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UNUSUALLY HIGH PCH COUPLING CONSTANTS IN CYCLOPROPENYLPHOSPHONIUM SALTS

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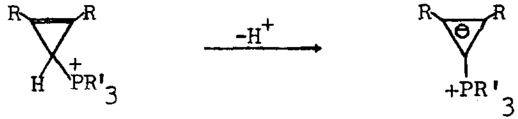
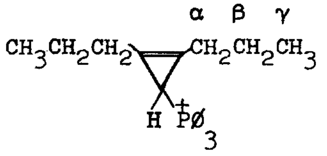
We have prepared a series of cyclopropenylphosphonium salts(I) of interest as precursors of the antiaromatic(2) 4π electron system II. At this time we report the proton magnetic resonance spectra data on these salts. Of particular interest are the PCH coupling constants. To our knowledge they are the first reported measurements of cyclopropene geminal coupling constants and they are abnormally large, exceeding in magnitude J_{PCH} values for phosphorus derivatives of any type.

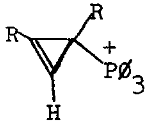
I



II

III



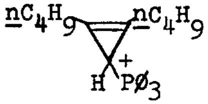
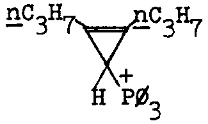
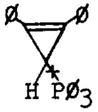
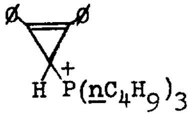
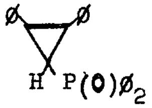


IV

Reaction of di-n-propylcyclopropenyl perchlorate and triphenylphosphine cleanly gives the phosphonium perchlorate III. The PMR spectrum (CD_3CN, 100 MHz) exhibits a one-proton doublet at τ7.13 with J = 51.2 Hz. That the product is III and not the isomeric salt IV is demonstrated not only by the high field position of the doublet but also by the presence of two equivalent n-propyl groups: τ 7.66 (4H, symmetrical multiplet); τ 8.58 (4H, sextet, J~7 Hz); and τ 9.22 (6H, triplet, J = 7.2 Hz). The chemical shift values agree well with those reported for the α, β, and γ protons, respectively, in model

Table I

Chemical Shifts and Coupling Constants of Methine Protons[a]

Cpd.	τ	$^{J}_{PCH}$	Solvent
	7.23	52.0 Hz	CD_3CN
	7.13	51.2	CD_3CN
	6.08	47.1	CD_3CN[b]
	7.33	42.8	CD_3CN
	7.21	40.8	$CDCl_3$[c]

[a] All spectra obtained at 100 MHz except as indicated; values accurate to ± 0.2 Hz; all salts are perchlorates at concentrations $< 10\%$; no apparent concentration effects.

[b] 60 MHz

[c] sparingly soluble CD_3CN

1,2-di-n-propylcyclopropenes containing an electron-withdrawing group in the 3-position(3).

The phosphonium salts in Table I were similarly prepared utilizing the appropriate phosphine and disubstituted cyclopropenyl perchlorate. In all compounds listed J_{PCH} greatly exceeds values generally characteristic of phosphonium salts (11-16 Hz) (4,5) as well as values quoted for phosphorus compounds of diverse functionality (0-36 Hz) (6). The coupling constant is sensitive to the nature of the substituents on the ring and on phosphorus.

The relationship between structure and both sign and magnitude of proton-phosphorus coupling constants is a subject of much current discussion (4-10). Some trends are discernible and when applied to the data here they allow tentative conclusions to be offered. Of prime interest are the abnormally

Table II

Chemical Shifts and Coupling Constants of the Methine Proton in Diphenylcyclopropenyltriphenylphosphonium Salts (I, R=R'=Ø)

Anion	$CDCl_3$	CD_3CN	DMSO-d_6
BF_4^-	τ 5.96 (J, 48.4 Hz)	6.07 (47.0)	5.56 (46.6)
ClO_4^-	6.07 (47.6)	6.08 (47.2)	
Br^-	5.39 (48.0)	5.92 (47.6)	

large coupling constants listed in Table I. The geminal coupling constant, J_{PCH}, can either be positive or negative. In phosphonium salts where phosphorus is bound to $\underline{sp}^3$ hybridized carbon, the corresponding J_{PCH} is negative in sign (5,8,9). Recent analysis of the spectra of two vinyl phosphonium salts demonstrated that the geminal (21-24 Hz) and vicinal vinyl proton-phosphorus coupling constants have the same sign (10). Since the vicinal proton-phosphorus coupling constant, J_{PCCH}, is taken to be positive (6,8), there is an apparent sign reversal for J_{PCH} in phosphonium salts where phosphorus and proton are bound to an $\underline{sp}^2$ hybridized carbon. From this we tentatively conclude that J_{PCH} in the cyclopropenyl salts is positive in sign. If the above is correct then the larger positive J_{PCH} in the cyclopropenyl salts as compared to those in the vinyl phosphonium salts is not unreasonable. The carbon-13-proton coupling constant in 1-methylcyclopropene indicates approximately 35% $\underline{s}$ character for the methylene carbon-hydrogen bond(11). Available data suggest that J_{PCH} becomes more positive as the $\underline{s}$ character of the carbon atom bonding orbital to phosphorus increases (8). Additional data is needed on compounds structurally related to those reported here before more definite correlations can be made.

Table II summarizes the effect of anion and solvent on τ and J_{PCH} for the methine proton in diphenylcyclopropenyltriphenylphosphonium salts. The results are generally in accord with those obtained in studies of tetraalkyl/aryl phosphonium salts (4). The chemical shifts are solvent dependent and there is a discernible dependence on solvent of J_{PCH} in the case of the fluoroborate salt. Both τ and J_{PCH} were found to be independent of halide ion in the tetraalkyl/aryl phosphonium salts (4). Our results show that such lack of dependence on anion is not general.

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