Carbon-13 Nuclear Magnetic Resonance of Organophosphorus Compounds. III. Phosphorus Heterocycles

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^{13}C Chemical shifts and ^{13}C–^{31}P nuclear spin coupling constants have been determined for different patterns of ring methyl substitution in 32 phosphetane oxides, 3 phosphetane sulfides, 12 phosphetanium salts, a phospholane oxide, 3 phospholene oxides, and a phosphorianane oxide, as well as for trimethyl- and triethylphosphine oxides. The data are consistent with fixed, puckered conformations for four of the phosphetane ring substitution patterns and rapidly interconverting puckered forms for the single symmetrically substituted phosphetane. Variations of shifts and couplings as a function of ring substitution for several exocyclic phosphorus substituent pairs generally follow one another, but there are sizable deviations from this overall additivity. Seventeen cis–trans pairs of isomers are present in the above compounds. Strong stereospecificities in shift and coupling are apparent in the phosphetanes, especially for the one-bond coupling to carbon in phosphorus substituents and the three-bond coupling to the β-bound methyl carbon. These stereospecificities are useful in determining cis–trans isomer ratios in mixtures.

In spite of its low natural abundance (1%) and its much lower sensitivity, ^{13}C nmr holds promise of great value in the study of organophosphorus chemistry. ^{31}P spectra for most organophosphorus compounds provide only one chemical shift parameter, while the couplings to ^{13}C, and often those to ^{1}H, can be more easily and accurately determined from their respective spectra. A significant amount of experimental and theoretical work has been done in recent years, mainly concerning ^{13}C–^{31}P nuclear spin couplings.[2-18] Now with the development of more powerful techniques,[18]C nmr spectra can be obtained in natural abundance for molecules very much larger than those previously studied. In part I[2] a systematic inquiry was made into the effects of substitution on a carbon bound to phosphorus in a series of organophosphonates. Now we extend the inquiry into a class of compounds where different substitution patterns are allowed for carbon and phosphorus. Interesting compounds for this purpose are phosphorus heterocycles. The simplest available rigid systems are the four-membered ring compounds, the phosphetanes.

One of the earliest studies in phosphetane chemistry was that of Jungermann.[19] Useful synthetic extensions were developed by Cremer,[20] and in the last few years a great number of investigations have been centered on the stereochemistry of nucleophilic displacement reactions and the general chemistry of phosphetanes.[21] In addition, X-ray investigations have established the structures and stereochemistry of several phosphetane compounds.[22] These, coupled with the prodigious amount of work on stereoselective reactions,[21a,e-i,k-n,p-x] enable stereochemical assignments of most of the compounds treated in this work.

Results

The carbon chemical shifts (Tables I–VIII) are most easily assigned in the symmetrical 2,2,3,4,4-pentamethylphosphetanes in Table I. The large ^{13}C–^{31}P coupling and high shift (low shielding), as well as the twofold intensity, allow C-2 and C-4 to be identified. The high shift of C-3 is characteristic of a tertiary carbon. C-7 gives a shift normal for a free methyl bound to a carbon atom and has unit intensity. The remaining two doublets belong to the methyls bound to C-2

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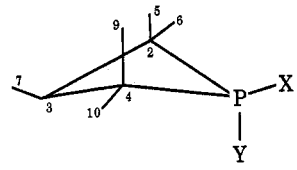
TABLE I

ALIPHATIC ^{13}C CHEMICAL SHIFTS AND ^{13}C–^{31}P NUCLEAR SPIN COUPLING CONSTANTS FOR 1-X, 1-Y 2,2,3,4,4-PENTAMETHYLPHOSPHETANE OXIDES, SULFIDES, AND SALTS[a]

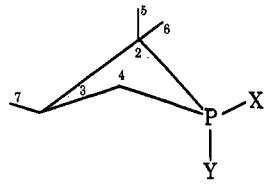


Compd	X	Y	C-2,4	C-3	C-5,9	C-6,10	C-7	X	Y
			Chemical shifts						
1	O	OH	48.77	42.90	18.18	24.03	6.96		
2	O	OCH_3	44.43	37.10	18.11	23.83	6.86		
3	OCH_3	O	44.23	37.65	18.28	24.49	8.15		
4	O	CH_3	45.41	42.61	17.28	24.71	7.31		9.79
5	CH_3	O	44.05	46.89	19.83	24.66	9.71	11.47	
6	O	Ph	46.68	44.88	18.90	24.00	7.33		
6a	O	*p*-C_6H_4F	47.23	45.33	19.01	24.35	7.50		
7	Ph	O	46.45	48.03	20.41	24.81	8.69		
8	O	Cl	57.35	42.79	18.27	26.09	7.37		
9	Cl	O	57.05	46.20	20.74	24.50	9.38		
10	O	Bz	46.96	43.80	18.06	25.40	7.18		31.90
11	Bz	O	46.96	47.39	19.71	24.20	8.64	33.05	
12	O	*t*-Bu	47.50	45.71	20.49	25.61	7.20		35.83 26.58
13	*t*-Bu	O	47.50	47.68	20.37	24.51	7.42	38.64 26.49	
14	S	Ph	46.62	51.06	22.52	25.48	9.55		
15	Ph	S	45.79	48.73	21.70	26.09	8.23		
16	CH_3	CH_3	38.07	51.42	18.96	24.43	8.75	4.94	4.15
17	CH_3	Ph	41.41	53.49	20.57	25.43	9.69	5.93	
17a	CH_3	*p*-C_6H_4F	41.98	53.44	21.04	26.03	9.67	8.01	
18	Ph	CH_3	42.11	50.43	20.17	24.94	8.08		6.90
19	CH_3	Bz	39.82	51.94	19.90	25.54	9.37	3.49	25.99
20	Bz	CH_3	40.40	50.93	19.50	24.66	8.69	26.65	2.15
21	Bz	Bz	42.28	50.82	19.76	25.02	8.06	26.20	25.05
			Coupling constants						
1	O	OH	76.6	11.7	3.2	5.3	21.9		
2	O	OCH_3	74.2	10.9	2.9	6.6	23.8		
3	OCH_3	O	73.5	10.4	5.5	3.7	18.5		
4	O	CH_3	59.4	6.3	4.6	3.6	23.0		40.9
5	CH_3	O	59.4	10.0	2.2	4.4	12.6	36.9	
6	O	Ph	58.7	6.2	4.6	3.5	23.1		
6a	O	*p*-C_6H_4F	58.3	6.2	4.7	3.9	23.4		
7	Ph	O	58.4	11.2	1.3	4.6	16.9		
8	O	Cl	56.8	1.6	3.8	6.8	30.1		
9	Cl	O	55.4	1.8	5.4	5.3	20.5		
10	O	Bz	56.9	5.7	4.6	3.8	22.9		34.8
11	Bz	O	56.9	11.8	2.0	5.6	15.5	30.7	
12	O	*t*-Bu	51.0	5.2	4.8	3.2	21.2		35.9 1.0
13	*t*-Bu	O	51.0	12.5	1.1	4.4	16.6	31.2 0.7	
14	S	Ph	47.9	5.4	1.7	4.2	20.9		
15	Ph	S	47.3	6.9	2.5	2.2	21.5		
16	CH_3	CH_3	45.2	11.2	2.5	3.7	18.1	29.1	34.7
17	CH_3	Ph	45.2	10.2	2.1	3.7	17.6	31.1	
17a	CH_3	*p*-C_6H_4F	45.8	9.5	1.9	4.0	18.9	30.6	
18	Ph	CH_3	45.3	10.5	3.1	3.4	22.2		35.9
19	CH_3	Bz	44.0	10.2	3.1	3.1	16.8	28.2	21.9
20	Bz	CH_3	44.3	10.2	2.8	4.2	19.1	18.6	34.3
21	Bz	Bz	41.0	9.1	2.5	4.0	19.4	17.8	23.4

[a] Chemical shifts, in parts per million, were determined to ±0.01 ppm from 60% enriched $^{13}CH_3I$ present in the lock capillary. The shifts were subsequently placed on the tetramethylsilane-^{13}C scale by subtracting 20.97 ppm, a value found for the shift of TMS-^{13}C, from the same lock capillary, in a 2:2:1 **25**:$CHCl_3$:TMS solution. The TMS was at natural abundance in ^{13}C. A positive value for the chemical shift represents a higher frequency shift, or deshielding of the carbon atom. Bz = benzyl, CH_2Ph; Ph = phenyl; *t*-Bu = *tert*-butyl.

TABLE II

ALIPHATIC ^{13}C CHEMICAL SHIFTS AND ^{13}C–^{31}P NUCLEAR SPIN COUPLING CONSTANTS FOR 1-X, 1-Y 2,2,3-TRIMETHYLPHOSPHETANE OXIDES AND SALTS[a]

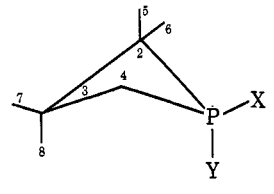


Compd	X	Y	C-2	C-4	C-3	C-5	C-6	C-7	PCH_3
			Chemical shifts						
22	O	OH	52.20	40.74	30.62	17.42	23.15	15.19	
23	O	OCH_3	52.93	39.71	30.27	16.65	22.05	14.12	
24	OCH_3	O	52.93	39.71	30.27	17.27	20.71	15.82	
25	O	Ph	49.96	37.42	30.97	16.89	23.67	14.75	
26	Ph	O	48.41	34.56	34.47	19.40	23.52	15.97	
27	CH_3	Ph	45.53	25.35	40.49	18.13	23.94	15.87	9.43
28	Ph	CH_3	44.91	24.86	38.72	17.75	23.31	15.92	6.29
			Coupling constants						
22	O	OH	81.8	67.7	18.1	4.2	4.9	23.4	
23	O	OCH_3	79.3	65.8	18.3	2.6	7.4	27.8	
24	OCH_3	O	79.3	65.8	18.3	6.1	2.	12.1	
25	O	Ph	63.3	52.5	11.9	4.4	3.2	28.3	
26	Ph	O	63.1	52.3	16.0	2.6	4.5	16.5	
27	CH_3	Ph	48.6	47.7	17.1	1	3.7	21.2	31.5
28	Ph	CH_3	48.5	46.1	15.9	1	3.9	23.7	37.3

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

TABLE III

ALIPHATIC ^{13}C CHEMICAL SHIFTS AND ^{13}C–^{31}P NUCLEAR SPIN COUPLING CONSTANTS FOR 1-X, 1-Y 2,2,3,3-TETRAMETHYLPHOSPHETANE OXIDES, SULFIDE, AND SALT[a]



Compd	X	Y	C-2	C-4	C-3	C-5	C-6	C-7[b]	C-8[b]	P-CH_3
			Chemical shifts							
29	OH	O	53.34	48.19	32.17	20.02	20.02	26.11	26.11	
30	OCH_3	O	54.47	47.86	31.97	19.48	20.45	26.73	26.24	
31	Ph	O	50.81	41.46	35.04	19.16	21.55	26.30	27.19	
32	Ph	CH_3	46.82	30.88	44.00	20.78	21.00	26.75	27.03	10.04
33	Ph	S	49.33	42.74	39.19	21.38	22.91	26.80	28.19	
			Coupling constants							
29	OH	O	81.8	67.7	14.6	4.8	4.8	15.3	15.3	
30	OCH_3	O	78.2	64.4	13.8	6.9	4.0	9.2	0.9	
31	Ph	O	62.8	52.0	11.9	4	2	11.3	13.6	
32	Ph	CH_3	47.2	46.0	14.0	3.0	4.4	14.2	8.0	34.2
33	Ph	S	49.7	44.8	10.5	1.9	3.1	9.4	13.9	

[a] See footnote *a*, Table I. [b] Tentative assignment.

and C-4. The shift difference between them is primarily due to different methyl–methyl steric interactions and ring puckering rather than the cis or trans orientation with respect to the phosphorus substituents. This is evident in **1**, where rapid proton exchange renders the substituents on phosphorus identical, or in **16**, where they are in fact identical. In view of the generally smaller shift experienced by sterically crowded (as opposed to uncrowded) carbon,[23] as well as the small shift experienced by axial methyl carbons,[24] the methyl carbons of smaller shift are assigned to the pseudoaxial C-5 and C-9. Our calculations[25] based on reported X-ray fractional coordinates of 1-chloro-2,2,3,4,4-pentamethylphosphetane oxide,[22c] 1-phenyl-2,2,3,4,4-pentamethylphosphetane oxide,[22d] and 1-phenyl-1,2,2,3,4,4-hexamethylphosphetanium bromide[22b] show that the neighbor heavy atom interatomic contact distances for C-5 and C-9 are significantly shorter than those for C-6 and C-10. With this basic assignment the remaining exocyclic carbon shifts are easily assigned to the basis of

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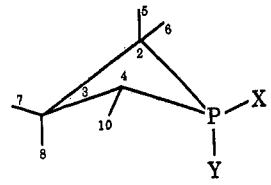
(24) D. K. Dalling and D. M. Grant, *ibid.*, **89**, 6612 (1967).

(25) Calculations of heavy atom interatomic distances were done using data from ref 22b–d using the molecular geometry program MGEOM, J. S. Wood, 1964. We thank Dr. Roger Eiss (OGC) for assistance in performing these calculations.

TABLE IV

ALIPHATIC ^{13}C CHEMICAL SHIFTS AND ^{13}C–^{31}P NUCLEAR SPIN COUPLING CONSTANTS FOR 1-X, 1-Y 2,2,3,3,4-PENTAMETHYLPHOSPHETANE OXIDES AND SALT[a]

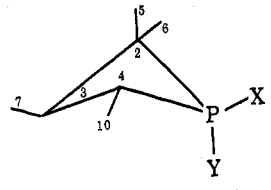


Compd	X	Y	C-2	C-4	C-3	C-5	C-6	C-7[b]	C-8[b]	C-10	PCH_3
			Chemical shifts								
34	OH	O	52.57	51.02	35.57	21.33	18.36	24.57	20.61	7.38	
35	O	OCH_3	53.00	50.13	35.64	20.13	18.28	23.73	20.58	7.34	
36	OCH_3	O	53.14	51.72	33.97	20.13	17.63	23.86	20.58	6.81	
37	Ph	O	49.20	43.10	41.74	22.92	17.66	24.38	22.11	6.56	
38	Ph	CH_3	46.24	36.33	46.95	22.17	19.67	26.54	22.17	8.41	5.98
39	O	Cl	60.54	58.75	40.69	23.08	17.99	24.40	20.49	7.14	
40	Cl	O	60.04	57.74	35.54	20.72	19.96	25.24	20.49	8.70	
			Coupling constants								
34	OH	O	78.9	72.8	10.6	3.1	6.2	28.9	1.8	7.5	
35	O	OCH_3	74.7	69.7	10.1	4.8	5.3	26.5	5.2	6.9	
36	OCH_3	O	74.2	67.8	10.1	2.6	6.8	30.3	1.8	7.6	
37	Ph	O	61.2	58.4	15.1	0.8	4.4	24.9	1.6	5.9	
38	Ph	CH_3	45.8	44.7	9.7	2.8	3.4	22.1	2.8	6.4	33.3
39	O	Cl	58.6	53.5	6.2	4.1	6.6	33.1	1.9	9.0	
40	Cl	O	57.8	51.7	2.9	3.8	6.8	35.1	1.9	9.5	

[a] See footnote *a*, Table I. [b] Tentative assignment.

TABLE V

ALIPHATIC ^{13}C CHEMICAL SHIFTS AND ^{13}C–^{31}P NUCLEAR SPIN COUPLING CONSTANTS FOR 1-X, 1-Y 2,2,3,4-TETRAMETHYLPHOSPHETANE OXIDES AND SALT[a,b]



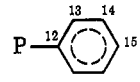
Compd	X	Y	C-2	C-4	C-3	C-5	C-6	C-7	C-10	PCH_3
			Chemical shifts							
41	OH	O	49.52	47.74	39.88	17.51	22.32	12.50	11.52	
42	OCH_3	O	50.18	48.17	38.84	16.70	21.72	11.63	11.06	
43	Ph	O	48.68	38.38	36.02	18.14	24.71	9.32	8.38	
44	Ph	CH_3	43.77	29.48	43.91	20.48	25.99	11.97	10.75	8.22
			Coupling constants							
41	OH	O	80.1	73.4	14.0	2.8	6.5	31.9	8.0	
42	OCH_3	O	76.1	70.4	13.8	2	6.7	31.8	8.1	
43	Ph	O	60.4	56.2	12.5	4.8	2.8	17.5	6.2	
44	Ph	CH_3	46.7	46.5	13.7	2.8	2.5	11.9	5.5	30.5

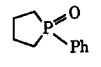
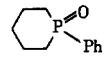
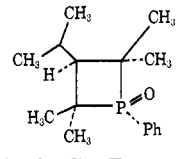
[a] See footnote *a*, Table I. [b] Pseudoequatorial C-10 trans to pseudoequatorial X assumed as conformation.

intensity, ^{13}C–^{31}P coupling, and nature of the exocyclic phosphorus substituents. The phosphorus-bound methyls in **16** were assigned using material in which one of the exocyclic CH_3 groups had been stereospecifically replaced by CD_3 (see Materials section). The resonances in Table II were assigned in much the same manner except that C-2 and C-4 possess different shifts. The general effect of replacing hydrogen on an aliphatic carbon with methyls is to increase the shift of the carbon atom.[24] Hence, the more shifted carbon is assigned C-2. The compounds listed in Table III reflect the placement of an equal number of methyls above and below the four-membered ring. Proton exchange in **29** makes C-5 and C-6 identical as well as C-7 and C-8. The small chemical shift difference in Table III between C-5 and C-6, also C-7 and C-8, reflects, in part, the difference in cis or trans orientation relative to the phosphorus substituents. This is largest when the atoms bound to phosphorus are different, as in **31**. Although there is uncertainty in assignment of the methyl shifts, the coupling constants provide some help, at least for C-5 and C-6 when compared with similar couplings in Tables I, II, and IV. The shifts and couplings for C-7 and C-8 in **30**, **31**, **32**, and **33** are so similar that the assignment may be the reverse of that shown. Assignments for C-2, C-4, and C-3 follow from the reasoning for compounds in Table II. All of the compounds in Table IV have a doublet with a moderately large coupling to phosphorus in the region of 24 ppm, an area characteristic of the pseudoequatorial C-6 or C-10 in

TABLE VI

AROMATIC ^{13}C CHEMICAL SHIFTS AND ^{13}C–^{31}P NUCLEAR SPIN COUPLING CONSTANTS FOR PHENYL-SUBSTITUTED OXIDES SULFIDES, AND SALTS[a,b]



Compd	X	Y	C-12 δ	C-12 $^1J_{CP}$	C-13[c] δ	C-13[c] $^2J_{CP}$	C-14[c] δ	C-14[c] $^3J_{CP}$	C-15 δ	C-15 $^4J_{CP}$
6	O	Ph	129.94	59.5	133.32	9.0	128.85	9.7	132.33	2.9
6a	O	*p*-C_6H_4F	124.58	62.6	135.06	9.4	115.50	11.0	165.15	3.2
7	Ph	O	131.88	54.5	132.65	8.8	129.12	10.1	132.37	2.7
14	S	Ph	129.45	46.4	134.75	9.4	128.89	11.1	132.34	2.2
15	Ph	S	132.23	58.3	131.38	8.8	128.86	10.7	135.13	0.0
17	CH_3	Ph	119.15	54.9	135.01	8.5	131.28	11.7	135.79	0.0
17a	CH_3	*p*-C_6H_4F	113.62	59.6	137.03	9.7	117.43	12.8	166.09	3.6
18	Ph	CH_3	120.68	48.9	133.81	8.5	131.55	11.3	135.65	0.0
25	O	Ph	[1]31.40	72.3	131.02	9.7	128.99	10.6	132.11	2.9
26	Ph	O	[1]33.06	57.6	131.02	9.7	128.85	11.9	132.11	2.9
27	CH_3	Ph	[1]19.36	64.7	133.90	10.7	131.37	11.7	135.97	5.0
28	Ph	CH_3	[1]20.52	58.4	133.90	10.7	131.26	11.5	135.85	4.7
31	Ph	O	133.78	67.8	131.56	9.7	129.18	10.8	132.34	2.9
32	Ph	CH_3	121.79	62.2	134.24	10.2	131.27	12.0	135.62	2.5
33	Ph	S	134.40	54.6	131.11	10.3	128.95	11.3	131.62	2.9
37	Ph	O	133.10	63.1	131.51	9.3	129.30	10.9	132.47	3.1
38	Ph	CH_3	120.85	58.4	132.92	10.2	131.22	11.7	135.63	7.4
43	Ph	O	134.49	64.6	130.80	8.0	128.67	10.5	131.82	4.6
44	Ph	CH_3	118.90	59.9	133.70	9.4	130.67	11.8	135.38	3.5
45			136.66	86.6	131.01	9.4	129.43	11.1	132.13	2.5
46			135.31	95.4	130.87	10.0	129.15	11.6	132.01	2.3
49			134.29	92.6	130.89	9.2	129.58	11.2	132.60	2.6
52			128.69	62.4	133.16	8.7	128.42	10.2	132.04	2.8

[a] See footnote *a*, Table I. [b] ^{13}C–^{19}F couplings—for **6a**: C-15, 253.2 H; C-14, 21.0 Hz; C-13, 9.4 Hz; and C-12, 2.6 Hz. For **17a**: C-15, 258.1 Hz; C-14, 21.8 Hz; C-13, 9.7 Hz; and C-12, 3.4 Hz. [c] Assignments for C-13 and C-14 made by noting **6** → **6a** and **17** → **17a** shifts and comparing with the analogous benzene → fluorobenzene changes as reported by H. Spieseke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

Table I. C-7 in Table IV is similar to these in that it is bound to a tertiary carbon. X-Ray studies[22f] of **37** show a stable puckered ring with C-10 in the lower energy pseudoequatorial position. Since C-8 is present, C-6 should have a smaller shift than that in Tables I and II due to the additional methyl–methyl interaction. Also, C-5 should have a greater shift than C-5 in Tables I and II, since the C-5–C-9 steric interaction is missing. The couplings for C-5 and C-6 in **34** are similar to those in **1** if the order of shift is reversed from that in Tables I and II. It may be that the above two factors combine sufficiently to reverse the shift order of C-5 and C-6 in **34** with respect to **1**. The magnitude of the C-6 coupling in **34** is close to that of C-10, as indicated above. Upon considering **37** the same reasoning holds. C-6 has a coupling of 4.6 Hz in **7** and 4.4 Hz in **37**. Reversing the chemical shift order of C-5 and C-6 in going from **2** to **36** predicts the carbon having the smaller shift to have a larger coupling, in agreement with the experimental results. The insensitivity of C-8 coupling in all cases in Table IV (except for **35**) as well as the variability of C-5 coupling with substituent allowed a tentative assignment of these carbons to be made.

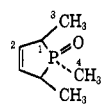
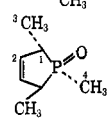
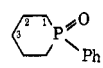
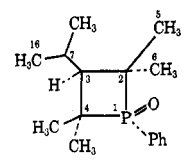
Table VII lists the aliphatic carbon shifts and ^{13}C–^{31}P couplings for compounds of interest in analyzing the data for the four-membered ring compounds.

Discussion

The overall chemical shifts in the pentamethylphosphetane systems in Table I are understandable in terms of an increased shift to be expected for C-2 and C-4 for α- and β- methyl substitution and a major shift of C-3 arising from the addition of one α-methyl and four β-methyls. The C-2 and C-4 shifts seem to be approximately related to the electronegativity of the exocyclic phosphorus substituents. The most shifted C-2 and C-4 carbons are in **1**, where both exocyclic phosphorus-bound atoms are oxygen, while the least shifted are in **16**, where both groups are methyls. The range of C-3 shifts is greater than that of any carbon in Table I, even

TABLE VII

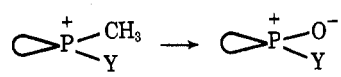
ALIPHATIC AND OLEFINIC ^{13}C CHEMICAL SHIFTS AND ^{13}C–^{31}P NUCLEAR SPIN COUPLING CONSTANTS FOR SEVERAL ACYCLIC AND CYCLIC OXIDES[a]

Compd			C-1	C-2	C-3	C-4
45		δ	30.30	25.72		
		J	66.8	7.9		
46		δ	25.85	30.35	153.14	126.92
		J	71.0	10.4	24.0	92.0
47		δ	36.89	133.83	14.86	16.02
		J	65.4	13.4	4.0	59.7
48		δ	39.02	133.51	14.05	7.58
		J	64.9	14.3	3.7	58.8
49		δ	28.73	22.54	26.98	
		J	65.2	6.0	6.8	
50	$(CH_3)_3P{=}O$	δ	18.58			
		J	68.3			
51	$(CH_3CH_2)_3P{=}O$	δ	20.72	6.15		
		J	65.6	4.9		
52		δ		47.18	58.98	
		J		57.8	7.1	
			C-5	C-6	C-7	C-16
		δ	18.70	26.68	27.88	23.06
		J	5.4	4.3	26.4	0.0

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

TABLE VIII

CHANGES IN ^{13}C CHEMICAL SHIFT



Transition	Ring	Y	Isomer	ΔC-2	ΔC-4	ΔC-Y	ΔC-3	ΔC-5	ΔC-6	ΔC-7
4 → 16		CH_3	trans	7.3	7.3	5.6	−8.8	−1.7	0.3	−1.4
5 → 16		CH_3	cis	6.0	6.0	6.5	−4.5	0.9	0.2	1.0
6 → 17		Ph	trans	5.3	5.3	10.8	−8.6	−1.7	−1.4	−2.4
7 → 18		Ph	cis	4.3	4.3	10.2	−2.4	0.1	−1.1	0.6
10 → 19		Bz	trans	7.1	7.1	6.2	−7.7	−1.4	0.5	−1.8
11 → 20		Bz	cis	6.6	6.6	6.4	−3.5	0.2	−0.5	−0.0
25 → 27		Ph	trans	4.4	12.1	12.0	−9.5	−1.2	−0.3	−1.1
26 → 28		Ph	cis	3.5	9.7	12.5	−4.2	−1.6	0.2	0.0
31 → 32		Ph		4.0	8.7	12.0	−8.9	−1.7	0.6	−0.6
37 → 38		Ph	cis	3.0	6.8	12.2	−5.2	0.8	−2.0	−1.2
43 → 44		Ph	cis	4.9	8.9	15.6	−7.9	−2.3	−1.3	−2.6

though it is three bonds removed from the substituent. Its trend with electronegativity is opposite to that of the C-2 and C-4 carbons. On the whole, C-3 shows more sensitivity to exocyclic phosphorus substituent than C-2 or C-4. It is difficult to rationalize these C-3 shifts on the basis of either attenuated inductive effect (wrong direction) or direct steric effects (too far away).

The C-2, C-4, and C-3 methyls in Table I are also three and four bonds away from the phosphorus substituents but are much less affected by changes in these substituents than C-3. C-7 is less shifted than an isolated equatorial methyl.[24] The decreased shift is adequately predicted using shift parameters for methyl-methyl interactions in methylcyclohexanes.[24] Taking the shift of an isolated equatorial methyl carbon as 24 ppm and adding the effect of two axial C-2 and C-4 methyls (−12 ppm) and two equatorial C-2 and C-4 methyls (−4 ppm), we calculate a shift of 8 ppm for C-7, agreeing well with the observed C-7 shifts in Table I.

The chemical shifts in Table II reflect the less crowded situation when the C-9 and C-10 methyls are replaced by hydrogens. C-4 is affected more dramatically and, interestingly, to a different degree in the

oxides and salts. For example, C-4 decreased in shift by 9 ppm in going from **6** to **25** but 16 ppm in going from **17** to **27**. The C-3 shifts are affected similarly, however, in the above cases, showing a decreased shift of ~13–14 ppm upon removal of the two β-methyl groups. C-7 is also increased in shift by 6 to 8 ppm in both oxide and salt as the steric crowding of the two β-methyl groups is removed. If we were considering the analogously substituted cyclobutane we would expect concomitant shift increase of the pseudoequatorial methyl on C-1. However, in the structurally similar **27**, the phosphorus-bound methyl carbon is increased in shift by only half of the 6-ppm change experienced by C-7. This lower sensitivity in shift probably results from the larger P–C bonds, which cut down on the methyl–methyl steric perturbations. Note that the pseudoaxial phosphorus exocyclic methyl in **28** is only shifted −0.6 ppm in going from **18** to **28**.

In going to Table III we introduce the effect of another methyl group at C-3. This has primary effect on C-7, which is strongly shifted by ~11 ppm. The absence of the unique ring carbon methyl group makes C-5 and C-6 much more alike in terms of steric interactions and thus shifts.

In Tables I and IV we see that chlorine as an exocyclic phosphorus substituent produces a severe shift of C-2 and C-4. The effect is not propagated too far, since all the other carbons have shifts similar to those in compounds having carbon or oxygen as exocyclic phosphorus substituents.

An accurate set of substituent parameters should be able to describe the variation of shift with ring structure for different sets of exocyclic phosphorus substituents. There does seem to be some consistency in overall pattern to within a few parts per million. However, some complete reversals of significant size are apparent and no accurate set of substituent parameters can be extracted from the data.

Aromatic carbon chemical shifts are given in Table VI. C-12 is not very sensitive to phosphetane ring substitution in at least this one type of oxide.

In comparing pairs of oxides and salts in which the only difference is the replacement of oxide by methyl, we may assess the uniformity of shift differences and note any dependence on phosphetane ring structure. C-3 shows highly sensitive behavior in the transition oxide → salt. This is documented in Table VIII, where differences in shifts are noted for compounds in which the oxide oxygen is replaced by methyl: in the *trans*-2,2,3,4,4-pentamethylphosphetane case ΔC-2 is smaller in magnitude than ΔC-3. The reverse is true for the corresponding cis isomer. C-4 is more severely affected than C-2 for cases in which C-4 has less than two attached methyl groups. Note that putting two methyl groups on C-3 does not lower ΔC-3 to the same level as ΔC-2. C-5 and C-6 are barely affected by the transition, even though they are, as is C-3, three bonds away from the substituents. Exocyclic phosphorus substituents are shifted in the same direction as C-2 and C-4. Methyl and benzyl give Δ values close to those for C-2 and C-4, but Δ values for phenyl (C-12) are 2–4 times those for C-2 or C-4.

^{13}C–^{31}P Coupling Constants.—The phosphetane oxides and salts provide significant new data concerning the sensitivity of ^{13}C–^{31}P couplings to substituent and structural effects. Several compounds in Table VII can serve as unstrained acyclic and cyclic reference compounds. The one-bond ^{13}C–^{31}P coupling in $(CH_3)_3$-P=O is decreased slightly in going to **51**, where methyl is replaced by ethyl. Conversion to the six-membered ring compound **49** does not affect the coupling significantly. There is a slight increase in coupling in contracting the ring to **45**, but the smaller C-4 coupling to phosphorus in **25** is evidence that contraction to a four-membered ring structure results in a sizable decrease in the corresponding coupling.

The phosphetane backbone can contribute a number of coupling constants for assessing the effect of exocyclic phosphorus substituent variation on ^{13}C–^{31}P couplings. There appears to be a loose relationship between substituent electronegativity and C-2 (C-4) couplings in Table I. The sensitivity of the C-4 coupling to methyl substitution on C-4 is fairly small in the salts (*e.g.*, a change of only 1–2 Hz for **17** or **18** → **27** or **28**) in contrast to some of the oxides, where changes up to 10 Hz occur. Interestingly, the number of hydrogens on the phosphorus-bound exocyclic carbon influences the C-2 (C-4) couplings to a higher degree than those of the exocyclic carbons themselves, *i.e.*, 59.4 (**4**), 56.9 (**10**), and 51.0 Hz (**12**). Note that the C-2 and C-4 couplings in the oxides are much more sensitive to change in phosphorus substituent than those in the salts. The small values for C-5, C-6, C-9, and C-10 couplings in Table I are not a consequence of unusual or strained geometry, since the analogous coupling to the *tert*-butyl methyl carbons in **12** is also small (1.0 Hz). The couplings to C-3 in Table I are typically larger and more variable, even though it is again a two-bond coupling. One surprising aspect is the magnitude of the three-bond couplings to C-7 in Table I. In fact, in **20** this coupling is larger than the one-bond coupling to the benzyl carbon. The magnitude of this coupling is not especially sensitive to the exocyclic phosphorus substituent for a series of cis or series of trans isomers (except for chloro), although it is generally lower when the oxide is converted into the corresponding salt. Chlorine bound to phosphorus has some interesting effects. Even though chlorine is more electronegative than carbon, the C-2 and C-4 couplings are greater for phenyl or methyl as phosphorus substituents as opposed to chloro. The major effect is felt in the C-3 coupling, which is reduced, and the C-7 coupling, which is enhanced.

The coupling for C-7 seems most sensitive to ring structure. The drop in coupling in going to the 2,2,-3,3-tetramethyl is not a result of placing another methyl on C-3, since similar values are found for rings in Tables II and IV. Rather, this must result from one or the other of two dynamical possibilities. Either the ring geometry is changed or the puckered form is undergoing rapid interconversion. A static puckered form is difficult to accept because of the similarity in the C-5/C-6 shifts and also the C-7/C-8 shifts. The results in Tables I, II, IV, and V are very consistent in showing a large three-bond coupling for C-7. Since these rings are puckered[22] to relieve steric interactions, the C-7 coupling is an indicator of coupling to be expected for a pseudoequatorial methyl carbon bound to C-3. Hence, static puckered rings corresponding to compounds in Table III should show C-7 and C-8 cou-

plings similar to compounds in Table IV. The choice then is between possibly a flattened ring and interconverting puckered forms. The differences in C-7 and C-8 couplings should then be composed of two factors: (1) the portion of time spent in each conformer, and (2) the cis–trans nature with respect to the substituents. It is conceivable that both structural possibilities are in effect with some ring flattening present, affecting the expected magnitude of the C-7 and C-8 couplings. It is very difficult to draw on other four-membered ring systems for analogies, since both puckered[26a-i] and flat[26g-j] examples have been found for rings symmetrically substituted on the carbon skeleton. However, since *all* the carbon-bound substituents on the ring are methyls, a flat molecule would be expected to be a fairly high energy conformer, since all the methyls would be eclipsed with each other. Thus, on the basis of couplings and conformer energetics, rapidly interconverting conformers are favored. It is difficult to estimate the fraction of each conformer, since the larger P–C bonds in the ring remove, to some extent, the degree of steric interaction associated with the exocyclic phosphorus substituents.

The C-12 coupling is sensitive to phosphetane ring substitution. The sensitivity of aromatic carbon coupling to phosphetane ring substitution virtually disappears in going to the ortho, meta, and para carbons in the oxides. A similar situation prevails in the salts, except that the para coupling is much more variable, ranging over 7.4 Hz. Replacing oxide by sulfide results in decreases in C-12 and C-2/C-4 couplings. This effect is also apparent in going from trimethylphosphine oxide (68.3 Hz) to trimethylphosphine sulfide (56.1 Hz[6]). The effect is not promulgated over more than one bond, since the remaining couplings are unaffected. In fact, since the shifts of the remaining carbons are also unaffected, the primary perturbation in going from oxide to sulfide seems to be felt only at the phosphorus.

^{13}C Shifts and ^{13}C–^{31}P Couplings in Cis–Trans Isomers.—In those compounds with unsymmetrical methyl substitution, cis and trans isomers are possible. X-ray studies[22] of several of the compounds in Table I, on both cis and trans isomers, have shown that C-7 is in a pseudoequatorial position and that the ring backbone is essentially independent of the stereochemistry of particular compounds. A trans oxide will be defined as having the oxide oxygen in a cis configuration with respect to C-7. Therefore, **6** is a trans oxide and **7** a cis oxide. Likewise, **17** is a trans salt (1-phenyl and 3-methyl trans) and **18** is a cis salt (1-phenyl and 3-methyl cis). It is also convenient to assign **20** as a cis salt (1-benzyl and 3-methyl are cis) and **19** as a trans salt. The availability of cis and trans isomers allows examination of changes in shifts and couplings in the cases where only the exocyclic phosphorus substituents are modified, in this case merely switched. This switch can possibly have steric implication and reflect more subtle influences on shifts and couplings. There does not appear to be any isomeric dependence for the C-2 and C-4 carbon shifts or couplings other than a slight shift increase in the trans oxides and in salts **17** (*vs.* **18**) and **19** (*vs.* **20**). C-3 is uniformly more shifted in the cis oxide and, in the cases where the phosphorus substituents are carbon and oxide, the C-3 coupling is typically about 1.5–2.5 times greater in the cis isomer than in the trans. Essentially no stereospecificity is observed for the C-3 coupling in the salts except for the ΔC-3/ΔC-2 ratio in Table VIII. The only instances in which the C-5, C-6, C-9, and C-10 carbons show significant stereospecific shift behavior are in the oxides **4** and **5**. We have previously reported the stereospecific nature of the C-7 and one-bond exocyclic carbon couplings in some of the compounds in Tables I and II.[3] The difference between one-bond couplings of the same phosphorus-bound exocyclic carbon in cis and trans pairs is substantial, uniform in direction, and fairly unrelated to the other exocyclic phosphorus substituent in both aromatic and aliphatic cases. This last fact indicates that the size of the exocyclic group bound to phosphorus is probably not too important in causing this difference in coupling. The three-bond C-7 coupling is unusually stereospecific (up to 15.7 Hz for **23** and **24**) in that the relative orientation of the coupled atoms *remains fixed* while groups α to one of the coupled atoms interchange positions (this is also the situation for the C-3 couplings discussed above). Normally, stereospecific ^{31}P–^{1}H long-range couplings result from sensitivity of the coupling to relative orientation of the coupled atoms.[27] The degree of difference of exocyclic phosphorus substituents is directly related to the magnitude of the stereospecificity. It does seem unlikely that through-space steric or electronic effects are directly responsible, since C-7 and the phosphorus exocyclic group cis to it are well separated (4.8 Å in **26**).[25] C-7 is uniformly increased in shift in the cis oxides with respect to the trans oxides and decreased in shift in the cis salt (*e.g.*, **18**) with respect to trans salt (*e.g.*, **17**). The phosphorus-bound methyl carbons exhibit orientation-dependent chemical shift, as seen in **4** *vs.* **18**, **19**, *vs.* **20**, and **27** *vs.* **28**. In all cases except **17** *vs.* **18** the trans methyl is of smaller shift than the cis methyl in the same isomer pair. The couplings are all consistently stereospecific, however. Phenyl, benzyl, and *tert*-butyl behave similarly in stereospecificity. Stereospecific C-12 shifts are shown in **6** *vs.* **7**, **17** *vs.* **18**, **25** *vs.* **26**, and **27** *vs.* **28**, where C-12 in trans phenyl has a

(26) (a) Cyclobutane, S. Meiboom and L. C. Snyder, *J. Amer. Chem. Soc.*, **89**, 1038 (1967); (b) octafluorocyclobutane, H. P. Lemaire and R. L. Livingston, *ibid.*, **74**, 5732 (1952); (c) *cis*- and *trans*-1,2-dibromo-1,2-dicarbomethoxycyclobutane, I. L. Karle, J. Karle, and K. Bitts, *ibid.*, **88**, 2918 (1966); (d) *cis*-1,3-cyclobutanedicarboxylic acid, E. Adman and T. N. Margulis, *Chem. Commun.*, 641 (1967); *J. Amer. Chem. Soc.*, **90**, 4517 (1968); (e) *N*-methyl-*N*-*tert*-butyl-3-hydroxyazetidinium methanesulfonate, E. L. McGandy, H. M. Berman, J. W. Burgner, II, and R. L. Van Etten, *ibid.*, **91**, 6173 (1969); (f) L-azetidine-2-carboxylic acid, H. M. Berman, E. L. McGandy, J. W. Burgner, II, and R. L. Van Etten, *ibid.*, **91**, 6177 (1969); (g) octahydroxycyclobutane, C. M. Bock, *ibid.*, **90**, 2748 (1968); (g) tetraphenylcyclobutane, J. D. Dunitz, *Acta Crystallogr.*, **2**, 1 (1949); (i) *trans*-1,3-cyclobutanedicarboxylic acid, T. N. Margulis and M. S. Fischer, *J. Amer. Chem. Soc.*, **89**, 223 (1967); (j) 1,1-debenzyl-3,3-dimethylazetidinium bromide, R. L. Snyder, E. L. McGandy, R. L. Van Etten, L. M. Trefonas, and R. L. Towns, *ibid.*, **91**, 6187 (1969).

(27) (a) L. D. Hall and R. B. Malcomb, *Chem. Ind.* (*London*), 92 (1968); (b) J. P. Albrand, D. Gagnaire, J. Martin, and J. B. Robert, *Chem. Commun.*, 1469 (1968); (c) J. P. Albrand, D. Gagnaire, J. Martin, and J. B. Robert, *Bull. Soc. Chim. Fr.*, 40 (1969); (d) J. Nelson, R. Spratt, and B. J. Walker, *Chem. Commun.*, 1509 (1970); (e) J. G. Verkade and R. W. King, *Inorg. Chem.*, **1**, 948 (1962); (f) E. J. Boros, K. J. Coskran, R. W. King, and J. G. Verkade, *J. Amer. Chem. Soc.*, **88**, 1140 (1966); (g) D. W. White and J. G. Verkade, *J. Magn. Resonance*, **3**, 111 (1970); (h) D. W. White, R. D. Bertrand, G. K. McEwen, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 7125 (1970); (i) W. G. Bertrand and J. H. Hargis, *ibid.*, **92**, 7136 (1970); (j) L. D. Quin and T. P. Barket, *J. Amer. Chem. Soc.*, **92**, 4303 (1970); see also J. P. Albrand, D. Gagnaire, M. Picard, and J. B. Robert, *Tetrahedron Lett.*, 4593 (1970).

smaller shift than C-12 in cis phenyl. The five-membered ring isomers **47** and **48** show minor differences in coupling but significant differences in α carbon and exocyclic phosphorus methyl shifts, reflecting the dissymmetry above and below the plane of the ring.

Assuming that C-10 is pseudoequatorial in all compounds in Table IV, as shown in **37**,[22f] the stereospecificity of C-7 coupling is reversed from that in compounds of Tables I and II for two sets of isomers and also reduced in magnitude. Since just addition of another methyl to C-3 or C-4 produces this effect, isolation and characterization of isomers of the compounds in Table V may help to clear up the function of ring substitution on stereospecificity of C-7 coupling.

Theoretical Analysis.—Although the complexity and number of the compounds used here makes detailed calculation impractical, some of the ideas developed in theoretical studies of ^{13}C chemical shifts and nuclear spin couplings might prove useful in developing an understanding of the experimental results.

^{13}C chemical shifts have been the subject of much theoretical investigation,[28-37] usually starting from Ramsey's formulation[38] and employing approximations of varying severity.

Since no calculations have been done on the phosphetanes, we are restricted to only qualitative estimates of the origin of the observed shifts. In cases where the phosphetane backbone remains fixed for various substituents on phosphorus, all the phosphetane carbon shifts are for carbons at least two bonds away from the substituent. Carbon charge density variation may be the controlling factor in determining these carbon shifts. For a given ring configuration the observed range of shifts for different phosphorus substituents would then be primarily due to differences in charge densities resulting from the range of electronegativities of the substituents. At first glance, the full positive charge present on phosphorus in the salts would lead to a prediction of a large C-2/C-4 shift, since this would represent a type of very powerful inductive withdrawal of charge. However, C-2 and C-4 have smaller shifts in the salts than in the oxides. It could be that the oxides are better represented as P-(IV) rather than "P(V)," *i.e.*, P^+-O^- instead of P=O.

If charge density polarization is the dominant mechanism for changes in the paramagnetic contribution to the chemical shift, some definite reversals are to be noted in the expected order of shifts. Note that C-2 and C-4 have a *higher* shift in **4** or **6** than in **2**. In fact, with the exception of chloro as a substituent, the C-2/C-4 shift in Table I is fairly insensitive to phosphorus substituent. When chloro is omitted the range of C-2/C-4 shifts is only 4.4 ppm, as opposed to 12.4 ppm for analogous $^{13}CH_3CH_2X$ shifts.[39] Carbons three bonds away from substituents in 1-substituted bicyclo[2.2.2]octanes have been reported to have shifts in the same direction as carbons two bonds away, but are significantly more attenuated.[39] The compounds in Table I show that the trend in C-3 is opposite that of C-2/C-4 and is actually more sensitive to the character of the substituent. This is difficult to explain on the basis of attenuated inductive effect and may be the result of alternating positive and negative charge densities around the phosphetane ring.

Theoretical analysis of $^{13}C-^{31}P$ nuclear spin couplings has been hampered by the until recent paucity of experimental data and the difficulty of doing detailed calculations involving a second-row element. The only available theoretical treatments of $^{13}C-^{31}P$ couplings have been by Cowley and White,[15] who calculated $^{13}C-^{31}P$ couplings in CH_3PH_2, CF_3PH_2, and $CH_3PH_3^+$ by a parameterized LCAO-SCF-MO theory in the Pople-Santry[16] approximation, Jameson and Gutowsky,[17,18] who developed a general qualitative model of spin coupling based on the contact contribution and core polarization, and Gray (part I),[2] who used the finite perturbation INDO-SCF-MO theory of Pople, McIver, and Ostlund[40] to calculate $^{13}C-^{31}P$ couplings in a series of phosphonates. In this last investigation the relationship between "s character" and $^{13}C-^{31}P$ coupling was examined. The coupling followed the calculated bond order but varied about twice as fast. In the phosphetanes, substituents are varied on phosphorus, whereas in the phosphonates the site of variable substitution was on the phosphonate carbon. The relationship between one-bond coupling to phosphorus and $C_{2s}-P_{3s}$ bond order in this different kind of bonding situation is a subject for further theoretical analysis, but treatments of spin coupling involving carbon[2,40,41] offer good promise that changes in couplings involving carbon, especially for carbons not undergoing substitution, reflect to a degree changes in the valence s-orbital bond order between the coupled atoms.

The C-2 and C-4 couplings in Table I cover a range of over 35 Hz (25 Hz in the oxides alone). Even if the $C_{2s}-P_{3s}$ bond order does not proportionately follow the observed couplings, the range of couplings in the oxides must point toward sizable differences in $C_{2s}-P_{3s}$ bond order throughout the oxides. Since the substituent variation is on phosphorus, it is likely that the main contribution to a change in bond order is from changes in the P_{3s} orbital contribution to the bonding orbital. There does not appear to be a drastic change in the observed couplings in proceeding to the salts. If this can be interpreted as resulting from a small change in the bond order for the coupled atoms, then prediction of sizable P(IV) character for the oxides is reinforced.

The smaller values for coupling to exocyclic alkyl carbons on phosphorus relative to the C-2 and C-4 carbons are interesting, especially in view of the frequently assumed correlation of bond angle with carbon hybridization. The $C_3-C_{2,4}-P$ angles in the phos-

(28) T. Yonezawa, I. Morishima, and H. Kato, *Bull. Chem. Soc. Jap.*, **36**, 1398 (1966).
(29) B. V. Cheney and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 5319 (1967).
(30) J. E. Bloor and D. L. Breen, *ibid.*, **89**, 6835 (1967).
(31) T. Tokuhiro, N. K. Wilson, and G. Fraenkel, *ibid.*, **90**, 3622 (1968).
(32) W. Adam, A. Grimison, and G. Rodriguez, *J. Chem. Phys.*, **50**, 645 (1969).
(33) T. Tokuhiro and G. Fraenkel, *J. Amer. Chem. Soc.*, **91**, 5005 (1969).
(34) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961).
(35) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).
(36) J. Mason, *J. Chem. Soc. A*, 1038 (1971).
(37) R. Ditchfield, D. P. Miller, and J. A. Pople, *J Chem. Phys.*, **54**, 4186 (1971).
(38) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950); **83**, (1951); **86**, 243 (1952).
(39) G. E. Maciel and H. C. Dorn, *J. Amer. Chem. Soc.*, **93**, 1268 (1971).
(40) (a) J. A. Pople, J. W. McIver, Jr., and N. S. Ostland, *Chem. Phys. Lett.*, **1**, 456 (1967); (b) *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).
(41) (a) 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); (b) P. D. Ellis and G. E. Maciel, *ibid.*, **92**, 5829 (1970).

phetanes are 84–88°,[21] considerably distorted from normal tetrahedral values. The C_2–P–C_4 angles are also distorted (82–86°).[21] These values are suggestive of angles for hybrids of considerable p character, arguing for small one-bond couplings. There is a small reduction in the one-bond coupling for the α-ring carbon in going from the larger five- and six-membered rings to an analogous four-membered ring coupling like the C-4 coupling in **25** or **26**. However, this reduction amounts to only a few hertz, nothing like a reduction based on hybridization arguments for C-2 and C-4. Note that the C-12 coupling in this same trend goes from 92.6 Hz in **49** to 86.6 Hz in **45** to 55–75 Hz in the various phosphetanes, pointing toward reduced P_{3s} orbital contribution to this coupling in this bond as the ring contracts.

Since the stereospecificity in exocyclic one-bond coupling is somewhat insensitive to the size of the group containing the coupled carbon or its electronic nature, it seems that the effect must arise from differences in the phosphorus bonding orbitals directed toward the substituents. Analogous stereospecificities have been noted for ^{13}C–^1H couplings in bicyclobutane[42] and 3-phenyl-1-azabicyclo[1.1.0]butane,[43] as well as ^{13}C–^{19}F couplings in some methyl-substituted 2,2-difluoronorbornanes.[44] Approximate MO methods based on the Fermi contact contribution have proved successful in calculation of ^{13}C–^{13}C and ^{13}C–^1H couplings[41] and have been able to account for the stereospecificity of the ^{13}C–^1H coupling in bicyclobutane.[41b] A notable property of these calculations is that the ^{13}C–^{13}C and ^{13}C–^1H couplings closely parallel the calculated s-orbital bond order for *structural* rather than *substituent* changes. If this pattern holds for the ^{13}C–^{31}P couplings in the structurally different cis and trans isomers here, the greater exocyclic coupling for the pseudoaxial bond predicts a corresponding greater s-orbital bond order for this bond than the pseudoequatorial bond.

Experimental Section

^{13}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 ^{13}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 $^{13}CH_3I$ 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 Hz/sec.

Most of the data were taken using a modification of the standard Varian equipment. In these situations the ^{13}C center band was derived from a 251-MHz signal, digitally divided by ten and amplified, which 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 generated 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 $CHCl_3$ except for those which are liquid at room temperature. The salts were examined as saturated solutions in water except for **44**, which was run in $CHCl_3$, and **21**, for which glacial acetic acid was used. The ambient probe temperature under proton decoupling was not measured but was usually significantly higher than room temperature. The chemical shifts in Tables I–VI are with respect to tetramethylsilane-^{13}C. In practice all shifts are recorded with respect to the $^{13}CH_3I$ in the lock capillary and are accurate to ±0.01 ppm for comparisons of shifts for the particular compound studied. For comparison with other compounds they have been corrected to the TMS scale by the shift (20.97 ppm) of TMS-^{13}C from $^{13}CH_3I$ (lock capillary), determined in a 1:2:2 TMS:$CHCl_3$:**25** solution. Even though all the solutions in this work (except for **4** and **21**) were approximately 1:1 oxide:$CHCl_3$ or salt:H_2O, some change in bulk susceptibility is to be expected in going from one sample to another with the largest change expected for changing from $CHCl_3$ to H_2O.

Materials.—Compound **1** was prepared according to the procedure of Jungermann and coworkers.[19e] The phosphinic esters **2** and **3** were made by a previously described method;[21g] likewise, the materials **4**, **6**, **7**, **16–18**, **20**, **25–28**, **31**, and **32** were synthesized by reported routes.[20] The synthesis of derivatives **10**, **37**, **45**, **46**, and **49** has recently appeared.[21a] The phospholene 1-oxides **47** and **48** were obtained by following the procedure of Quin.[27j] The phosphine oxides **50** and **51** are commercially available (*e.g.*, K and K Laboratories, Plainview, N. Y.). The phosphinic acid chlorides **8** and **9** were prepared by reported, general procedures.[19e,21g]

The ^1H nmr given below were recorded on a Varian A-60 spectrometer with TMS as an internal standard. Microanalyses were carried out by Alfred Bernhardt, Elbach, West Germany. All melting and boiling points are uncorrected. All of the reactions were carried out under a nitrogen atmosphere and were stirred mechanically or with a magnetic stirring bar.

1,2,2,3,4,4-Hexamethylphosphetane 1-Oxide (5).—The preparation of the cis isomer **5** followed that for the trans isomer **4** except for the mode of quenching of the reaction intermediate with water.[20] If the anhydrous intermediate (namely, the 1-chloro-1,2,2,3,4,4-hexamethylphosphetanium tetrachloroaluminate salt) in methylene chloride was added dropwise to an excess of rapidly stirred ice–water, a *ca.* 7:3 ratio of **5**:**4** was formed. This is in contrast to previously reported results;[20] more careful experimental work using methylphosphonous dichloride (Ethyl Corp.) gave a 90% yield of product (previously, 23%). The pure cis isomer **5** has a melting point of 99–101° (sealed capillary tube).

Anal. Calcd for $C_9H_{19}OP$: C, 62.05; H, 11.00. Found: C, 61.99; H, 10.94.

1-*tert*-Butyl-2,2,3,4,4-pentamethylphosphetane 1-Oxide (12).—To 90 g (0.46 mol) of 1-chloro-2,2,3,4,4-pentamethylphosphetane 1-oxide[19e] in 1 l. of dry ether cooled to −40°, 440 ml (0.55 mol) of 1.24 *M* *tert*-butyllithium in pentane was added dropwise over 1.5 hr. The reaction mixture was allowed to warm to room temperature, stirred for several hours, and cooled again to −30°. A saturated solution of sodium sulfate in water (50 ml) was added followed by sufficient anhydrous magnesium sulfate to pick up excess water. The reaction was warmed to 25° and the inorganic salts were filtered and washed with additional dry ether. Evaporation of the ether gave the crude solid. Additional material was obtained by trituration of the inorganic salts with methylene chloride. The crude product was recrystallized from cyclohexane to give 56 g (56% yield) of white needles, mp 147–149°. The analytical sample was recrystallized from cyclohexane and then sublimed at 100° (0.1 mm).

Anal. Calcd for $C_{12}H_{25}PO$: C, 66.63; H, 11.65; P, 14.32. Found: C, 66.51; H, 11.45; P, 14.52.

From the method of its synthesis this compound is presumed to be the trans isomer (1-*tert*-butyl and 3-methyl). The ^1H nmr showed only one isomer to be present. Treatment of a mixture of the isomeric acid chlorides **8** and **9** with *tert*-butyllithium by this same procedure gave a mixture of **12** and **13**, mp 94–120° from petroleum ether (bp 30–60°). An nmr (methylene chloride) showed all of the characteristic peaks expected for both isomeric oxides.

1-Benzyl-2,2,3,4,4-pentamethylphosphetane 1-Oxide (10 and 11).—An isomeric mixture of **10** and **11** was prepared in a manner

(42) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).

(43) A. G. Horfmann and D. A. Robertson, *J. Amer. Chem. Soc.*, **89**, 5974 (1967).

(44) J. B. Gutzner, M. Jantelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *ibid.*, **92**, 7107 (1970).

identical[21a] with that of the pure trans isomer **10** by treatment of a mixture of **8** and **9** with benzylmagnesium chloride. The isomeric oxides were recrystallized from cyclohexane. An nmr (pyridine) showed the presence of two isomers; the benzyl protons for **10** appeared at τ 6.57 (2 H, d, J_{PCH} = 11 Hz) and those for **11** at τ 6.61 (2 H, d, J_{PCH} = 11 Hz).

1-Phenyl-2,2,3,4,4-pentamethylphosphetane 1-Sulfide (14).—Treatment of a predominance of the trans phosphetane[20] precursor *in refluxing benzene with 1 equiv of molecular sulfur* gave a precipitate which was recrystallized from cyclohexane to give white needles, mp 96–100°, in good yield. Fractional recrystallization from cyclohexane gave the pure trans isomer, mp 100.5–102°. The product is presumed (by its mode of synthesis) to be the trans isomer (1-phenyl and 3-methyl). The nmr ($CDCl_3$) indicated one major isomer to be present: τ 1.6–2.7 (5 H, m), 7.4 (1 H, dq, J_{HCCH} = 7 Hz, J_{PCCH} = 2 Hz), 8.62 (6 H, d, J_{PCCH} = 20.0 Hz), 8.92 (6 H, d, J_{PCCH} = 19.0 Hz), 9.00 (3 H, dd, J_{HCCH} = 7, J_{PCCCH} = 1.2 Hz).

Likewise, the cis sulfide **15** was made by treatment of a predominance of the cis phosphetane with sulfur in benzene to give a 60% yield of product. Recrystallization from cyclohexane gave needles, mp 85–90°. Several recrystallizations from petroleum ether gave nearly pure cis isomer, mp 91–93°. The nmr ($CDCl_3$) showed absorption at τ 2.05–2.72 (5 H, m), 7.28–8.0 (1 H, dq), 8.54 (6 H, d, J_{PCCH} = 20 Hz), 8.66 (6 H, d, J_{PCCH} = 18 Hz), 9.05 (3 H, dd, J_{HCCH} = 7.5, J_{PCCCH} = 1.2 Hz).

1-Trideuteriomethyl-1,2,2,3,4,4-hexamethylphosphetanium Bromide (16).—About 2 g of the trans isomer **4** was dissolved in 35 ml of 3 *M* sodium deuteroxide solution and heated on a steam bath for 4 days. The solution was acidified and extracted repeatedly with chloroform. The chloroform was dried and evaporated to give a quantitative yield of **4** with a CD_3 substituent on phosphorus trans to the 3-CH_3 group. Reduction and quaternization following previous methods[20] gave the salt **16** (1-CD_3 and 3-CH_3 trans). The position of the label was consistent with the result of a previous study, which indicated that the cis 1-methyl of **16** (note that the word trans in ref 21f must be changed to cis and vice versa because of subsequent stereochemical revision; see ref 21h) underwent H–D exchange more rapidly than the trans 1-methyl in **16**.

1-Benzyl-1,2,2,3,4,4-hexamethylphosphetanium Bromide (19).—The corresponding *trans*-1-benzyl-2,2,3,4,4-pentamethylphosphetane[21a] was treated with methyl bromide in benzene–ether to give an 80% yield of the phosphetanium salt. Recrystallization from acetonitrile gave needles, mp 212–218°. The nmr ($CDCl_3$) showed absorption at τ 5.25 (2 H, d, J_{PCH} = 15 Hz), 6.8–7.2 (1 H, m), 7.82 (3 H, d, J_{PCH} = 13.5 Hz), 8.31 (6 H, d, J_{PCCH} = 19 Hz), 8.60 (6 H, d, J_{PCCH} = 19 Hz), 8.98 (3 H, dd, J_{HCCH} = 7.5, J_{PCCCH} ≈ 1 Hz). The elemental analysis was previously performed on a mixture of isomers (**19** plus **20**).[20]

1-Methoxy-2,2,3,3-tetramethylphosphetane 1-Oxide (30) and the Corresponding Acid 29.—To a mixture of 67 g (0.5 mol) of anhydrous aluminum chloride and 69 g (0.5 mol) of phosphorus trichloride in 200 ml of methylene chloride at 0–5°, 49 g (0.5 mol) of 2,3,3-trimethyl-1-butene in 500 ml of methylene chloride was added dropwise with stirring over 3 hr. The mixture was stirred overnight at room temperature and then quenched by pouring it over 400 g of ice. The two layers were quickly separated and the methylene chloride was dried over anhydrous sodium sulfate. Evaporation of the solvent gave 83 g of crude, viscous liquid. Direct hydrolysis of the crude liquid with 4 *M* sodium hydroxide solution gave the phosphinic acid **29** in 60% yield; isolation of the acid was achieved by acidification of the basic, aqueous layer with hydrochloric acid followed by extraction of the product with methylene chloride. The white, crystalline acid **29** was purified by sublimation at 145° (0.1 mm) to give material with mp 186–188°.

The above crude, viscous liquid (phosphinic acid chloride) in 300 ml of benzene was treated with 45 g of triethylamine followed by dropwise addition of 15.3 g of methanol in 125 ml of benzene over 1 hr. The mixture was then brought to reflux for 2 hr. Evaporation of the benzene followed by distillation of the residue gave 40.1 g of solid, platelike material, mp 50–52° (23% overall yield). The ester **30** was recrystallized from petroleum ether and sublimed at room temperature under vacuum (0.2 mm) to give the purified sample, mp 52–55°. The nmr (benzene) showed peaks at τ 6.45 (3 H, d, J_{POCH} = 11 Hz), 9.00 (3 H, d, J_{PCCH} = 19.0 Hz), 8.82 (3 H, d, J_{PCCH} = 19.5 Hz), 9.02 (3 H, s), 9.03 (3 H, s), 7.68–7.98 (2 H, four peaks observed).

Anal. Calcd for $C_8H_{17}O_2P$: C, 54.53; H, 9.73; P, 17.58. Found: C, 54.59; H, 10.02; P, 17.56.

1-Methoxy-2,2,3,3,4-pentamethylphosphetane 1-Oxide (35) and 36 and Associated Derivatives 34, 40, and 39.—To a mixture of 13 g (0.1 mol) of anhydrous aluminum chloride and 14 g (0.1 mol) of phosphorus trichloride in 100 ml of methylene chloride, 11.2 g (0.1 mol) of 3,4,4-trimethyl-2-pentene in 100 ml of methylene chloride was added dropwise over 1.5 hr; the mixture was cooled to 0° and stirred during the addition. The mixture was poured over 200 g of ice and the layers were quickly separated. The organic layer was dried and evaporated to give 18.5 g of brown semisolid. Recrystallization from cyclohexane gave 9.8 g (50% yield) of the acid chloride **40**, mp 112–115°. The nmr ($CDCl_3$) showed absorption at τ 6.75 (1 H, dq, J_{HCCH} = 7.5, J_{PCH} ≈ 14.5 Hz), 8.50 (3 H, d, J_{PCCH} = 22.5 Hz), 8.69 (3 H, d, J_{PCCH} ≈ 23 Hz), 8.72 (3 H, dd, J_{HCCH} = 7.5, J_{PCCH} = 26 Hz), 8.90 (6 H, broad singlet).

A mixture of 1 g of **40** and 10 ml of 1 *N* sodium hydroxide was stirred for 12 hr. The mixture was extracted with benzene and the benzene extracts were discarded. The aqueous layer was then acidified with concentrated hydrochloric acid and extracted with methylene chloride. The methylene chloride was dried and evaporated to give 0.8 g of yellow oil which solidified on standing. This material was sublimed several times at 100° (0.1 mm) to give a pure sample of **34**, mp 104–105°.

Anal. Calcd for $C_8H_{17}O_2P$: C, 54.53; H, 9.72. Found: C, 54.29; H, 9.60.

The ester **36** was prepared from **40** using the following procedure. To 0.1 mol of sodium methoxide in 100 ml of dry methanol, 19.5 g (0.1 mol) of **40** in 100 ml of methanol was added over 1 hr. The temperature was maintained at 20° by external cooling. The reaction was stirred overnight, the solvent was evaporated, and the residue was extracted with three 150-ml portions of methylene chloride. Evaporation gave a crude liquid, which was distilled to render 18.5 g of liquid which solidified on standing. This material was recrystallized from petroleum ether to give the hygroscopic, crystalline ester **36**, mp 105–107°. The nmr (benzene) showed peaks at τ 6.32 (3 H, d, J_{POCH} = 10 Hz), 8.77 (3 H, d, J_{PCCH} = 19 Hz), 9.08 (3 H, d, J_{PCCH} ≈ 19 Hz), 9.11 (3 H, dd, J_{HCCH} = 7.5, J_{PCCH} = 21 Hz), 9.2 (6 H, broad peak), 7.4 (1, H, six peaks, J_{HCCH} = 7.5, J_{PCH} ≈ 14.5 Hz).

The stereochemistry of the acid chloride **40** is assumed (by synthetic analogy) to be trans (1-chloro and 4-methyl groups). The formation of the ester **36** from **40** is assumed to go with retention of configuration.

The isomeric acid chloride **39**, present in a mixture with **40**, was prepared by slow, dropwise addition of the acid **34** in benzene to a tenfold excess (mole) of thionyl chloride in benzene at 50–55°. The product was formed in high yield; the nmr showed the presence of both isomers, **40** and **39**. The mixture was dissolved in dry benzene and treated with 1 equiv of triethylamine and methanol at room temperature followed by heating at reflux temperature. The product was distilled, bp 62–65° (0.15 mm); the nmr (benzene) showed two isomeric esters, **35** and **36**, to be present in a 7:3 ratio, respectively. The ester **35** gave a characteristic doublet at τ 6.39 (3 H, d, J_{POCH} = 10.5 Hz) which was upfield from the corresponding doublet of **36** (τ 6.32).

1-Phenyl-1,2,2,3,3,4-hexamethylphosphetanium Bromide (38).—The corresponding trans (1-phenyl and 4-methyl) phosphetane[21a] was treated with methyl bromide in benzene–ether solution to give the phosphetanium salt in high yield, mp 198–200°. The ^1H nmr and ^{31}P–^1H decoupled nmr were consistent with the structure and showed only one isomeric compound to be present.

Anal. Calcd for $C_{15}H_{24}BrP$: C, 57.15; H, 7.28; P, 9.84. Found: C, 57.04; H, 7.39; P, 9.79.

The quaternization is assumed[20] to go with retention of configuration to give the trans salt **38** (1-phenyl and 4-methyl are trans).

1-Hydroxy-2,2,3,4-tetramethylphosphetane 1-Oxide (41) and Ester (42).—The acid chloride precursor to **41** was prepared by the standard, general procedure;[19e,21a] it was obtained in 56% yield by addition of 4,4-dimethyl-2-pentene to phosphorus trichloride and aluminum chloride in methylene chloride. The nmr (benzene solution) indicated that most of the product consisted of a single isomer. The acid chloride, 1.0 g, was treated with 10 ml of 10% sodium hydroxide solution overnight. The reaction mixture was extracted with benzene and the aqueous layer was acidified with concentrated hydrochloric acid. The solution was extracted with methylene chloride. Evaporation of

the solvent gave an oil which solidified on standing. Recrystallization from cyclohexane gave 0.75 g (83%) of the acid **41**, mp 71–74°. The nmr ($CDCl_3$) gave peaks at τ −1.7 (1 H, s), 7.3–8.0 (1 H, m), ~8.8 (3 H, d, J_{PCCH} = 19 Hz), 8.87 (3 H, d, J_{PCCH} = 20 Hz), 8.81 (3 H, dd, $J_{HCCH} \approx 7$, $J_{PCCH} \cong 21$ Hz), ~9.0 (3 H, dd, $J_{HCCH} \cong 7$ Hz), ~8.3–8.9 (1 H, m, partially obscured by overlap).

Anal. Calcd for $C_7H_{15}O_2P$: C, 51.84; H, 9.32. Found: C, 51.96; H, 9.00.

The phosphinic acid chloride was treated with 1 equiv of sodium methoxide solution in methanol; the temperature was kept at 20°. An 85% yield of the ester **42** was obtained, bp 62–63° (0.1 mm). The nmr (benzene) showed the product to be a single isomer: τ 6.35 (3 H, d, J_{POCH} = 10 Hz), 7.28–8.05 (1 H, m), 8.88 (3 H, d, J_{PCCH} = 19 Hz), 8.93 (3 H, d, J_{PCCH} = 18.5 Hz), 8.95 (3 H, dd, J_{PCCH} = 20, J_{HCCH} = 7 Hz), 9.20 (3 H, broad d, J_{HCCH} = 7 Hz). An additional hydrogen was obscured by the upfield methyl signals.

1-Phenyl-2,2,3,4-tetramethylphosphetane 1-Oxide (43) and 1-Phenyl-1,2,2,3,4-pentamethylphosphetanium Iodide (44).—These compounds were prepared by analogous and standard procedures.[20,21a] The oxide was obtained as a viscous liquid in 22% yield by treatment of phenylphosphonous dichloride and aluminum chloride with 4,4-dimethyl-2-pentene in methylene chloride. The nmr (CCl_4) showed peaks at τ 1.9–2.6 (5 H, m), 9.14 (3 H, d, J_{PCCH} = 19.5 Hz), 8.71 (3 H, d, J_{PCCH} = 17 Hz), 8.68 (3 H, dd, J_{PCCH} = 19, J_{HCCH} = 8 Hz), 8.97 (3 H, broad d, $J_{HCCH} \cong 7$ Hz), ~6.3–7.2 (1 H, m), ~7.3–8.1 (1 H, m).

The phosphetane oxide **43** was reduced with trichlorosilane–pyridine in 60% yield and then treated with methyl iodide to give the pure salt **44** in 55% yield. The iodide salt was recrystallized from acetonitrile–ethyl acetate to give pale yellow needles, mp 209–213° dec. The nmr ($CDCl_3$) showed peaks at τ 7.35 (3 H, d, J_{PCH} = 13.5 Hz), 8.37 (3 H, d, J_{PCCH} = 21.0 Hz), 8.74 (3 H, d, $J_{PCCH} \cong 22$ Hz), 8.81 (3 H, dd, J_{HCCH} = 7.5, J_{PCCCH} = 1.3 Hz), 8.44 (3 H, dd, J_{PCCH} = 22, J_{HCCH} = 7.0 Hz), 5.5–6.3 (1 H, m), 6.5–7.3 (1 H, m), 1.5–2.5 (5 H, m, aromatic).

Anal. Calcd for $C_{14}H_{22}IP$: C, 48.29; H, 6.37; I, 36.45. Found: C, 48.36; H, 6.51; I, 36.30.

1-Phenyl-2,2,3,3-tetramethylphosphetane 1-Sulfide (33).—The phosphetane precursor[20] was treated with an excess of sulfur in refluxing benzene for 5 hr. The solution was filtered and the solvent was evaporated to give a residue which was recrystallized from cyclohexane. The purified product (50% yield) had mp 118.5–120.5° after several recrystallizations from petroleum ether. The nmr ($CDCl_3$) gave peaks at τ 1.93–2.8 (5 H, m), 6.6–7.9 (2 H, m), 8.62 (3 H, s), 8.98 (3 H, s), 8.63 (3 H, d, J_{PCCH} = 21.5 Hz), 9.03 (3 H, d, J_{PCCH} = 20.5 Hz).

1-Hydroxy-2,2,3-trimethylphosphetane 1-Oxide (22) and the Corresponding Isomeric Esters 23 and 24.—The acid chloride precursor to **22** was prepared using the generally described procedure;[19c,21a] 3,3-dimethyl-1-butene was employed as the olefin. The acid chloride was quite sensitive to hydrolysis and was obtained as a mixture with the acid **22**. The crude mixture was stirred with saturated sodium carbonate solution overnight; it was then filtered; and the filtrate was acidified with concentrated hydrochloric acid. Extraction with methylene chloride followed by evaporation of the solvent gave **22** as a viscous liquid. The nmr (CH_2Cl_2) was consistent with the expected product: τ −1.9 (1 H, s), 7.02–8.48 (3 H, m), 8.80 (3 H, d, J_{PCCH} = 19 Hz), 8.89 (3 H, d, J_{PCCH} = 20 Hz), 8.97 (3 H, d, J_{HCCH} = 7 Hz).

The acid was treated with thionyl chloride in benzene at 50° and the resultant mixture was converted to a mixture of isomeric esters [bp 40–41° (0.1 mm)] **23** and **24** by the methanol–triethylamine method.[21g] The nmr was in accord with these structures.

Anal. Calcd for $C_7H_{15}O_2P$: C, 51.84; H, 9.32. Found: C, 52.16; H, 9.10.

1,1-Dibenzyl-2,2,3,4,4,4-pentamethylphosphetanium Bromide (21).—The phosphetane precursor was treated with benzyl bromide in ether–benzene to give a 56% yield of the phosphonium **21**, mp 219.5–222.5°, from acetonitrile. The nmr was consistent with the expected structure.

Anal. Calcd for $C_{22}H_{30}BrP$: Br, 19.71. Found: Br, 19.66.

1-Phenyl-3-isopropyl-2,2,4,4-tetramethylphosphetane 1-Oxide (52).—The requisite olefin, 2,4-dimethyl-3-isopropyl-2-pentene, for the synthesis of **52**, was prepared by dehydration of triisopropylcarbinol. The alcohol was made by the slow addition of diisopropyl ketone in dry petroleum ether to isopropyllithium (Alpha Inorganics, Inc.) in pentane at 0–5°. After the addition was complete the solution was treated with saturated ammonium chloride solution. Fractional distillation gave a 50% yield of the desired alcohol, bp 193.5–196°, $n^{22}D$ 1.4475.[45] Dehydration was carried out with anhydrous copper sulfate; the alcohol was heated to 110–120° under vacuum (120 mm) to give a mixture of olefins, bp 148–151°.[23] Glpc analysis (6 ft × 0.25 in. column at 70°, 30% SE-30/Chromosorb) showed two major components. The component (40%) with the longer retention time (7.3 min) was collected. The nmr (neat) was consistent with the desired olefin: τ 7.1–7.6 (2 H, m), 8.32 (6 H, s), 8.98 (12 H, d, J_{HCCH} = 7 Hz).

Anal. Calcd for $C_{10}H_{20}$: C, 85.62; H, 14.38. Found: C, 85.63; H, 14.36.

For the synthesis of **52** the crude mixtures of olefins (directly from the dehydration) was used. This was treated with phenylphosphonous dichloride–aluminum chloride in the usual way;[20] water was added dropwise to the reaction to quench it. The initial product was a viscous liquid; treatment with petroleum ether followed by recrystallization (five times) from this solvent gave the phosphetane oxide **52**, mp 140–142°. The nmr ($CDCl_3$) showed peaks at τ 1.58–2.65 (5 H, m), 8.5 (6 H, d, J_{PCCH} = 16.0 Hz), 8.76 (6 H, d, 19.5 Hz), 9.0 (6 H, d, J_{HCCH} = 6 Hz).

Anal. Calcd for $C_{16}H_{25}OP$: C, 72.69; H, 9.53. Found: C, 72.73; H, 9.40.

It is assumed that the 1-phenyl and 3-isopropyl groups are trans. Quenching the reaction by adding it dropwise to water gave the cis isomer, mp 113–115°.

Registry No.—**1**, 35210-25-4; **2**, 26490-21-1; **3**, 26490-22-2; **4**, 33530-51-7; **5**, 28672-43-7; **6**, 16083-91-3; **6a**, 35624-12-5; **7**, 20047-46-5; **8**, 26674-18-0; **9**, 25145-33-9; **10**, 33530-55-1; **11**, 35624-07-8; **12**, 35624-08-9; **13**, 35624-09-0; **14**, 30664-59-6; **15**, 30664-60-9; **16**, 16084-01-8; **17**, 24436-07-5; **17a**, 35623-38-2; **18**, 35623-39-3; **19**, 35623-40-6; **20**, 35623-41-7; **21**, 31120-05-5; **22**, 35623-43-9; **23**, 34136-12-4; **24**, 34136-11-3; **25**, 34136-10-2; **26**, 34136-09-9; **27**, 35589-66-3; **28**, 35589-67-4; **29**, 35623-47-3; **30**, 35623-48-4; **31**, 16083-92-4; **32**, 16083-99-1; **33**, 35623-51-9; **34**, 35623-52-0; **35**, 35623-53-1; **36**, 35623-54-2; **37**, 35623-55-3; **38**, 35623-56-4; **39**, 35623-57-5; **40**, 35623-58-6; **41**, 35623-59-7; **42**, 35623-60-0; **43**, 35623-61-1; **44**, 35623-62-2; **45**, 4963-91-1; **46**, 703-03-7; **47**, 35623-32-6; **48**, 35623-33-7; **49**, 4963-95-5; **50**, 676-96-0; **51**, 597-50-2; **52**, 35623-35-9.

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