a standard drybox an excess of KH was loaded into the reaction side of the vessel through the ground-glass joint. Under nitrogen this vessel was removed to the vacuum line and evacuated. At −196° 0.4 mmol of 1-$CH_3B_5H_8$ and 0.3 ml of $(CD_3)_2O$ were condensed into the reaction tube. The tube was then warmed to −78° and the reaction was allowed to proceed until evolution of gas ceased. The vessel was immersed in liquid nitrogen, the hydrogen was removed, and 0.1 ml of $CHCl_3$ was condensed into the flask. The vessel was inverted. A −78° bath covered the nmr tube and an area above the frit. As the solution melted, it dropped to the frit. At no time was the solution above −78°. After filtration the solution in the nmr tube was frozen and the tube was sealed with a torch and removed.

For 1.0-mmol samples or larger a test tube type apparatus containing a magnetic stirring bar and fitted with an nmr tube side arm was employed. The sample was prepared as above. When the reaction stopped, the entire vessel including side arm was immersed in a −78° bath. The necessary amount of solution was then tipped into the nmr tube. The vessel was frozen and the nmr tube was sealed with a torch and removed.

For boron-11 nmr studies both tetrahydrofuran and dimethyl ether were used as solvents.

The hydrogen from samples was Toepler-pumped and measured. Yields were in excess of 97% of the theoretical value.

The deprotonation reactions of 2-$CH_3B_5H_8$, 1-$ClB_5H_8$, and 1-$BrB_5H_8$ were carried out in a similar manner as above.

**Protonation of the Anions.** The appropriate anion was prepared on the vacuum line on a 1.00-mmol scale in $(CH_3)_2O$ according to procedures described in the previous section. An excess of HCl was introduced at −196°. The reaction tube was warmed to −78° and stirred for 1 hr. The mixture was fractionated, and the boron hydride was isolated. The vessel was maintained at −78° until the solvent had been removed. Yields for the neutral boranes varied from 85 to 96%.

**Preparation of $(n\text{-}C_4H_9)_4N[1\text{-}CH_3B_5H_7]$ and $(n\text{-}C_4H_9)_4N[1\text{-}ClB_5H_7]$.** A 1.00-mmol sample of $(n\text{-}C_4H_9)_4NI$ and 1.00 mmol of KH were weighed into a reaction vessel in the drybox. The vessel was removed to the vacuum line and evacuated. About 2.0 ml of THF and 1.00 mmol of either 1-$CH_3B_5H_8$ or 1-$ClB_5H_8$ were condensed into the reaction tube. The vessel was warmed to −78°. When the reaction was completed, the hydrogen was removed and 4.0 ml of $CH_2Cl_2$ was condensed in at −196°. The vessel was warmed to −35° and stirred for 1 hr. Approximately 8–10 ml of diethyl ether was then introduced. Under nitrogen at −196° the vessel was attached to a filtration extractor on the line and evacuated. The solution was filtered at −78°. Again under nitrogen the bottom vessel containing the filtrate was removed and replaced with a test tube vessel fitted with an nmr tube side arm. The system was evacuated and pumped on for 1 hr. About 1 ml of methylene chloride was condensed in onto the frit at −78° and the tetra-*n*-butylammonium salt was allowed to wash through to the lower vessel. A portion of the sample was tipped at −78° into the nmr tube. The tube was frozen and removed. The solid on the frit was identified as KI by its X-ray powder pattern.

**Relative Acidities of the Boranes.** In reaction procedures described above proton competition reactions in THF were prepared between the various pairs of neutral boranes and anions. The appropriate anion was prepared on a 0.50-mmol scale at −78°. The neutral borane was introduced in an equivalent amount and the mixture was allowed to equilibrate at −78° for 1 hr before the nmr sample was removed. The following pairs of reactions were carried out and the resulting boron-11 nmr spectra were studied from −78° to ambient temperature: $B_5H_9$ and K[1-$CH_3B_5H_7$]; 1-$CH_3B_5H_8$ and $KB_5H_8$; $B_5H_9$ and K[2-$CH_3B_5H_7$]; 2-$CH_3B_5H_8$ and $KB_5H_8$; 1-$CH_3B_5H_8$ and K[2-$CH_3B_5H_7$]; 2-$CH_3B_5H_8$ and K[1-$CH_3B_5H_7$]; $B_5H_9$ and K[1-$ClB_5H_7$]; 1-$ClB_5H_8$ and $KB_5H_8$. The respective species in solution could be determined by the chemical shifts of the resonances observed. Solutions containing 1-$CH_3B_5H_8$ and 2-$CH_3B_5H_8$ and their corresponding anions were fractionated. Boron-11 nmr spectra revealed the presence of both neutral species in solution for this mixture.

**Registry No.** $B_5H_8^-$, 31426-87-6; 1-$CH_3B_5H_7^-$, 36900-66-0; 1-$ClB_5H_7^-$, 36900-67-1; 1-$BrB_5H_7^-$, 36900-68-2; 2-$CH_3$-$B_5H_7^-$, 37035-65-7.

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# Nuclear Magnetic Resonance Spectroscopy. Spin-Spin Coupling of Carbon to Phosphorus, Mercury, Nitrogen, and Other Elements[1a,b]

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Spin-spin coupling between carbon and phosphorus, mercury, nitrogen, and boron has been observed in proton-decoupled $^{13}C$ spectra. One-bond couplings involving carbon are generally positive and two-bond couplings are negative; however, if unhybridized p orbitals are used in the bonding, such as with phosphorus(III) or fluorine, one-bond couplings are negative and two-bond couplings are positive. A comparison of the magnitudes of carbon–phosphorus and carbon–nitrogen couplings with carbon–carbon couplings shows a significant negative contribution to the coupling constants which suggests that average energy approximation should not be used for this kind of comparison. Carbon–mercury couplings correlate well with carbon–carbon or proton–mercury couplings in similar bonding situations.

Prior to the advent of field frequency controlled spectrometers, studies of coupling between carbon and nuclei other than hydrogen and fluorine were rare.[2] Indor techniques could be used to study the couplings involving methyl carbons,[3] and carbon enrichment allowed observation of the couplings in the carbon spectrum,[4] but with the requirement of simple molecules or inconvenience of labeled

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[1] (a) Supported in part by the National Science Foundation and by the Public Health Service, Grant No. GM-11072 from the Division of General Medical Sciences. (b) Preliminary communication: F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 91, 4940 (1969). (c) National Science Foundation predoctoral fellow, 1965–1968.

[2] E. F. Mooney and P. H. Winston, *Annu. Rev. NMR Spectrosc.*, 2, 176 (1969).

[3] K. A. McLaughlan, *Chem. Commun.*, 105 (1965).

[4] K. Frei and H. J. Bernstein, *J. Chem. Phys.*, 38, 1216 (1963).

**Table I.** $^{13}C$ Nuclear Magnetic Resonance Parameters of Phosphorus-Containing Compounds

| Compd | Carbon | $^{13}C$ chem shift[a] | $J_{CP}$, Hz |
|---|---|---|---|
| Methylphosphine | $CH_3$ | −4.6 | 9.3 |
| Dimethylphosphine | $CH_3$ | 6.9 | 11.6 |
| Trimethylphosphine | $CH_3$ | 17.1 | 13.5[b] |
| Phosphacyclopentane | C2 | 31.6 | 5.4 |
| | C3 | 21.2 | 9.95 |
| Tetramethyldiphosphine | | 11.2 | *c* |
| Triphenylphosphine | C1 | 137.8 | 12.4[d] |
| | C2 | 134.0 | 19.5 |
| | C3 | 128.8 | 6.7 |
| | C4 | 128.5 | 0 |
| Tetrabutylphosphonium bromide | C1 | 18.7 | 47.6 |
| | C2 | 23.7 | 4.3 |
| | C3 | 24.1 | 15.4 |
| | C4 | 13.3 | 0 |
| Methyltributylphosphonium iodide | C1 | 20.4 | 48.0 |
| | C2 | 23.7 | −4.55 |
| | C3 | 23.9 | 15.7 |
| | C4 | 13.5 | 0 |
| | $CH_3$ | 5.1 | 41.8 |
| Methyltriphenylphosphonium iodide | C1 | 119.3 | 88.4 |
| | C2 | 133.2 | 10.9 |
| | C3 | 130.3 | 12.8 |
| | C4 | 135.0 | 2.9 |
| | $CH_3$ | 9.5 | 51.7 |
| Tri-*n*-butyl phosphate | C1 | 76.5 | −5.9 |
| | C2 | 32.8 | 6.5 |
| | C3 | 19.1 | 0 |
| | C4 | 13.7 | 0 |
| Di-*n*-butyl phosphate | C1 | 65.4 | −5.6 |
| | C2 | 32.8 | 6.0 |
| | C3 | 19.0 | 0 |
| | C4 | 13.6 | 0 |

[a] Chemical shifts are in ppm downfield from the methyl of tetramethylsilane. [b] V. H. Elser and H. Dreeskamp, *Ber. Bunsenges. Phys. Chem.*, **73**, 619 (1969), report − 14 Hz. [c] The average of the two carbon–phosphorus coupling constants is 4.3 Hz. The spectrum is a AA′X type. [d] The results of this work agree with those of H. J. Jakobsen and O. Manscher, *Acta Chem. Scand.*, **25**, 680 (1971), but not those of O. A. Gansow and B. Y. Kimura, *Chem. Commun.*, 1621 (1970).

syntheses. Neither couplings to phenyl groups nor long-range couplings in aliphatic systems had been studied.

Using the DFS-60 spectrometer, we have previously reported couplings between carbon and fluorine[5a] and carbon and carbon[5b] and one-bond coupling in the tetramethyl derivatives of group IV.[5c] We report here studies of the coupling of carbon and phosphorus, mercury, and some nuclei with spin greater than $^1/_2$.

## Experimental Section

Most of the samples were obtained from commercial sources and were used without further purification. Phosphonium salts were prepared from the corresponding phosphines and alkyl halides.[6] The methylphosphines were available from previous studies.[7] Samples of di-*n*-propyl- and diisopropylmercury were supplied by Dr. B. M. Monroe. Tri-*n*-propyl- and triisopropylboron were supplied by Dr. D. J. Pasto. Carbon-13 spectra were obtained in the external-lock mode of a Varian DFS-60 spectrometer with single-frequency proton decoupling. Liquid samples were diluted about 10% with a convenient reference. Solids were examined as saturated solutions in either methanol or water.

## Results

**Phosphorus.** The $^{13}C$ chemical shifts and carbon–phosphorus coupling constants of the compounds studied are listed in Table I. The chemical shifts of the α carbons of phosphates are similar to those of the α carbons in alcohols and therefore present no problems in identification. Methyl carbons appear as perturbed quartets and methylene carbons as triplets under partial decoupling conditions. However, if the carbons are significantly coupled to phosphorus, the partially decoupled spectra are quite complex. The protons on the β and γ carbons appear as a single broad band, and both methylene carbons appear in the same region of the $^{13}C$ spectrum. For phosphates, the expectation that four-bond carbon–phosphorus coupling will be negligible identifies the doublet as the β carbon and the singlet as the γ carbon.[8]

We could determine the relative signs of carbon–phosphorus coupling constants by partial decoupling only when both the carbon and its directly bonded protons were significantly coupled to phosphorus. This limitation made it impossible to determine the sign of the three-bond carbon–phosphorus coupling, because the phosphorus–proton coupling through four bonds is small.

Where the interior methylenes of butyl groups are both coupled to the phosphorus and have similar chemical shifts, the β and γ carbons can be distinguished by the symmetry of the degradation of the $^{13}C$ resonances when the decoupler is offset from the optimum frequency. The β carbon, whose protons are coupled to phosphorus, shows an unsymmetrical effect, while both peaks in the γ carbon resonance broaden symmetrically.

**Mercury.** The carbon–mercury coupling constants of a series of disubstituted mercury compounds are given in Table II. Irradiation of the low-field portion of the proton spectrum sharpens the upfield mercury satellite of the $^{13}C$ resonance of the β carbon and *vice versa*, showing that the sign of the geminal carbon–mercury coupling constant is opposite to the (positive) vicinal mercury–proton coupling. The sign of the vicinal carbon–mercury coupling could not be determined, but as with mercury–proton coupling, the magnitude is greater than that of the geminal coupling.

**Table II.** Carbon–Mercury Coupling in Disubstituted Mercury Compounds (Hz)

| Substituent | $^1J_{CHg}$ | $^2J_{CCHg}$ | $^3J_{CCCHg}$ | $^4J_{CCCCHg}$ |
|---|---|---|---|---|
| Methyl | 692 | | | |
| Ethyl | 648 | 24 | | |
| *n*-Propyl | 659 | −25.2 | 102.6 | |
| *n*-Butyl | 656 | 26.3 | 100 | 0 |
| Isopropyl | 633.6 | 32.2 | | |
| Vinyl | +1159 ± 2 | | | |
| Phenyl | 1186 | 88 | 101.6 | 17.8 |

**Nitrogen.** The measurement of spin-spin coupling involving nitrogen is hampered because the major isotope of nitrogen has a spin of 1, and most coupling is either partially or completely washed out by quadrupole relaxation. The nitrogens in the tetraalkylammonium ions have long relaxation times and for these ions, the proton-decoupled $^{13}C$ resonances are 1:1:1 triplets. The $^{13}C$-$^{14}N$ couplings in the tetramethyl- and tetraethylammonium ions are 5.15 and 2.85 Hz. The lines of the triplets are noticeably broader than

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(5) (a) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 2361 (1971); (b) F. J. Weigert and J. D. Roberts, *ibid.*, **94**, 6021 (1972); (c) F. J. Weigert, M. Winokur, and J. D. Roberts, *ibid.*, **90**, 1566 (1968).

(6) (a) M. Grayson and P. T. Keough, *J. Amer. Chem. Soc.*, **82**, 3919 (1960); (b) W. A. Henderson, Jr., and S. A. Buckler, *ibid.*, **82**, 5794 (1960).

(7) G. M. Whitesides, J. L. Beauchamp, and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 2665 (1963).

(8) The β-carbon couplings are quite prominent in nucleotides: D. E. Dorman and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **65**, 19 (1970).

the lines from an internal reference, but the coupling is resolvable.

**Boron.** The resonances of the carbons directly bonded to boron in triisopropyl- and tri-*n*-propylboron have line widths of 130 and 80 Hz, respectively, which, presumably, result from large carbon-boron couplings which are incompletely relaxed by the quadrupole mechanism. The boron of the tetraphenylboride anion is in a symmetrical environment and is expected to have a long relaxation time. The substituted carbon (insensitive to the proton-decoupling frequency) is a 1:1:1:1 quartet with a carbon-boron coupling constant of 49.5 Hz. A coupling of 2.6 Hz was observed to the meta carbons, but no coupling could be resolved to either the ortho or the para carbons, though both resonances were slightly broadened.

## Discussion

Karabatsos[9] extended the valence-bond theory of geminal proton-proton couplings to geminal carbon-proton coupling. The couplings could be related by

$$J_{\mathrm{CH}} = aJ_{\mathrm{HH}} \tag{1}$$

where, for $sp^3$-hybridized carbon $a = 0.3$; for $sp^2$, $a = 0.4$; and for sp, $a = 0.61$. Smith[10] extended this comparison further to geminal X-C-H coupling of the tetramethyl derivatives of group IV. Weigert, Winokur, and Roberts[5c] showed that Smith's equation could also be applied to one-bond C-X coupling

$$J_{\mathrm{CX}} = \left(\frac{\alpha_{\mathrm{CX}}}{\alpha_{\mathrm{CC}}}\right)^2 \left(\frac{\Delta E_{\mathrm{c}}}{\Delta E_{\mathrm{x}}}\right) \left(\frac{n_{\mathrm{x}}Z_{\mathrm{x}}^*}{n_{\mathrm{c}}Z_{\mathrm{c}}^*}\right)^3 \left(\frac{g_{\mathrm{x}}}{g_{\mathrm{c}}}\right) J_{\mathrm{CC}} \tag{2}$$

where $\alpha^2$ is the hybridization of the carbon orbital forming the C-X bond, $\Delta E$ is an average excitation energy, $Z_{\mathrm{x}}^*$ is an effective nuclear charge of X, $n_{\mathrm{x}}$ is the period to which atom X belongs, and $g$ is the magnetogyric ratio. The same $Z^*$ used by Smith to correlate geminal X-C-H coupling also explains one-bond C-X coupling.[5c] The validity of eq 2 depends on the similarity of the fragments of the wave functions being compared, however, neither the negative sign of one-bond carbon-fluorine or carbon-phosphorus coupling is predicted from eq 2.

The valence s orbitals of both phosphorus and fluorine are of lower energy than the corresponding p orbitals and, thus, hybridization should be unfavorable. Pople and Santry[11] have shown that under these conditions the average energy approximation is not valid and negative one-bond couplings can occur. Although phosphorus-proton coupling in the phosphines can be discussed in terms of the smaller s character of the phosphorus orbitals,[12] the negative sign of the carbon-phosphorus coupling invalidates further comparisons. Both two-bond carbon-phosphorus and carbon-fluorine[5b,13] couplings are positive.

By symmetry, the four orbitals used in forming the carbon-phosphorus bonds in phosphonium ions are expected to be $sp^3$ hybrids and the coupling constants to follow more normal patterns (Table III). The signs, at any rate, are in agreement with this expectation, as one-bond coupling is positive and two-bond coupling is negative. While the magnitude of the geminal coupling is in good agreement with that calculated from typical geminal proton-phosphorus couplings using (1), the one-bond coupling constant is much smaller than would be predicted by application of eq 2 to the phosphorus-proton coupling in phosphonium ions. Although the signs of the vicinal carbon-phosphorus couplings are not known, their magnitudes are also not in agreement with those calculated using (2); only here, the experimental values are larger than the calculated ones. Correlations between the two- and three-bond carbon-phosphorus coupling constants in triphenylphosphine are no better than the comparisons in the aliphatic cases (Table IV). The larger coupling between the phosphorus and C1 of the phenyl group in the methyltriphenylphosphonium ion arises from the increased s character in the carbon orbital.

**Table III.** Chemical Shifts in Boron-Containing Compounds

| Compd | Carbon | Chem shift[a] |
|---|---|---|
| Tri-*n*-propylboron | α | 18.4 |
| | β | 17.8 |
| | γ | 31.7 |
| Triisopropylboron | α | 20.5 |
| | β | 17.8 |

[a] In ppm downfield from TMS.

**Table IV.** Correlation of Carbon-Phosphorus and Phosphorus-Proton Coupling in Aliphatic Systems

| Bonding situation | Phosphorus-proton coupling, X = H, Hz[a] | carbon-phosphorus coupling, X = C, Hz | |
|---|---|---|---|
| | | Calcd[b] | Obsd |
| P-X | +180 | +54 | −11 |
| $\overset{+}{\mathrm{P}}$-X | +550 | +165 | +50 |
| P-C-X | +3 | +1 | +12 |
| $\overset{+}{\mathrm{P}}$-C-X | −14 | −4.2 | −4.5 |
| P-C-C-X | +12 | +3.6 | 12 |
| $\overset{+}{\mathrm{P}}$-C-C-X | +11 | +3.3 | 15 |

[a] Reference 12. [b] From eq 1 with $a = 0.3$.

When the bonding orbitals of the coupled atoms have similar energies and hybrid orbitals are formed, such as for carbon and mercury, simplified theories of coupling, such as (2), may explain the observed trends. Thus, the one-bond carbon-mercury coupling may be estimated from typical carbon-carbon coupling constants, assuming that the mercury orbital forming the carbon-mercury bond is an sp hybrid, neglecting changes in the average excitation energy[14] and carbon orbital hybridization and using Smith's value of 22.7 for $Z^*$. The calculated value depends on the carbon-carbon bond chosen as the model but, assuming a value of 36 Hz (from neopentane),[5c] the calculated value for $J_{\mathrm{CHg}}$ is 650 Hz, in good agreement with that observed. The geminal mercury-proton coupling in diethylmercury is −88 Hz, predicting 0.3(−88) = −26 Hz for two-bond carbon-mercury coupling—again in excellent agreement with experiment. The one-bond carbon-mercury coupling in diphenyl- or divinylmercury is most greatly influenced by the change in the hybridization of the carbon orbital forming the bond to mercury. Carbon-mercury coupling in diphenylmercury may be favorably compared with mercury-proton coupling in divinylmercury, as shown in Table V. The vicinal carbon-mercury coupling constants in the dialkylmercury compounds

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[9] G. J. Karabatsos, J. D. Graham, and F. M. Vane, *J. Amer. Chem. Soc.*, 84, 37 (1962).

[10] G. W. Smith, *J. Chem. Phys.*, 39, 2031 (1963).

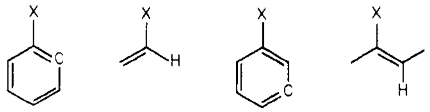
[11] J. A. Pople and D. P. Santry, *Mol. Phys.*, 8, 1 (1964).

[12] S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Amer. Chem. Soc.*, 88, 2689 (1966).

[13] M. A. Cooper, H. E. Weber, and S. L. Manatt, *J. Amer. Chem. Soc.*, 93, 2369 (1971).

[14] Typically, changes in the "average excitation energy" have been related to bond strengths.[9] A more valid procedure would be to consider electronic transitions. Although the carbon-mercury bond has a low dissociation energy, it has higher excitation energy.

**Table V.** Comparison of Couplings Involving Carbon in Phenyl Derivatives with those Involving Protons in Vinyl Derivatives



| | $J_{CCX}$, Hz | | $J_{CCCX}$, Hz | |
|---|---|---|---|---|
| X | Obsd | Calcd[a] | Obsd | Calcd[a] |
| H[b] | +1.0 | +1.0 | +7.4 | +7.6 |
| F[c] | +21.0 | + 33.9 | +7.7 | +21.0 |
| Hg | 88 | + 52 | 102 | +118 |
| P | 19.5 | +4.7 | 6.7 | +12.1 |

[a] From eq 1 with $a = 0.4$. [b] F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2967 (1967). [c] Reference 5a.

**Table VI.** A Comparison of Vicinal C-X Coupling and Vicinal H-X Coupling in Aliphatic Systems

| X | $J_{HCCX}$, Hz | $J_{CCCX}$, Hz | X | $J_{HCCX}$, Hz | $J_{CCCX}$, Hz |
|---|---|---|---|---|---|
| H | 7 | 5 | Hg | 115 | 100 |
| P | 13 | 12 | F | 25 | 19 |
| $P^+$ | 12 | 15 | | | |

are, however, much larger than would be expected from application of eq 1 to the vicinal mercury-proton coupling constants.

While calculating coupling constants involving mercury is impractical, the correlations presented here suggest that if we understand proton-proton coupling, we should at least qualitatively understand carbon-mercury coupling.

## Generalizations

The average energy approximation appears to be valid for carbon-carbon couplings but invalid for carbon-fluorine couplings.[10] The magnitudes of the carbon-nitrogen couplings are generally not encouraging for application of eq 2. If we neglect changes in the average energy term, the $^{13}C-^{15}N$ coupling would be predicted to be 0.8 times the carbon-carbon coupling for an analogously hybridized bond. Here we can compare acetylenes (175 Hz)[4] and acetonitrile (17.5 Hz),[3] neopentane (36 Hz)[5c] and the tetramethylammonium ion (5.7 Hz), or benzenes (57 Hz)[5b] and pyridine (0.45 Hz).[15] One-bond carbon-phosphorus couplings in phosphonium ions are also smaller than would be predicted by eq 2. The one-bond coupling constants may be internally consistent with s bond order correlations, but when comparisons are made with carbon-carbon coupling, the failure of the average energy approximation becomes more obvious.

Vicinal coupling in aliphatic compounds is very similar to the corresponding H-X vicinal coupling constants for the limited number of X considered (Table VI). The factors which influence the vicinal coupling for the case X = H have been discussed[16] but no conclusion as to the exact nature of the failure of eq 1 was reached.

**Registry No.** Methylphosphine, 593-54-4; dimethylphosphine, 676-59-5; trimethylphosphine, 594-09-2; phosphacyclopentane, 3466-00-0; tetramethyldiphosphine, 3676-91-3; triphenylphosphine, 603-35-0; tetrabutylphosphonium bromide, 3115-68-2; methyltributylphosphonium iodide, 1702-42-7; methyltriphenylphosphonium iodide, 2065-66-9; tri-*n*-butyl phosphate, 126-73-8; di-*n*-butyl phosphate, 107-66-4; tri-*n*-propylboron, 1116-61-6; triisopropylboron, 1776-66-5; methyl, 593-74-8; ethyl, 627-44-1; *n*-propyl, 628-85-3; *n*-butyl, 629-35-6; isopropyl, 1071-39-2; vinyl, 1119-20-6; phenyl, 587-85-9.

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(15) R. L. Lichter and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 5218 (1971).

(16) G. J. Karabatsos and C. E. Orzech, Jr., *J. Amer. Chem. Soc.*, **87**, 560 (1965).

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# Reaction of Octafluorocyclotetraphosphonitrile with Methyllithium

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Octafluorocyclotetraphosphonitrile reacts with methyllithium to give methyl, dimethyl, trimethyl, and tetramethyl derivatives and finally octamethylcyclotetraphosphonitrile. All five dimethyl derivatives were found, and two of them (geminal and trans-antipodal) were characterized completely by $^{31}P$, $^{1}H$, and $^{19}F$ nmr spectroscopy. Trimethylation was exclusively geminal; of the five trimethyl derivatives, the geminal-vicinal and geminal-antipodal compounds have been characterized in detail with the help of their decoupled $^{1}H$ and $^{19}F$ nmr spectra. The single tetramethyl derivative isolated exemplifies a novel orientation pattern in phosphonitrilic chemistry, *viz.*, geminal substitution followed by reaction at an antipodal site. The orientation pattern and the bond length inequalities observed in the structure of *gem*-dimethylhexafluorocyclotetraphosphonitrile are interpreted in terms of perturbation theory applied to a delocalized $\pi$-electron system.

## Introduction

Very many phosphonitrilic derivatives have been prepared by reactions of chlorophosphonitriles with nucleophiles, and different orientation patterns have been distinguished. At the same time, theories of the $\pi$-electron structure of these molecules have been developed and have been used for the interpretation of molecular structure and energetics, though there has hitherto been no systematic attempt to apply the theory to strictly chemical problems, such as the orientation of substituents or the rates of the reactions by which they are introduced. This is partly because reactivity is not a

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