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ON THE CONTRASTING MAGNITUDE OF GEMINAL PHOSPHORUS-HYDROGEN COUPLING IN CYCLOPROPENYL AND CYCLOPROPYL PHOSPHORUS DERIVATIVES

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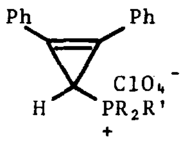
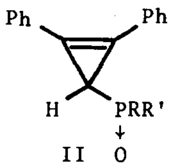
A recent report (2) on the unusually high geminal phosphorus-hydrogen coupling constants observed in cyclopropenyl phosphorus derivatives prompts us to present, in preliminary form, our results comprising a more extensive study of this phenomenon.

As indicated in Table I, we have determined the PCH coupling constants for a variety of cyclopropenyl phosphorus derivatives (Ia-f and IIa-e) and contrast the magnitude of these couplings with those observed for several selected cyclopropyl phosphorus derivatives. The J_{PCH} values for the cyclopropenyl systems range from 37.4 to 68.7 Hz-the latter value which we believe to be the highest geminal phosphorus-hydrogen coupling yet observed. By comparison, the PCH values for the cyclopropyl phosphorus derivatives III-V, apparently the first reported geminal phosphorus-hydrogen couplings for this system, are strikingly smaller than those observed in the cyclopropenyl system and may in themselves be considered to be unusually low for phosphonium salts and phosphine oxides.



I



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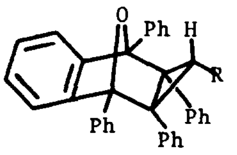


III

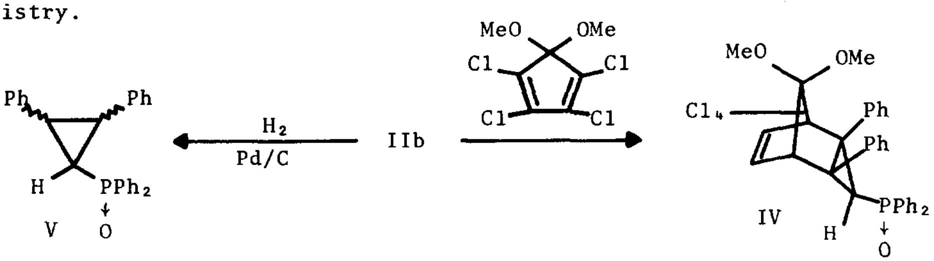
Table I

Chemical Shifts and Coupling Constants of Protons Geminal to Phosphorus

		J_{PCH}	τ^a
Ia	R=R'=OPh	67.2	6.50
Ib	R=R'=Ph	49.8	5.98
Ic	R=Ph; R'=Me	47.0	6.46
Id	R=R'=n-Bu	44.2	7.15
Ie	R=Ph; R'=t-Bu	49.4 [b]	6.45
If	R=Ph; R'=diphenylcyclopropenyl	47.8	6.65
IIa	R=R'=OMe	42.0 [c]	7.95
IIb	R=R'=Ph	41.5	7.11
IIc	R=Ph; R'=t-Bu	40.0	7.32
IId	R=Ph; R'=Me	37.4	7.53
IIe	R=Ph; R'=diphenylcyclopropenyl	38.0	7.46
IIIa	R=Ph_3P^+; ClO_4^-	0.0	5.62
IIIb	R=n-Bu_3P^+; ClO_4^-	0.9	6.78
IIIc	R=$Ph_2(O)P$	4.6	6.10
IV		5.9	7.70
V		6.8-11.0	7.9

[a] All spectra are 60 MHz with $CDCl_3$ as solvent, except where noted; [b] TFA; [c] CCl_4

The preparation of compounds Ib-If and IIb-IIIb from Table I are described in an earlier communication. (3) Quasi-phosphonium salt Ia was prepared by addition of a chloroform solution of triphenyl phosphite to an equimolar amount of diphenylcyclopropenyl perchlorate in chloroform. The phosphonate ester IIa was prepared by a modification of the Arbusov reaction involving addition of an ether solution of trimethyl phosphite to a suspension of diphenylcyclopropenyl perchlorate and sodium chloride in ether. (4) The cyclopropane derivatives IIIc and IV are obtained from the Diels-Alder reaction of IIb with 1,3-diphenylisobenzofuran and the dimethylketal of tetrachlorocyclopentadieneone, respectively. Hydrogenation of IIb afforded the cyclopropylphosphine oxide V of undetermined stereochemistry.



V

IIb

IV

To our knowledge, the geminal phosphorus-hydrogen coupling constants reported here are the largest yet observed. (5) The only phosphorus-hydrogen couplings, through carbon, which approach this magnitude are those reported for trans vinylic systems of the type R_3P-C=C-H. (6,7,8) The data in Table I clearly indicate the sensitivity of J_{PCH} in cyclopropenyl phosphorus derivatives to changes in substitution on phosphorus. This observation of the dependence of J_{PCH} on phosphorus substituents is in agreement with the results of Ionin in systems of the type R_2C=CHP(O)R^1_2 (9) and H_2C=C=CHP(O)R_2; (10) however, it is in direct contrast to the results of Griffin and Gordon (11) for the standard $R_3\overset{+}{P}$-Me salts, which showed no change in J_{PCH} when R was varied from *n*-butyl to phenyl. These results are also at variance with those of Millar, (12) who established that substitution on carbon, not phosphorus, had the major effect on J_{PCH} in the system $R_2Me\overset{+}{P}CH_2X$. Comparison of PCH values for phosphonium salts Ia-Id clearly indicates that an increase in the electronegativity of the substituents on phosphorus produces a corresponding increase in J_{PCH} for these systems. A further examination of the PCH values in Table I reveals a striking difference in magnitude of phosphorus-hydrogen coupling for cyclopropyl and cyclopropenyl phosphorus derivatives, the cyclopropyl couplings being almost an order of magnitude smaller.

Before attempting to explain the trends observed in the geminal phosphorus-hydrogen couplings of these phosphorus derivatives, absolute or relative signs must be considered for the couplings. Although signs have not been determined experimentally, strong arguments may be advanced for assigning a positive sign to the cyclopropenyl J_{PCH}. Phosphonium salts in which phosphorus is bound to an *sp*^{3} hybridized carbon have negative geminal phosphorus-hydrogen coupling constants; (12,13) however, these geminal coupling constants become more positive as the electronegativity of the groups on *sp*^{3} hybridized carbon is increased. (12) This increase in J_{PCH} is attributed to an increase in the *s* character (14) of the carbon hydrogen bonds. Lancaster (15) has analyzed the spectra of two vinyl phosphonium salts and a vinylphosphonate ester (J_{PCH}, 21-24 Hz) and found the relative signs of the geminal and vicinal phosphorus-hydrogen coupling constants to be the same. Since the vicinal coupling has been determined to be positive in analogous systems, (16) the geminal coupling can be assigned a positive sign.

With the above assignment made, the cyclopropyl and cyclopropenyl phosphorus derivatives fit quite well in the developing trend. Since the *s* character of cyclopropyl carbon-hydrogen bonds is intermediate between that for sp^3 and sp^2 hybridized carbon, J_{PCH} for cyclopropyl phosphorus derivatives would be expected to be intermediate, which is the observed result. The geminal carbon-hydrogen bond in the cyclopropenyl system can be assigned an approximate value of 35% *s* character;(17) therefore, J_{PCH} values for this system would be expected to be larger than those for the corresponding vinyl systems in agreement with the present observations. The data presented here, together with that of other workers, thus reveals a consistent increase of geminal·phosphorus-hydrogen coupling with increasing *s* character of the carbon-hydrogen bond, as well as carbon-phosphorus bond.

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