and MDPA as there was no need to introduce a third contribution in order to interpret the spectra.

From a more pragmatic viewpoint the present NMR data corroborate the various procedures used to separate ^{13}C contact and pseudocontact shifts where the assumption is made that ^{1}H shifts are purely of dipolar nature.[5,22] This assumption should be checked through studies using several lanthanides, as contact contributions are not always negligible for protons.[18] The Gd^{3+} induced shifts, recently reported for the first time by Ajisaka and Kainosho,[6] afford in principle a new method of separation of the two forms of shifts; however, this ion leads to enormous line broadening for DPA complexes as well as for various LSR adducts and shifts are difficult or impossible to measure. Finally it should be pointed out that the variable temperature method outlined for $Yb(DPA)_3$ has to be applied with reservation as the $\langle S_z \rangle$ factor of various lanthanides may follow a Curie–Weiss dependence instead of a simple T^{-1} law.

Acknowledgment. We gratefully acknowledge research support from the National Science Foundation, the National Institutes of Health, and the F.N.R.S. of Belgium.

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^{13}C Nuclear Magnetic Resonance of Organophosphorus Compounds. X. Ring-Size Variation in Heterocyclic Phosphines, Phosphonium Salts, and Phosphine Oxides

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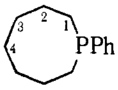
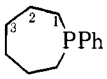
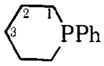
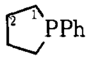
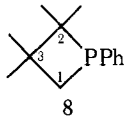
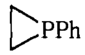
Abstract: ^{13}C chemical shifts and ^{13}C–^{31}P nuclear spin couplings are reported for phosphorus heterocycles with exocyclic substitutions: phenyl, diphenyl, benzylphenyl, and phenyloxide. These saturated heterocycles extend from three-membered (only for the phosphine) through eight-membered rings, using di-*n*-butyl analogues as examples of unconstrained relatives. Sign determination for several of the ^{13}C–^{31}P couplings in the phosphines has been made, including the only *positive* one-bond couplings yet observed for directly bonded ^{13}C–^{31}P couplings in P(III) organophosphorus compounds. Dihedral angle dependence of two-bond ^{13}C–^{31}P couplings in phosphines is observed, both in sign and magnitude. Proton chemical shifts for several of the phosphines were measured and assigned from data obtained from ^{13}C-{^{1}H} double resonance data, cases in which this was impossible from direct observation of the proton NMR spectrum. A very large −39.7 Hz coupling was observed for the methylene carbon in the three-membered ring phenylphosphorinane, a coupling larger than the (−)38.7 Hz coupling to the directly bonded phenyl carbon. This is in contrast to the near zero *positive* coupling to the corresponding methylene in a four-membered ring analogue, which yet has a very similar phenyl coupling. In addition to the ring size data, new results are reported for various ring methylation patterns of phenylphosphetanes and phenylbenzylphosphetanium salts.

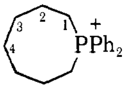
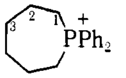
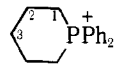
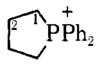
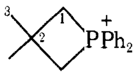
Cyclic molecules have been traditionally interesting because of their restricted number of populated conformations. Variable temperature experiments have permitted estimates of these populations and uncovered stereochemical specificities in physical properties. Although the great majority of magnetic resonance work has been in ^{1}H NMR, the last decade has produced an accelerating number of ^{13}C NMR investigations in which the increased chemical shift dispersion has greatly extended the power of the NMR method. We have pursued[2-8] the study of phosphorus heterocycles because of the attractive, multifaceted nature of phosphorus which provides stable compounds that can be studied in different oxidation states and a nuclear spin which allows an additional and very sensitive probe of molecular electronic structure through its couplings to the naturally abundant ^{13}C. In this work we systematically analyze the ^{13}C shifts and ^{13}C–^{13}P couplings for four types of exocyclic phosphorus substitution: an oxide, two salts, and a phosphine. For each of these phosphorus substitutions a sizable variation of (saturated) ring size is examined, using

Table I. ^{13}C Chemical Shifts and $^{13}C-^{31}P$ Couplings in Phenyl-Substituted Phosphines[a]

Carbon	Ph_2PPh[b] 1	1 2 3 4 ($P-CH_2CH_2CH_2CH_3$) Ph(*n*-Bu)PPh 2	(*n*-Bu)$_2$PPh 3	 4	 5	 6	 7[c]	 8	 9[d]
				^{13}C Chemical Shifts					
1		27.86	28.52	28.02	29.89	24.79	27.15	28.74	11.04
2		28.12	28.40	24.77	25.16	23.65	27.74	41.26	
3		24.14	24.48	26.77	28.27	28.04		40.16	
4		13.74	13.82	25.50					
Ph-1	137.39	139.39	139.78	142.94	141.94	141.34	142.55	140.75	138.88
Ph-2	133.71	132.57	132.44	131.53	130.27	130.49	130.25	130.76	131.68
Ph-3	128.51	128.18	128.20	128.14	128.21	128.30	128.16	128.09	128.74
Ph-4	128.65	128.12	128.43	127.69	127.75	127.07	127.03	127.24	128.88
				$^{13}C-^{31}P$ Coupling Constants					
1		(−)13.7	(−)13.4	(−)17.0	(−)15.0	−14.8	−14.0	+0.6 ± 0.05	−39.7
2		+16.1	+14.7	+12.3	+10.6	+2.4	−4.7	1.5	
3		12.4	12.2	5.3	4.6	2.5[e]		3.9	
4		0.0	0.0	2.1					
Ph-1	−12.51	(−)14.8	(−)17.7	(−)14.4	(−)15.6	(−)19.1	(−)25.0	(−)35.4	(−)38.7
Ph-2	+19.65	+18.1	+18.4	+18.9	+17.5	+14.5	+15.6	+15.6	+20.3
Ph-3	+6.80	(+)5.4	(+)6.7	+6.3	+5.8	(+)4.7	(+)4.8	(+)4.7	(+)7.0
Ph-4	0.33	<0.5	1.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5

[a] Chemical shifts (10% C_6D_6) in ppm from TMS-^{13}C (internal 1-5%) accurate to ±0.02 ppm. Couplings accurate to ±0.1 Hz except where noted. Signs in parentheses are assumed based on sign determinations on similar compounds. Signs without parentheses were determined using selective off-resonance decoupling as in ref 9 and 12. [b] Reference 9: 10% DMSO-d_6, 10% TMS. [d] Run at ca. −80 °C, 50% C_2D_6CO, 10% TMS. [e] Sign opposite to corresponding $^4J_{PH}$.

Table II. ^{13}C Chemical Shifts and $^{13}C-^{31}P$ Couplings in Diphenyl-Substituted Phosphonium Salts[a]

Carbon	$(n\text{-}Bu)_2\overset{+}{P}Ph_2$ 10	 11	 12	 13	 14	 15
			^{13}C Chemical Shifts			
1	21.18	19.97	22.89	20.45	25.42	40.29
2	24.00	20.21	22.05	21.75	26.19	37.41
3	23.55	26.58	27.70	24.12		31.54
4	13.59	22.74				
Ph-1	118.55	120.23	120.24	118.63	119.64	120.27
Ph-2	133.71	133.14	132.46	132.65	133.50	132.85
Ph-3	130.79	131.73	130.40	130.41	130.89	130.11
Ph-4	135.13	134.57	134.43	134.61	135.27	134.98
			$^{13}C-^{31}P$ Coupling Constants			
1	49.3	48.2	49.9	48.1	52.5	53.2
2	4.5	4.8	1.5	6.1	6.7	19.1
3	16.0	1.7	1.4	6.4		12.1
4	0.7	0.7				
Ph-1	82.6	83.6	82.0	83.2	80.2	68.0
Ph-2	9.6	9.3	9.9	9.4	10.5	11.8
Ph-3	12.2	12.1	12.6	11.5	12.6	12.6
Ph-4	2.7	3.0	1.9	2.8	3.1	2.6

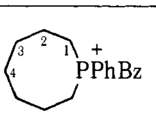
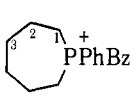
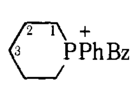
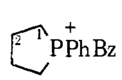
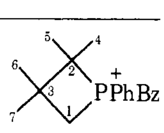
[a] Chemical shifts (in $CDCl_3$) in ppm from TMS-^{13}C (internal 1−5%) accurate to ±0.02 ppm. Couplings accurate to ±0.2 Hz except where noted.

one acyclic compound to represent the case of infinite ring size. In addition, new data on phosphetanes and phosphetanium salts are presented for various methylation patterns to further explore the sensitivity of shifts and couplings to neighbor substitution and to compare these sensitivities as a function of phosphorus oxidation state.

Results

Phosphines. ^{13}C chemical shifts and $^{13}C-^{31}P$ nuclear spin coupling constants for the phosphines are given in Table I. Listed here are the results of Jakobsen et al.[9] for triphenylphosphine, including signs of couplings. **2** and **3** are given to provide a smooth transition from **1** to **4**. Although there is no difficulty in assigning the methyl carbon in **2** and **3**, there can be confusion in the methylene assignments. A series of inversion-recovery[10] (T_1) ^{13}C spectra on **3** showed the expected increase of T_1 along the *n*-butyl chain[11] consistent with the proposed assignment. Further, the interior methylenes are also subject to two β effects, whereas the C-3 methylene has only one β effect and thus should be more shielded. The effect of selective spin-state irradiation[12] in the proton spectrum was observed only for C-2 in **2** and **3**. This is consistent with the large $^3J_{PH}$ coupling observed in aliphatic phosphines. In contrast, $^2J_{PH}$ is expected to be small (0.05 Hz in $(CH_3CH_2)_3P$)[13] in the mobile *acyclic* phosphines and thus should show no effect under selective spin-state irradiation (see below for a more detailed discussion of this technique). This selective irradiation also confirmed the coupling assignments for the *n*-butyl carbons in **2** and **3** since both members of the $^{13}C-^{31}P$ doublet

Table III. ^{13}C Chemical Shifts and $^{13}C-^{31}P$ Couplings in Phenylbenzyl-Substituted Phosphonium Salts[a]

Carbon	$(n\text{-Bu})_2\overset{+}{P}PhBz$ 16	 17	 18	 19	 20	 21
			^{13}C Chemical Shifts			
1	18.91	17.37	20.15	17.05	22.24	30.05
2	23.79	19.80	21.23	20.98	25.83	49.11
3	23.81	26.45	27.95	24.36		43.54
4	13.45	22.42				
Ph-1	117.40	117.64	118.43	116.39	118.91	118.51
Ph-2	132.72	133.14	132.51	132.70	132.39	133.38
Ph-3	130.00	130.15	129.91	129.89	129.35	129.73
Ph-4	134.32	134.41	134.14	134.22	133.75	134.13
Bz-1	29.22	32.20	31.84	25.32	30.32	32.21
Bz-2	128.22	128.93	128.49	127.89	128.21	127.64
Bz-3	130.33	130.68	130.40	130.20	130.00	130.29
Bz-4	128.99	128.86	128.73	128.70	128.65	128.95
Bz-5	128.18	128.14	127.96	127.90	127.84	127.96
			$^{13}C-^{31}P$ Coupling Constants			
1	48.1	47.1	46.6	46.3	51.6	45.5
2	5.0	5.2	4.8	5.0	5.6	42.0
3	15.9	1.8	0	5.6		12.4
4	1.9	1.				
Ph-1	78.3	79.1	78.2	78.2	76.1	60.5
Ph-2	9.1	7.3	8.8	9.0	9.1	9.3
Ph-3	11.4	11.8	11.8	11.3	12.2	12.6
Ph-4	3.6	2.7	2.6	1.9	2.0	2.2
Bz-1	46.0	45.4	44.4	43.2	40.2	22.7
Bz-2	8.9	9.0	9.4	9.0	9.6	10.0
Bz-3	5.4	5.2	5.4	4.3	4.6	6.1
Bz-4	2.5	3.3	3.6	1.8	3.5	4.0
Bz-5	3.9	4.0	3.8	1.5	3.8	4.5

[a] See footnote *a*, Table II.

broaden (or sharpen) in a pairwise manner as a function of ^1H irradiation frequency. C-4 in **4** was easily assigned on the basis of intensity and C-3 in view of its small coupling and insensitivity to selective decoupling. C-3 in **5** was assigned similarly. C-1 and C-2 in **4** and **5** were identified on the basis of the incremental shielding to be expected at C-2 from a more effective γ interaction resulting from cyclization, the insensitivity of C-1 to selective decoupling (a large $^3J_{PH}$ is to be expected for the C-2 protons, whereas $^2J_{PH}$ can be small particularly for the less stereorigid rings), and the similarity of the assigned C-1 shifts to those in **2** and **3**. C-1 and C-2 in **6** were identified in the same manner. Here $^2J_{PC\text{-}2}$ is much smaller because C-2 is positioned at a larger average dihedral angle with respect to the phosphorus lone pair.[4] In fact, C-2 in **7** is, on the average, at an even larger dihedral angle, producing a *negative* $^2J_{PC}$ similar to that of the pseudoaxial C-4 methyl of **8**. The flatter five-membered ring of **7** decreases the γ interaction of C-2 and restores the more comparable C-1 and C-2 shifts found in **2** and **3**. C-1 in **8** was assigned via off-resonance decoupling. Phenyl resonances in **2–9** were assigned on the basis of chemical shift, intensity and the large coupling expected for the ortho carbon.[3]

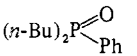
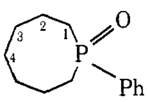
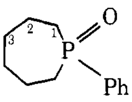
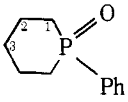
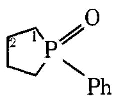
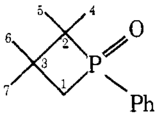
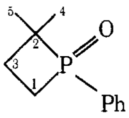
Phosphonium Salts. The diphenyl-substituted salts results are given in Table II. **10** simulates an arbitrarily large ring, while **11–15** exhibit the effect of closing the ring and compressing the C–P–C interior angle. The signals were assigned based on the large coupling to be expected for the α carbon, the intensities, and the shielding patterns as a function of distance from the phosphorus.[3]

The phenylbenzyl salts have the same shielding and coupling patterns and were sorted out on the basis of the expected couplings, shifts, and intensities[3] (see Tables III and V).

Phosphine Oxides. The oxides exhibited regular shielding and coupling patterns,[3] making assignment easy (Table IV). As in the salts, the C-3 carbons in the di-*n*-butyl compounds have characteristic large couplings (ethyl-substituted salts and oxides have small C-2 couplings).

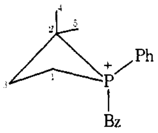
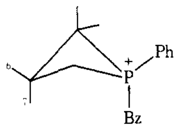
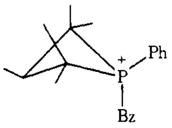
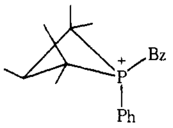
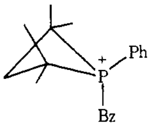
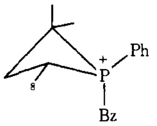
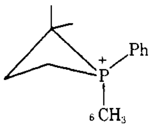
Sign Determinations. These were carried out using the techniques described by Jakobsen et al.[12] for $^{13}C-^{31}P$ couplings in organophosphorus compounds. Basically, the technique involves application of a coherent ^1H irradiating field such that one spin state in the $^{31}P-^1H$ doublet in the proton spectrum is irradiated more strongly than the other. If the irradiating field is weak it is referred to as "spin tickling". Under stronger irradiation some decoupling occurs and reduced couplings are observed, giving "off-resonance" spectra. For a three-spin system such as ^1H, ^{13}C, and ^{31}P there are two spin states in the proton spectrum corresponding to the $^{31}P-^1H$ coupling. For small residual "off-resonance" splittings, $J_r = J_{CH}\Delta f/(\gamma H_2/2\pi)$, where J_r is the reduced $^{13}C-^1H$ coupling constant, Δf the offset (in Hz) from exact ^1H irradiation, and $(\gamma H_2/2\pi)$ the strength of the ^1H decoupling field (in Hz). Since there are two Δf's (corresponding to the two $^1H-^{31}P$ spin states) the components of any $^{13}C-^{31}P$ doublet will give different J_r's. If $\Delta f = 0$ for one spin state but not the other, one line in the observed $^{13}C-^{31}P$ doublet will be perfectly decoupled (assuming $(\gamma H_2/2\pi)$ is large enough) while the other component will have a residual coupling (or broadening). This is illustrated in Figure 1 for the methylene carbon of **8**. The significance of this technique is that it allows a relative sign determination of $^nJ_{CP}$ and $^{n+1}J_{PH}$ (for protonated carbons). Under favorable circumstances quaternary carbons can also be examined[9] if there is a unique long-range $^{13}C-^1H$ coupling present where that proton is also coupled to the phosphorus. If a high-frequency ^1H irradiating field more efficiently decouples a

Table IV. ^{13}C Chemical Shifts and $^{13}C-^{31}P$ Couplings in Phenyl-Substituted Phosphine Oxides^{a}

Carbon	 $(n\text{-Bu})_2P(=O)Ph$ 23	 24	 25	 26	 27	 28^{b}	 29^{c}
			^{13}C Chemical Shifts				
1	29.78	29.30	31.76	28.73	30.30	41.46	28.64
2	23.56	20.21	21.66	22.54	25.72	50.81	48.76
3	24.00	27.24	29.56	26.98		35.04	26.69
4	13.55	23.38					
Ph-1	131.55	136.31	135.29	134.29	136.66	133.78	130.78
Ph-2	130.56	129.79	129.61	130.89	131.01	131.56	130.45
Ph-3	128.55	128.84	128.52	129.58	129.43	129.18	128.72
Ph-4	131.37	131.57	131.33	132.60	132.13	132.34	131.95
			$^{13}C-^{31}P$ Coupling Constants				
1	68.6	65.5	65.0	65.2	66.8	52.0	52.2
2	3.8	4.6	4.5	6.0	7.9	62.8	62.5
3	14.8	1.9	1.2	6.8		11.9	15.8
4	1.4	0.5					
Ph-1	85.8	93.5	92.6	92.6	86.6	67.8	71.1
Ph-2	7.7	8.7	9.0	9.2	9.4	9.7	9.6
Ph-3	10.9	11.1	11.4	11.2	11.1	10.8	10.5
Ph-4	2.8	2.7	2.1	2.6	2.5	2.9	2.4

^{a} See footnote *a*, Table II. ^{b} Taken from ref 3. In the 2,2,3-trimethyl versions the ring methylene has couplings of 52.5 (C-3 methyl and phenyl trans) and 52.3 (cis) while the substituted phenyl carbon has a coupling of 72.3 (trans) and 57.6 (cis) (65 Hz average).[3] For 28: C-4, 19.16 (4); C-5, 21.55 (2); C-6 26.30 (11.3); and C-7, 27.19 (13.6 Hz). ^{c} C-4 or C-5: 23.81 (3.7) or 22.77 (3.7 Hz).

Table V. ^{13}C Chemical Shifts and $^{13}C-^{31}P$ Couplings in Phosphetanium Salts^{a}

Carbon	 22	 21	 30	 31	 32	 33	 34
			^{13}C Chemical Shifts				
1	15.26	30.05	42.66	43.08	38.62	37.29	17.39
2	44.90	49.11	42.66	43.08	38.62	46.55	43.00
3	34.18	43.54	49.72	52.71	51.32	46.26	34.11
4	23.60^{b}	20.80^{b}	21.06	20.66	26.46	21.38^{b}	24.12^{b}
5	24.96^{b}	21.59^{b}	25.46	27.32	27.84	20.61^{b}	23.72^{b}
6		26.03	8.35	8.82		26.19	8.82
7		27.20				21.98^{b}	
8						10.17	
Ph-1	117.01	118.51	117.63	116.60	117.87	118.15	118.54
Ph-2	132.16	133.38	131.88	133.08	133.20	132.96	132.63
Ph-3	130.34	129.73	129.43	129.72	129.53	129.38	129.89
Ph-4	135.12	134.13	133.72	133.90	134.05	133.86	134.64
Bz-1	29.41	32.21	28.04	29.59	28.95	28.56	
Bz-2	127.82	127.64	*c*	*c*	127.67	127.38	
Bz-3	130.52	130.29	130.64	128.60^{d}	130.62	130.07	
Bz-4	129.43	128.95	128.20	128.18	128.45	128.49	
Bz-5	128.56	127.96	127.40	127.62	127.60	127.51	
			$^{13}C-^{31}P$ Couplings				
1	46.1	45.5	42.0	41.5	42.7	41.7	47.6
2	43.9	42.0	42.0	41.5	42.7	42.7	49.1
3	17.9	12.4	9.5	8.5	10.7	8.8	18.5
4	1.8^{b}	3.7^{b}	3.0	1	2.5	5.6^{b}	2.4^{b}
5	3.6^{b}	1^{b}	3.5	4.5	3.1	2.7^{b}	2.0^{b}
6		19.7	20.3	18.1		16.0	33.5
7		1.8				3.0^{b}	
8						15.4	
Ph-1	59.4	60.5	49.3	53.8	49.3	59.1	60.9
Ph-2	9.7	9.3	7.2	7.1	7.5	8.8	10.2
Ph-3	12.3	12.6	11.1	13.7	11.1	11.8	11.7
Ph-4	3.5	2.2	3.0	3.3	3.0	3.2	3.1
Bz-1	24.1	22.7	24.0	17.9	21.3	21.8	
Bz-2	10.3	10.0	*c*	*c*	9.5	9.4	
Bz-3	5.6	6.1	5.2	5.8^{d}	5.4	5.5	
Bz-4	3.3	4.0	3.0	3.2	2.9	2.6	
Bz-5	3.0	4.5	3.6	2.9	3.3	2.9	

^{a} See footnote *a*, Table II. ^{b} May be interchanged. ^{c} Not resolved. ^{d} Tentative.

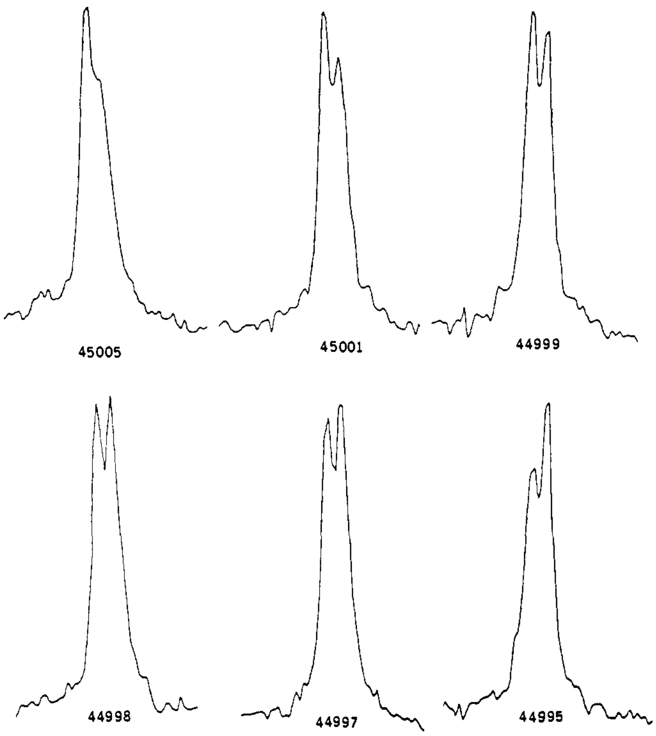


Figure 1. Variation of ^1H decoupling frequency for methylene carbon in 8. ^{13}C observing frequency increases to the left. Numbers are experimental settings (in Hz) of offset frequency in XL-100 Gyrocode spin decoupler and are appropriate for irradiation of methylene protons (exact resonance at 44 998 Hz). The observed doublet arises from the directly bonded $^{13}C-^{31}P$ spin-spin coupling which is $+0.6 \pm 0.05$ Hz. Spectra were obtained on an XL-100 WG12/S-124XL-16K Fourier transform spectrometer using coherent, high-power decoupling, acquisition times of 8 s and no exponential filtering. Each spectrum represents 16 accumulations.

high-frequency component of a $^{13}C-^{31}P$ doublet the signs of the $^{13}C-^{31}P$ coupling and $^{31}P-^1H$ coupling are the same. Better decoupling of the low-frequency ^{13}C component shows that the couplings are of opposite sign. This knowledge is of great value in assignments for phosphines, particularly cyclic phosphines wherein the dihedral angle dependence of $^2J_{PCH}$ allows the sign determination of $^1J_{PC}$. Albrand et al.[13] have detailed the dihedral angle dependence of $^2J_{PCH}$ in phosphines: when the proton is cis to the phosphorus lone pair $^2J_{PCH}$ is large and positive (ca. +25 Hz); at a dihedral angle of ~120° the coupling is ca. −5 Hz, while at 180° (trans) the coupling is ca. −1 Hz. Recent work by Bushweller and Brunelle[14] has shown a similar stereochemical dependence of the *magnitude* of $^3J_{PCCH}$ in *tert*-butylphosphines; however, the sign of $^3J_{PH}$ coupling remains always *positive*. This is in evidence in **8** which has been reported[15] to have α-methyl $^3J_{PCCH}$ couplings of 18 and 5.8 Hz. The larger coupling must be associated with the methyl cis to the phosphorus lone pair. In some earlier work[4] we reported the stereochemical dependence of the $^2J_{PC}$ in relatives of **8**. A methyl carbon cis to the phosphorus lone pair has a large (~35 Hz) coupling while a methyl in the other orientation has a small (2-5 Hz) coupling. Since $^3J_{PCCH}$ is positive for these methyls, selective proton spin-state irradiation behavior gives unambiguous signs for the $^2J_{PC}$ which turn out to have opposite sign. The large $^3J_{PCCH}$ coupling to the ortho phenyl carbon allowed sign determination for **4–9** in the same manner. As a bonus, this technique also provides the proton shift if a similar decoupling experiment is performed on the internal TMS. This has utility in cases where the proton spectrum is very complicated as in **4–9** (see Table VII).

Discussion

Chemical Shifts. Mann[16] has reported a large number of phosphine ^{13}C shifts which were found to parallel their corresponding hydrocarbon analogues. The normal large deshielding experienced by carbon bound to a heteroatom does not occur, a fact which leads to a congestion of resonances in the aliphatic region. In contrast, when phenyl is a substituent its substituted carbon is deshielded about 12–15 ppm while the ortho, meta, and para carbons are found within a 5-ppm spread near the shift of benzene. Featherman and Quin[17] have reported the ^{13}C shifts and $^{13}C-^{31}P$ couplings in a series of isomeric 4-phosphorinols, and recently reported[18] results on a series of various exo-cyclic substituted phosphorinanes and their sulfides. Their data for **6** are in substantial agreement with those reported here. No studies of phosphorus heterocycles larger than the six-membered ring have appeared.

Compound **3** was examined to provide an unconstrained model for **4–9**. Upon cyclization to the eight-membered ring C-1 is affected only slightly while C-2 is shielded as a result of more effective γ interactions. C-3 is deshielded through the added β effect arising from cyclization at C-4. Cyclization also has a dramatic effect on the substituted phenyl carbon, deshielding it over 3 ppm. The ortho and para carbons are, however, shielded by 1 ppm each. C-3 in **5** and **6** is similar in shift to C-2 in **2** or **3**, and may be taken as typical for a methylene (cyclooctane and cyclohexane have chemical shifts of 28 ppm while cycloheptane has a 29.4-ppm shift[19]). C-3 and C-4 in **4** are therefore about 1.5 and 2.5 ppm more shielded than expected.

There is an oscillatory regularity of C-1 and C-2 shifts as ring contraction proceeds **4** → **7**. Bond angles in these molecules should not be appreciably distorted and yet both carbons have greater shifts for ring sizes five and seven.

In general, conversion of the phosphines to their salts or oxides produces shifts similar to those previously observed.[5] One major question to be explored is the extent of separability possible between ring size effects and type of phosphorus coordination. Figure 2 exhibits the effects of ring contraction on various shifts. The oscillatory behavior is clearly present for C-1 in all oxidation states, with only minor deviations for ring size five and above. However, sharp differences in the five → four size transition are evident. Other ring systems (Figure 3) display similar behavior except that typically they show reverse six → five and mixed five → four ring size patterns. It is important to correct for the shielding produced from the α methyls on C-1 in **8a**, **22**, and **29**. This poses difficulties since there is no certainty that one α correction will be appropriate for all. Some estimates of this type of correction can be obtained from our previous work on substituted phosphetanes.[3] There, γ interactions ranging from 2 to 8 ppm can be calculated for various ring and exocyclic substitutions. Since these were for completely substituted carbons it seems appropriate that at least a 5 ppm shielding occurs for C-1 through the γ interaction of the C-4 methyls in **8a**, **22**, and **29**. Rather than a shielding for five → four ring size change in the oxide and salts, C-1 probably would be deshielded slightly for the oxide and shielded by a few parts per million for the salts. The phosphine C-1, however, would be still appreciably shielded in an unmethylated version of **8**, probably having a shift of 16 or 17 ppm. The magnitude of five → four shielding would then be unusual in its size, only matched by the 10 ppm *deshielding* for the five → four ring change for C-1 in cyclic ketones. The four → three ring size transitions are particularly interesting in light of the pattern of large shielding produced in carbocyclic or *N*-, *O*- and *S*-heterocyclic models. The 20–30 ppm shieldings experienced for

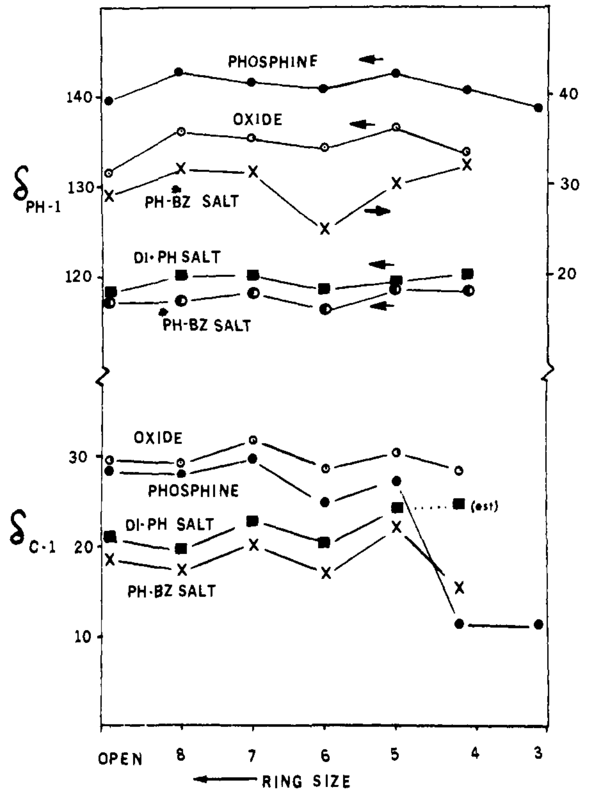


Figure 2. Variation of phosphorus-bound carbon chemical shifts as a function of ring size and type of phosphorus substitution.

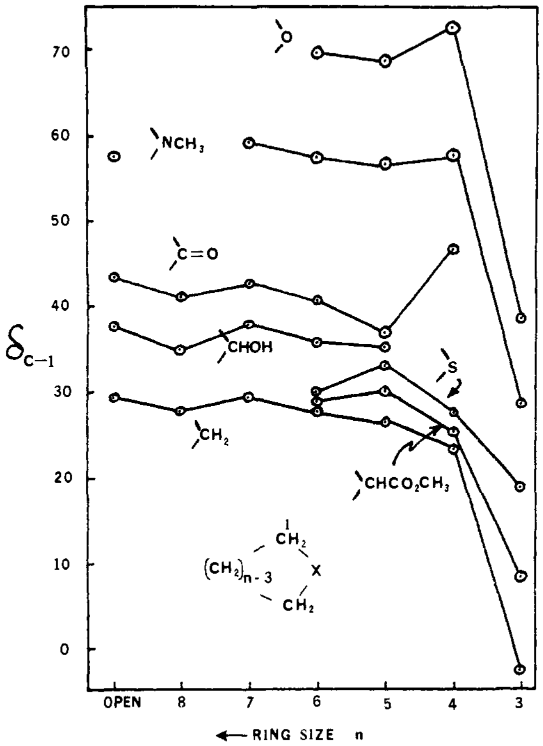


Figure 3. Variation of α carbon chemical shift with ring size for various types of substitution.

C-1 may be only appropriate for first-row elements (the sulfur heterocycle is shielded only about 9 ppm) perhaps indicating that the contraction to the three-membered ring causes less distortion because of the longer C-S or C-P bonds. More data are necessary to adequately test this proposition, particularly for the salts and oxide.

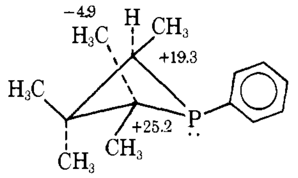
Exocyclic substituents might be expected to have different sensitivities to ring contraction. Few literature models are available to provide a calibration. In both the phosphine and oxide the substituted phenyl carbon gradually decreases in shift, with the exception of **7** and **27**. Conformation averaging tends to obscure details but the exocyclic pseudoaxial/pseudoequatorial shift difference is likely to be small; it has been found[5] to be 2.4 ppm in *cis*/*trans*-1-phenyl-2,2,3,4,4-pentamethylphosphetane for the substituted phenyl carbon. In all the phosphorus oxidation sates and the substitutions the exocyclic phosphorus-bound carbons show a similar pattern for the di-*n*-butyl → cyclopentyl ring contractions. The greater increase in shielding experienced by the benzyl methylene in the seven → six ring contraction may be due to a stronger γ interaction with the ring methylenes than present for the nonprotonated exocyclic phenyl carbons. The five → four ring contraction brings out a dependence of exocyclic directly bonded shift on phosphetane ring methylation. The benzyl carbon either is shielded or deshielded, depending upon the methylation at C-2.

The protons on C-1 have shifts (Table VII) which increase with ring closure and contraction. The contraction to the three-membered ring does produce the typical high shielding associated with cyclopropyl systems, however. There are also significant differences in methylene proton shifts in the eight-, seven- and six-membered rings, probably reflecting conformation effects. There does seem to be a 0.2-ppm shielding of the para proton in the phenyl groups of the three- and four-membered rings, relative to the larger heterocycles.

^{13}C–^{31}P Coupling Constants. Phosphines. We have previously reported the ^{13}C–^{31}P couplings for **1–3** and **6–8**.[8] Only minor changes in the couplings are observed upon replacement of phenyls with butyls in **1** → **3**.

The primary result of cyclization on the aliphatic carbons is the reduction of the $^3J_{PC}$. Some change is also noted in the two *one-bond* couplings: the C-1 coupling becomes (assumedly) more negative while the Ph-1 coupling becomes more positive. As the size of the heterocycle decreases all of the couplings tend to decrease in magnitude except that of the Ph-1 phenyl carbon which becomes even more negative. The dramatic reduction of the C-2 coupling from +12.3 in **4** to −4.7 in **7** is likely to be reflecting a change in the equilibrium orientation of that carbon with respect to the phosphorus lone pair. When C-2 is at a small dihedral angle with respect to the lone pair the $^2J_{PC}$ coupling is expected to be large and positive (up to as much as ~30 Hz)[4,20] and at large dihedral angle it can be small and negative, as borne out for the α methyls in **8**.

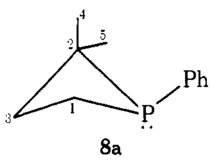
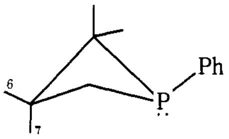
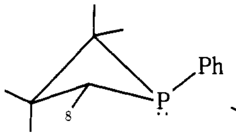
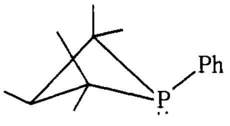
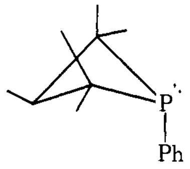
The most dramatic changes occur in the four- and three-membered rings where the C-1 coupling essentially vanishes or assumes a small value in the four-membered ring but becomes large and negative in the three-membered ring. Note that the phenyl one-bond coupling steadily becomes more negative throughout the entire ring contraction. Compound **8b** has been determined[21] to have the stereochemistry



8b

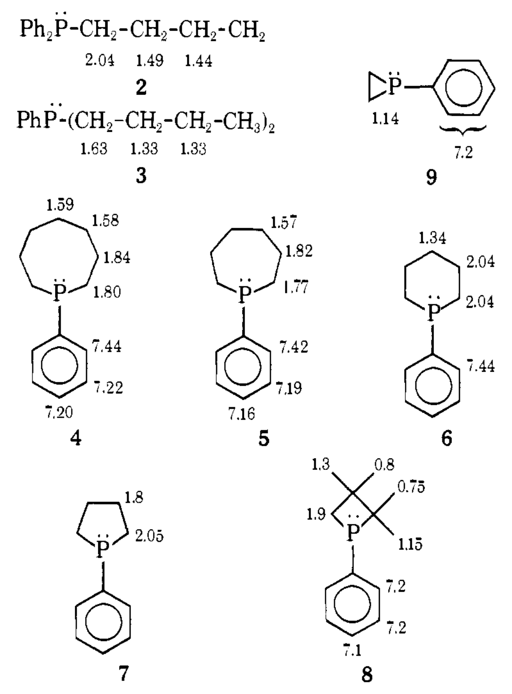
Since $^2J_{PCH}$ is for a trans relationship for the C-1 proton and phosphorus lone pair, the sign of that coupling is negative[13] and this allowed determination of the sign of the directly bonded methine $^1J_{CP}$. Since only this conformer

Table VI. ^{13}C Chemical Shifts and ^{13}C–^{31}P Couplings in Methyl-Substituted Phenylphosphetanes[a]

Carbon	 **8a**	 **8**	 **8b**	 **8c**[c]	 **8d**[c]
			^{13}C Chemical Shifts		
1	11.26	28.74	34.80	34.52	30.22
2	34.98	41.26[b]	38.75	34.52	30.22
3	37.68	40.16[b]	43.04	49.70	54.02
4	26.23	23.05	23.10	20.92	26.24
5	30.07	25.15	24.63	32.71	26.52
6		27.84[b]	22.10	8.12	9.96
7		26.13[b]	24.19		
8			13.02		
Ph-1		140.75	140.89	140.09	137.71
Ph-2		130.76	130.10	129.50	135.11
Ph-3		128.09	127.72	127.64	127.57
Ph-4		127.24	127.13	126.15	128.16
			^{13}C–^{31}P Coupling Constants		
1	2.2	+0.6 ± 0.05	+4.4	2.6	5.9
2	8.6	1.5[b]	2.9	2.6	5.9
3	1	3.9[b]	5.0	5.9	2.7
4	(−)2.1	−4.5	−4.9	(−)4.9	(+)31.8
5	(+)27.9	+25.5	+25.2	(+)27.8	(−)2.5
6		8.4[b]	10.5	13.5	0.0
7		5.5[b]	7.6		
8			+19.3		
Ph-1	~(−)35	(−)35.4	(−)36.7	(−)42.8	(−)41.3
Ph-2		+15.6	(+)14.6	(+)13.1	(+)20.2
Ph-3		(+)4.7	(+)4.5	(+)2.9	(+)6.6
Ph-4		0.0	0	1.8	1.1

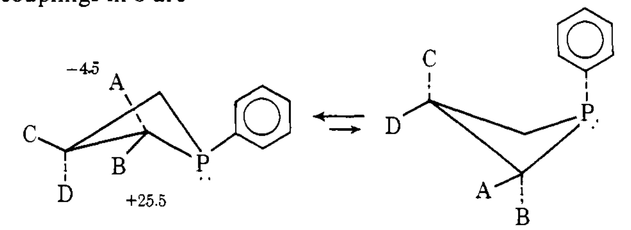
[a] See footnote *a*, Table II. [b] May be reversed. [c] From ref 5.

Table VII. Proton Shifts in Phosphines Obtained from Selective Decoupling[a] (ppm)



[a] Proton shifts with respect to internal TMS. See Experimental Section for details of method.

should be significantly populated it provides a measure of the degree of conformational flexibility of **8**. The α-methyl couplings in **8** are



virtually identical with those in **8b**, implying that the conformation equilibrium is decidedly to the left. In both conformers the methyl-methyl nonbonded interactions are identical so that the driving force in the equilibrium must be provided by the 1,3-phenylmethyl nonbonded interactions. These latter interactions are absent in **6** where comparable populations of both equatorial and axial phenyl are observed.[18]

The surprisingly small one-bond ring ^{13}C–^{31}P couplings in the four-membered rings (see Table VI) have no parallel in carbocyclic systems where the analogous ^{13}C–^{13}C couplings decrease monotonically in the ring size sequence six → five → four → three.[22] It could be argued that the only substantial changes occur at the phosphorus. This view must, however, also explain the relatively smooth trend in the phenyl $^1J_{PC}$ for **4** → **9** and the sensitivity of the phosphorus-bound phosphetane carbon coupling to various ring methylations (Table VI). This latter coupling has a range of 0.6 to 8.6 Hz.

In addition to the unusually large C-1 coupling in the three-membered heterocycle there are definite increases in the ortho and meta couplings, reversing definite trends established in **4** → **8**. The changes may be related more to electronic efforts than to conformational effects since their shifts, including the para carbon, are significantly different as well.

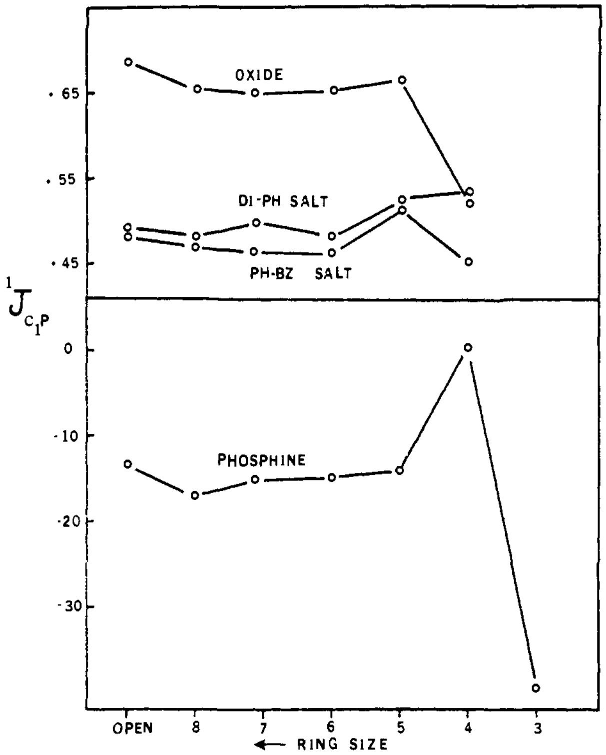


Figure 4. Variation of C-1 coupling to phosphorus as a function of ring size.

Salts and Oxides. Figure 4 compares the ring contraction behavior of the one-bond couplings for the three types of phosphorus heterocycles. Unfortunately, the three-membered ring analogues for the salts and oxide have yet to be synthesized. No large differences occur in the responses of the C-1 coupling to ring contraction until the five- to four-membered ring step where a wide divergence of direction and change occurs. The source does not lie in gross oxidation state since the two types of salts exhibit dissimilar effects. It might be argued that the variations in C-1 substitution within the various four-membered ring compounds lead to the differing five → four ring contraction patterns. It is true that single or double methylation of a C-1 carbon does affect the C-1 couplings, as documented in Table V. There is a systematic *decrease* in C-1 coupling of about 2-4 Hz in the phenylbenzyl salts (see Table V) and an *increase* of about 10 Hz in the oxides upon C-1 methylation. However, given a fixed methylation pattern for C-1, little sensitivity to neighboring C-2 or C-3 methylation is observed, leading to more certainty in taking the values observed for unmethylated C-1's as indicative of couplings appropriate for unmethylated four-membered rings. In view of this likelihood, the different patterns of five → four ring contraction coupling behavior for C-1 are indeed real.

The exocyclic one-bond phenyl and benzyl couplings are, however, remarkably similar in their ring contraction behavior. All become dramatically more negative in the five → four step. The only notable deviations are the *decrease* in coupling for the benzyl carbon on cyclization, the variety of seven → six steps, and the larger cyclization change shown by the phenyl carbon in the oxide.

A fundamental question yet to be answered for ^{13}C-^{31}P spin couplings is the extent of partitioning into the various mechanisms for spin coupling.[23-26] ^{13}C-^{1}H and ^{13}C-^{13}C couplings seem to be adequately explained in most cases using only the Fermi contact contribution. Our earlier[23] calculations of ^{13}C-^{31}P couplings in diethyl phosphonates succeeded in reproducing satisfactory agreement in signs, magnitudes, and trends for one-bond couplings. It is not clear, especially for P(III), that this is the only, or even predominant, mechanism. The qualitative theory of Jameson and Gutowsky[24] treats ^{13}C-^{31}P couplings in terms of a mixture of Fermi contact and "core polarization" mechanisms, the latter being responsible for *small* negative ^{13}C-^{31}P couplings in P(III) compounds. Detailed calculations will be necessary to rationalize the *large* negative couplings observed here and elsewhere. The oxide and salt one-bond couplings are much more likely to be dominated by the contract mechanism since they are four-coordinate and tetrahedral like the diethyl phosphonates.[23]

Recently Giessner-Prettre and Pullman[26] published Finite-Perturbation INDO-MO calculations on several organophosphorus compounds including $(CH_3)_3P$, $(CH_3)_3PO$, and $(CH_3)_4P^+$. The corresponding $^1J_{PC}$'s were calculated to be −16.9, +72.6, and +46.8 Hz, employing *only* the Fermi contact mechanism, in good agreement with experimental values. These encouraging results should permit at least overall interpretation within the contact mechanism although the extent of contributions from other spin coupling mechanisms remains to be proved.

Summerhays and Maciel[25] have rationalized small changes in ^{13}C-^{13}C couplings occurring in *tert*-butyl-, isopropyl-, ethyl-, and methyl-substituted carbon as resulting from hybridization changes brought about by bond angle distortions. The directly bonded CP coupling behavior in the phosphines may be also determined by changes in the bond angles. The one-bond exocyclic coupling does monotonically decrease with ring size, following the increase in the C-P-C exterior bond angle. The interior P-C-C and C-P-C bond angles *decrease* with decreasing ring size, nearing 90° in the four-membered ring where s-orbital participation in valence orbitals might be thought of as at a minimum. Further interior bond angle decrease in going to the three-membered ring would then allow contact contribution once again where, it is important to note, the sign still remains negative.

In comparing ring size change behavior for the variously substituted five → four cases, the range of five → four behavior observed may be too divergent to explain through bond angle arguments, possibly forcing consideration of oxidation-state dependent factors. It is interesting to note the smooth five → four transitions of the exocyclic one-bond couplings in contrast to the variety of five → four C_1 coupling transitions.

Even considering the normal richness of behavior found for CP couplings in organophosphorus compounds we must finally point out the unusual aspects of the observed results for the three-membered case **9**. The large C_1 coupling has no parallel in ^{13}C-^{13}C couplings where small in-ring couplings have previously been rationalized in terms of small s character and large exocyclic couplings in terms of large s character. No unusual increase is noted here, however, for the exocyclic one-bond coupling. In addition, **8** and **8b** offer the only situations where two carbons, bonded to the *same* phosphorus, have different coupling constant signs. Since positive C_1 couplings are observed it will be of considerable future interest to trace their contributing mechanism(s), since noncontact contributions of small magnitude may be always existent and only uncovered by the disappearance of the contact contribution. Hopefully, future calculation of the other coupling mechanism importance and bond angle dependence will somewhat illuminate this question.

Measurements. ^{13}C NMR spectra were obtained at 25.16 MHz using an XL-100WG/S-124XL16K Fourier transform spectrometer. Saturated (100-500 mg/ml) solutions of salts and oxides were run in 10-mm tubes in $CDCl_3$ using 1-5% internal TMS as reference. Phosphines were run neat with 10% C_6D_6 added for lock and 1-5% TMS as reference.

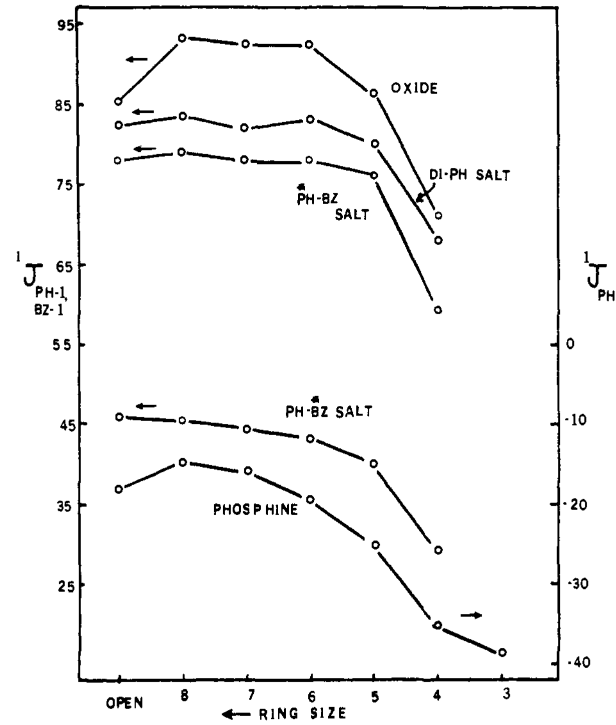


Figure 5. Variation of exocyclic one-bond couplings to phosphorus of phenyl and benzyl substituents as a function of ring size.

Sample temperatures were 35–40 °C. Spectral widths (4000 Hz) (1.0 s acquisition time) were employed normally for the chemical shift measurements while smaller spectral widths and 4–8 s acquisition times were used for coupling constant measurements. Line positions and chemical shifts were automatically generated via system software. Inversion-recovery experiments were made with the 180°–τ–90° pulse sequence using the standard two-pulse feature in the Varian FT/16D software. T_1's were not actually determined but rather the inversion-recovery behavior was used to sort out doublets of similar shift where.alternate assignments were possible.

Experimental Section

6, **7**, **8b**, **19**, **20**, **21**, **27**, **30**, **31**, and **33** were prepared using previously described methods;[21] likewise, samples of **8** and **28** were made by known procedures.[27] The salt, 1,1-diphenylphosphoranium bromide (**13**), was synthesized by Markl's method[28] and had mp 259–261 °C (lit.[28] mp 261–262 °C).

The preparations of di-(*n*-butyl)phenylphosphine (**3**) and *n*-butyldiphenylphosphine (**2**) were prepared by the procedure of Davies and Jones.[29]

Phosphonium Bromides. 10 and 16. Treatment of **2** with an excess of *n*-butyl bromide gave di(*n*-butyl)diphenylphosphonium bromide (**10**), mp 161–163 °C (lit.[30] mp 162–163 °C); similarly treatment of **3** in an ether solution of benzyl bromide gave a white precipitate (after standing for several days) of di(*n*-butyl)benzylphenylphosphonium bromide (**16**), mp 163–165 °C. A solution of **16** in $CDCl_3$ showed peaks in the ^1H NMR spectrum (TMS reference) at: δ 8.2–7.1 (10, H, m), 4.59 (2 H, d, J_{PCH} = 15 Hz), 3.3–2.5 (4 H, m), 1.9–1.2 (8 H, m), and 1.2–0.7 (6 H, m).

1,1-Diphenyl-3,3-dimethylphosphetanium Iodide (15). A solution of 0.3 mol of lithium diphenylphosphinide[32] in 200 ml of dry THF was added dropwise to a solution of 1,3-dichloro-2,2-dimethylpropane[33] (0.3 mol) in 600 ml of THF. No external cooling was required. The reaction mixture was stirred overnight, the THF was removed under vacuum and replaced by dry ether (100 ml), and 100 ml of 6% HCl was added. The ether layer was dried and concentrated to give a 92% yield of crude intermediate, 3-chloro-2,2-dimethylpropyldiphenylphosphine. Since this intermediate distilled (bp 130–140 °C (0.05 mm)) with decomposition, it was used in crude form for the subsequent reaction. The purity of the intermediate was conveniently monitored by ^1H NMR spectroscopy; a solution in $CDCl_3$ showed peaks at: δ 7.7–7.2 (10 H, m), 3.52 (2 H, s) 2.29 (2 H, d, J_{PCH} = 3.5 Hz), and 1.04 (6 H, s). Unreacted 1,3-dichloro2,2-dimethylpropane, if detected, was removed under vacuum (0.05 mm) at 50–60 °C.

A solution of the intermediate (0.1 mol) in 250 ml of dry benzonitrile was added dropwise to 15 g of NaI in 1 l. of refluxing benzonitrile (vigorously stirred) over a period of 20 h. The mixture was allowed to reflux 4 h longer and the benzonitrile was then removed by distillation under vacuum (0.1 mm). The crude, brown residue was recrystallized from acetonitrile-ethyl acetate to give 20 g (53% yield) of **15**. Three additional recrystallizations gave white, grainy crystals, mp 212–213 °C, which were submitted for elemental combustion analysis. The NMR spectrum ($CDCl_3$, TMS reference) showed absorption at δ 8.5–7.6 (10 H, m), 3.57 (4H, d, J_{PCH} = 14.5 Hz), and 1.50 (6 H, s).

Anal. Calcd for $C_{17}H_{20}PI$: C, 53.42; H, 5.27; I, 33.21. Found: C, 53.22; H, 5.19; I, 33.47.

Di(*n*-butyl)phenylphosphine Oxide (23). A solution of 4.4 g (0.02 mol) of the phosphine **3** in 30 ml of benzene was stirred and cooled to 5 °C; 1 equiv of H_2O_2 (30%) was added dropwise at a rate to maintain the temperature below 7 °C. The reaction was run under an atmosphere of nitrogen. After stirring overnight the benzene layer was dried (Na_2SO_4, anhydrous) and then evaporated to a liquid which was treated with 50 ml of petroleum ether (30–60 °C). On standing, needles formed but some liquid remained. The solid was filtered (drybox) and then heated under vacuum (60 °C (0.1 mm)) to remove volatile impurities; the desired product did not sublime. The impure, waxy, hygroscopic residue, mp 55–58 °C (lit.[34] mp 60–62 °C), showed peaks in the ^1H NMR ($CDCl_3$, TMS ref.) at δ 8–7.3 (5 H, m), 2.3–1.1 (12 H, m), and 1.1–0.7 (6 H, m).

1-Phenylphosphorinane 1-Oxide (26). The benzyl salt **19**, 3.5 g (0.01 mol), was dissolved in 50 ml of 2 N NaOH in 85% ethanol and heated at reflux for 5 days. The solvent was evaporated and the crude solid was sublimed and then recrystallized from cyclohexane to give the product (86% yield), mp 128–129.5 °C (lit.[31] mp 130 °C).

1,1-Diphenylphospholanium Bromide (14). 1-Phenylphospholane[35] was converted to 1,1-diphenylphospholanium bromide in quantitative yield by the method of Horner.[36] The product was initially obtained as an oil which, upon trituration with ether, gave crystals of mp 163–164 °C.

Anal. Calcd for $C_{16}H_{18}BrP$: C, 59.28; H, 5.65. Found: C, 59.29; H, 5.86.

1,1-Diphenylphosphepanium Bromide (12). This compound was prepared by a published procedure[37] in 74% yield, mp 248–250 °C (EtOH–EtOAc) (lit.[38] 245–247 °C).

1-Phenylphosphepane 1-Oxide (25). The oxide was prepared from 1,1-diphenylphosphepanium bromide by refluxing a solution of 22.0 g of the bromide and 63 ml of 2 N NaOH for 24 h. Benzene was removed from the reaction mixture by azeotropic distillation (4.8 ml); the aqueous solution was saturated with KOH and then continuously extracted with chloroform. After separation of the chloroform layer and its evaporation, the residue was sublimed at 120 °C (0.1 mm) to yield 86.5% of the oxide of mp 115.5–118 °C.

Anal. Calcd for $C_{12}H_{17}PO$: C, 69.21; H, 8.23; P, 14.87. Found: C, 69.39; H, 8.20; P, 15.06.

1,1-Diphenylphosphocanium Bromide (11). This salt was synthesized in accordance with a published method[37] in 20% yield, mp 222.5–223.5 °C (EtOH–EtOAc).

Anal. Calcd for $C_{19}H_{24}PBr$: C, 62.81; H, 6.66. Found C, 62.87; H, 6.68.

1-Phenylphosphocane 1-Oxide (24). This compound was prepared in 83% yield in the same manner as 1-phenylphosphepane 1-oxide as described above, mp 86–88 °C (sublimed at 120 °C (0.2 mm)).

Anal. Calcd for $C_{13}H_{19}OP$: C, 70.25; H, 8.61. Found: C, 70.21; H, 8.90.

1-Phenylphosphocane (4). This phosphine was prepared in 94% yield by phenylsilane reduction[39] of the corresponding oxide, bp 120–130 °C (15 mm) (kugelrohr).

1-Benzyl-1-phenylphosphocanium Bromide (17). The bromide salt was prepared as described above for 1-benzyl-1-phenylphosphepanium bromide: mp 182.2–182.8 °C (EtOH–EtOAc); yield, 93%.

Anal. Calcd for $C_{21}H_{28}BrP$: C, 64.45; H, 7.21. Found: C, 64.75; H, 7.45.

1-Phenylphosphepane (5). 1-Phenylphosphepane 1-oxide was reduced in 96% yield with phenylsilane by a procedure described elsewhere[38] to give the phosphine of bp 110-120 °C (0.035 mm) (kugelrohr).

1-Benzyl-1-phenylphosphepanium Bromide (18). 1-Phenylphosphepane from the above procedure was dissolved in about 75 ml of deoxygenated benzene and a twofold molar excess of benzyl bromide was added to the solution. After allowing the reaction mixture to stand overnight under nitrogen the crystals were removed to give a 93% yield of bromide salt, mp 164.5-165.3 °C (EtOH-EtOAc).

Anal. Calcd for $C_{19}H_{24}BrP$: C, 62.81; H, 6.65. Found: C, 62.83; H, 6.89.

1-Phenyl-1-benzyl-2,2,4,4-tetramethylphosphetanium Bromide (32). To 2.0 g (0.01 mol) of 1-phenyl-2,2,4,4-tetramethylphosphetane[40] in 50 ml of dry ether 1.7 g (0.01 mol) of benzyl bromide was added. The mixture was allowed to stand 2 days under a nitrogen atmosphere. The resultant white solid, 2 g (54%) was recrystallized from acetonitrile-ethyl acetate to give needles, mp 204-205 °C dec. The NMR ($CDCl_3$) spectrum showed peaks at δ 8-7.8 (10, H, m), 5.12 (2 H, J = 14 Hz), 3.6-2.0 (2 H, m), 1.99 (6 H, d, J_{PCCH} = 23 Hz), and 1.67 (6 H, d, J_{PCCH} = 21 Hz).

Anal. Calcd for $C_{20}H_{26}BrP$: C, 63.67; H, 6.95; Br, 21.18. Found: C, 63.72; H, 7.01; Br, 21.09.

1-Phenyl-2,2-dimethylphosphetane 1-Oxide (29). A 3-l. flask was equipped with a nitrogen inlet, thermometer, mechanical stirrer, and jacketed addition funnel. The flask was charged with 1.5 l. of methylene dichloride; after cooling 136 g (1.02 mol) of anhydrous $AlCl_3$ and 179 g (1.01 mol) of phenylphosphonous dichloride were added. A cooled solution of 3-methyl-1-butene dissolved in 1 l. of methylene chloride was placed in the water-cooled addition funnel and added dropwise to the above solution (cooled in an ice bath) over 4 h. The mixture was stirred overnight and then poured onto ice. The solvent layer was separated, dried (Na_2SO_4), and evaporated. The residue was distilled to give 60 g of product, bp 125 °C (0.3 mm). The distillate solidified on standing. The hygroscopic product was purified by sublimation, 50 °C (0.1 mm); a pure sample was obtained by recrystallization from a large volume of pentane to give square platelets, mp 63-66 °C (sealed capillary). The NMR ($CDCl_3$) showed peaks at δ 8-7 (5 H, m) 3-1.5 (4, H, m), 1.51 (3 H, d, J_{PCCH} = 16Hz), and 0.92 (3 H, d, J_{PCCH} = 19.5 Hz).

Anal. Calcd for $C_{11}H_{15}OP$: C, 68.03; H, 7.78. Found: C, 67.93; H, 7.77.

1-Phenyl-2,2-dimethylphosphetane (8a) and the Corresponding Quaternary Salts 34 and 22. The oxide (29) was reduced in the usual manner[27] with $Cl_3SiH-(C_2H_5)_3N$ or Cl_3SiH alone in benzene solution. Although the phosphetane was isolated by distillation, bp ≈45 °C (0.3 mm), extensive thermal decomposition occurs. The neat phosphine becomes viscous on standing at room temperature. Its lifetime in benzene solution is 2-3 days at 25 °C. The NMR (C_6D_6) spectrum showed peaks at δ 7.5-7 (5 H, m), 2.5-1.5 (4, H, m), 1.32 (3 H, d, J_{PCCH} = 18.7 Hz), and 0.71 (3 H, d, J_{PCCH} = 6.8 Hz). For convenience the undistilled phosphetane was separately treated with methyl bromide and benzyl bromide in ether to give the salts **34** and **22** in 73 and 57% yield, respectively.

After several recrystallizations from acetonitrile-ethyl acetate, the melting point of the former was 161-162.5 °C and the latter 219-220 °C dec.

Anal. Calcd for $C_{12}H_{18}BrP$: C, 52.76; H, 6.64; Br, 29.25. Found: C, 52.78; H, 6.88; Br, 29.15. Calcd for $C_{18}H_{22}BrP$: C, 61.90; H, 6.35; Br, 22.88. Found: C, 62.19; H, 5.95; Br, 22.75.

Acknowledgment. One of us (S.E.C.) wishes to acknowledge partial support from the Marquette University Committee on Research and the Alfred P. Sloan Foundation for a Research Fellowship (1971-1975). We thank Mr. Lloyd Wilkinson and Mr. Paul Kremer for the preparation of several samples and are most grateful for the generous synthesis and gift of the phosphirane (**9**) from Dr. Dorothy Denney and Miss Terry Cunningham (Rutgers University). We also appreciate the generous help given by Professor H. J. Jakobsen (University of Aarhus) in performing important decoupling simulations relevant to our phosphines.

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(40) We are grateful to Professor D. B. Denney, Rutgers University, for supplying a preparative procedure for the oxide precursor. The preparation of the oxide and phosphetane [see, *Chem. Commun.*, 272, 395 (1972)] will be submitted for publication by those workers.