_3$  one-bond couplings are apparently very different in magnitude, the oxidation state behavior makes them look very similar, apart from a constant offset of  $\sim 20$  Hz. The large difference between phosphine  $\rightarrow$  salt and salt  $\rightarrow$  oxide behavior indicates a substantial change in bonding character for the former, but much less for the latter. This may support the frequent assertion that phosphine oxides are really more like  $P^+-O^-$  than  $P=O$ .

Additivity ideas certainly suffer in considering the C-2/C-4 couplings. The couplings vary depending on X substituent and isomer. Of particular note is the large stereospecificity in C-2/C-4 coupling for  $X = Cl$  in the P(IV) compounds. If the correlation of <sup>13</sup>C-<sup>31</sup>P coupling and  $P_{3s}-C_{2s}$  bond order has at least some validity for four-coordinate phosphorus, this difference then shows a significant decrease in  $P_{3s}$  orbital character in the C-2/C-4 phosphorus bonds in the cis isomer with respect to the trans isomer.

Of special significance are the large negative couplings for exocyclic P(III)  $PCH_3$  and C-12. No halogen atoms<sup>33,34</sup> are used here to effect the change from what one would consider to be the "normal" small negative values. Even if further experimental work shows the C-12 and  $P-CH_3$  couplings to be of positive sign, the large magnitudes will still be exceptional for P(III)-bound carbon and provide a very stringent test for theoretical prediction.

The two-bond couplings exhibit a large stereospecificity in  $\alpha$ -methyl couplings which is analogous to that previously found for  $PCH_2$  two-bond couplings.<sup>35</sup> The only three-bond phosphetane ring carbon coupling is that for C-7. It is sensitive to both X substituent and isomer and difficult to rationalize. It is important

(24) A. J. Jones, D. M. Grant, J. G. Russell, and G. Fraenkel, *J. Phys. Chem.*, **73**, 1624 (1969).

(25) There does seem to be other evidence for this in comparing 1-phenyl-2,2,3,4,4-pentamethylphosphetane 1-oxide to 1-phenyl-2,2,4,4-tetramethylphosphetane 1-oxide. Here the C-5/C-9 shift (averaged over both isomers) in the latter is about 5.3 ppm smaller than the C-5/C-9 shift in the former (unpublished results). The pseudoequatorial C-7 methyl that is removed is analogous to the pseudoequatorial phosphorus-bound methyl removed in going from P(IV) to P(III).

(26) Part I: G. A. Gray, *J. Amer. Chem. Soc.*, **93**, 2132 (1971).

(27) A. H. Cowley and W. D. White, *ibid.*, **91**, 1917 (1969).

(28) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(29) C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, **51**, 2790 (1969).

(30) C. J. Jameson and H. S. Gutowsky, *J. Amer. Chem. Soc.*, **91**, 6232 (1969).

(31) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *Chem. Phys. Lett.*, **1**, 456 (1967); (b) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2960, 2965 (1968); N. S. Ostlund, M. D. Newton, J. W. McIver, Jr., and J. A. Pople, *J. Magn. Resonance*, **1**, 185 (1969).

(32) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 1, 11, 4151, 4497, 4506 (1970); P. D. Ellis and G. E. Maciel, *ibid.*, **92**, 5829 (1970).

(33) C. Schumann, H. Dreeskamp, and O. Stelzer, *Chem. Commun.*, 619 (1970).

(34) J. P. Albrand and D. Gagnaire, *Chem. Commun.*, 874 (1970).

(35) (a) J. P. Albrand, D. Gagnaire, and J. B. Robert, *Chem. Commun.*, 1469 (1968); (b) L. D. Hall and R. B. Malcomb, *Chem. Ind. (London)*, 92 (1968); (c) G. Mavel, *J. Chim. Phys.*, **65**, 1692 (1968); (d) J. P. Albrand, D. Gagnaire, J. Martin, and J. B. Robert, *Bull. Soc. Chim. Fr.*, 40 (1969); (e) L. D. Quin and T. P. Barket, *J. Amer. Chem. Soc.*, **92**, 4303 (1970); (f) W. G. Bentrude and J. H. Hargis, *ibid.*, **92**, 7136 (1970); (g) J. P. Albrand, D. Gagnaire, M. Picard, and J. B. Robert, *Tetrahedron Lett.*, 4593 (1970).

to remember that differences in C-2/C-4, C-3, and C-7 coupling between isomers are present *even though the relative spatial orientation of the coupled atoms remains the same*. It is not a case of dihedral angle dependence, as it is for the  $\alpha$  methyls. No satisfactory general model for this has emerged. The utility of the stereospecificities need not be hampered by lack of understanding of their precise mechanisms. Isomer identification is made quite easily, especially for the P(III) compounds, using the  $\alpha$ -methyl stereospecificities.

**Registry No.**—1-Chloro-2,2,3,4,4-pentamethylphosphetane 1-sulfide, 35623-65-5 (isomer A), 35623-66-6 (isomer B).

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## Investigations of Doubly Connected Phosphorus Cations. Diaminophosphenium Ions from 2-R-2-Phospha-1,3-diazacyclohexanes<sup>1</sup>

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Mass spectral analysis of a series of *N,N'*-dimethyl-2-R-2-phospha-1,3-diazacyclohexanes (R = Cl, OCH<sub>3</sub>, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub>) reveals a primary fragmentation pathway affording loss of the phosphorus R group and generation of a divalent phosphonium species as the major (base) fragment. Diequatorial orientation of the *N*-alkyl groups is important to stabilization of the cations, as deduced from the failure of certain bicyclic derivatives to provide phosphonium ions when the *N*-alkyl groups are locked in axial positions. Treatment of 2-chloro-2-phospha-1,3-diazacyclohexanes with PCl<sub>5</sub> gave an ionic species which is best interpreted (pmr, <sup>31</sup>P nmr, conductance measurements) in terms of a doubly connected phosphorus cation salt.

Higher and lower valent cations of many nonmetallic elements (*i.e.*, carbon, halogen, sulfur, nitrogen) have been well recognized and occupy a fundamental place in mechanistic organic chemistry with recent attention being given to pentavalent carbocations (carbonium ions)<sup>2</sup> and divalent nitrenium ions.<sup>3</sup> Somewhat surprisingly, however, very little is known of the behavior, or even existence, of lower valent phosphorus cations (phosphenium ions<sup>4</sup>), although tetracoordinate phosphonium species have played a significant role in phosphorus chemistry for many years.

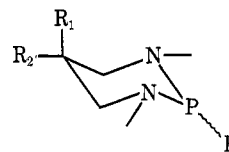
In the course of conformational analysis studies on 2-R-2-phospha-1,3-diazacyclohexanes,<sup>5</sup> electron impact spectra were recorded as an aid to characterization of these compounds. The observation of a primary fragmentation pathway leading to extremely stable divalent phosphorus cations prompted further exploration in this area, with interest in the factors governing the stability of such cations and possible implications of such species in the mechanisms of trivalent organophosphorus reactions.

### Results and Discussion

**Diaminophosphenium Ions in the Mass Spectrometer.**—The mass spectrum of phosphorus trichloride has been reported to display PCl<sub>2</sub><sup>+</sup> as the most abundant positive ion with a low appearance potential of approximately 12 eV.<sup>6</sup> Other trivalent phosphorus com-

pounds, *e.g.*, (CH<sub>3</sub>)<sub>3</sub>P,<sup>6</sup> Ph<sub>2</sub>PCl,<sup>7</sup> and (Me<sub>2</sub>N)<sub>3</sub>P,<sup>7</sup> also give rise to varying populations of divalent positive species by loss of one ligand. However, it is uncommon for the relative abundance of divalent ions derived in this fashion to be very large if further fragmentations are readily achievable,<sup>8</sup> that is, the significance of a high abundance of an individual ion becomes much greater as its opportunity for further decomposition is increased.<sup>9</sup> Along this line, triethylphosphine readily expels ethylene to form PH(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub><sup>+</sup> in abundant amounts, rather than giving up an ethyl group to form the divalent ion, P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub><sup>+</sup>.<sup>10</sup>

On the contrary, electron-impact spectra at 70 eV of various 2-R-2-phospha-1,3-diazacyclohexanes (1) bearing phenyl, ethyl, chloro, methyl, and methoxy substituents on phosphorus have disclosed a primary



- 1a, R<sub>1</sub> = R<sub>2</sub> = H; R = C<sub>6</sub>H<sub>5</sub>  
 b, R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>; R = C<sub>6</sub>H<sub>5</sub>  
 c, R<sub>1</sub> = H; R<sub>2</sub> = CH<sub>3</sub>; R = C<sub>6</sub>H<sub>5</sub>  
 d, R<sub>1</sub> = R<sub>2</sub> = H; R = C<sub>2</sub>H<sub>5</sub>  
 e, R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>; R = C<sub>2</sub>H<sub>5</sub>  
 f, R<sub>1</sub> = H; R<sub>2</sub> = CH<sub>3</sub>; R = C<sub>2</sub>H<sub>5</sub>  
 g, R<sub>1</sub> = R<sub>2</sub> = H; R = Cl  
 h, R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>; R = Cl  
 i, R<sub>1</sub> = R<sub>2</sub> = H; R = OCH<sub>3</sub>  
 j, R<sub>1</sub> = R<sub>2</sub> = R = CH<sub>3</sub>

(1) Extracted from the Ph.D. Thesis of B. E. M., Drexel University, June 1972.

(2) See G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972), and references cited therein.

(3) P. G. Gassman, *Accounts Chem. Res.*, **3**, 26 (1970).

(4) This nomenclature follows the system promoted by Olah (see ref 2) in which higher electron-deficient states of an element are designated "onium" and the lower "enium" ions.

(5) R. O. Hutchins, B. E. Maryanoff, J. Albrand, A. Cogne, D. Gagnaire, and J. B. Robert, *J. Amer. Chem. Soc.*, in press.

(6) See M. Halman, *Top. Phosphorus Chem.*, **4**, 49 (1967). Herein is contained some general information on the behavior of trivalent phosphorus compounds in the mass spectrometer; see pp 70-77.

(7) R. O. Hutchins and B. E. Maryanoff, unpublished results.

(8) See H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, pp 645-653.

(9) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York, N. Y., 1967.

(10) Y. Wada and R. W. Kiser, *J. Phys. Chem.*, **67**, 2290 (1964).