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UNUSUALLY LOW PCH COUPLING CONSTANTS IN THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF PHOSPHONIUM SALTS AND PHOSPHINE OXIDES

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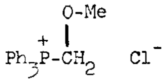
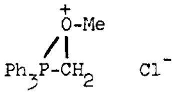
The geminal PCH coupling constants of the NMR spectra of phosphonium salts are commonly in the range 11 - 16 c/sec. However there are a few examples of unusually low values. Hendrickson, Maddox, Simms and Kaesz(1) observed one such example for the phosphonium salt (I) (J_{PCH} = 4 c/sec.) and put forward a tentative suggestion that fitted in with their general hypothesis that the s character of the phosphorus bonding orbitals was the major factor in determining the size of J_{PCH}. They considered that an electronegative group attached to phosphorus increases the s character of the phosphorus orbitals which point to alkyl carbon atoms and this in turn increases J_{PCH}. To explain the low coupling constant of (I) they suggested that the phosphorane form (II) made a contribution to the structure of the salt.



$Ph_3\overset{+}{P}-\overset{\overset{O-Me}{|}}{CH_2}\quad Cl^-$

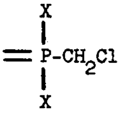
I



II

We assume from this that apart from reducing the positive charge, this contribution was expected to decrease the s character of the phosphorus bonding orbital directed towards the methylene carbon atom and the coupling constant accordingly.

Nixon and Schmutzler(2) examined a number of compounds with the partial structure (III) where X = electronegative atom or group and observed a range of values for J_{PCH} from 3.9 to 12.2 c/sec. Applying Hendrickson's ideas these workers expected the



$$=\overset{\overset{\textstyle X}{|}}{\underset{\underset{\textstyle X}{|}}{P}}-CH_2Cl$$

III

groupings to divert a large degree of s character into the orbitals of phosphorus which point towards the $-CH_2Cl$ group and thus to increase J_{PCH}, but their data showed that this is not generally the case.

Manatt, Juvinall, Wagner and Elleman(3) have determined the relative signs of PH, PCH and HPCH couplings for methyl-, dimethyl- and trimethylphosphine and found them all to be positive. The PCH couplings for triethylphosphine and the methylphosphines, which all have low s character ($<$10%) in the bonding orbitals of phosphorus, were close to zero and J_{PCH} was found to become more negative as the phosphorus atom bonding orbitals gain s character. The large HCP couplings of phosphonium salts (14.4 c/sec. for tetramethylphosphonium iodide) which should have phosphorus bonding orbitals possessing 25% s character, are therefore most certainly negative. From the large positive shift of J_{PCH} for trivinylphosphine (sp^2 hybridised carbon atom), it was deduced that the effect of the electronegative methoxyl group in (I) is to increase the s character of the bonding orbitals of carbon to phosphorus and cause a positive shift for J_{PCH}.

We have examined the spectra of a series of compounds of the type (IV), in which the electronegativity of the group X is varied. The parameters for the spectra are given in Table 1.

$$Ph_3\overset{+}{P}-CH_2X \quad Hal^-$$

IV

TABLE 1.

Coupling Constants and Chemical Shifts for the Aliphatic Protons
of the Triphenylphosphonium Salts.

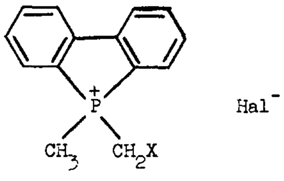
Salt	Solvent	PCH_2X ppm.	J_{PCH} c/sec.	Remarks
$Ph_3\overset{+}{P}CH_2OH\ Cl^-$	$CDCl_3$	4.49	0	singlet
	CF_3CO_2H	4.37	1.5	
$Ph_3\overset{+}{P}CH_2OMe\ Cl^-$	$CDCl_3$	4.18	4.0	See Hendrickson et al.(1)
	CF_3CO_2H	4.81	4.0	
$Ph_3\overset{+}{P}CH_2Cl\ Cl^-$	$CDCl_3$	3.68	6.0	
	CF_3CO_2H	4.93	6.3	
$Ph_3\overset{+}{P}CH_2Br\ Br^-$	$CDCl_3$	3.78	6.0	See Driscoll et al.(4)
	CF_3CO_2H	5.20	6.3	
$Ph_3\overset{+}{P}CH_2I\ I^-$	CF_3CO_2H	5.45	7.8	Spar Sol. $CDCl_3$

It has been reported(5) that the type of halide ion in methyltriphenylphosphonium salts does not affect the P-methyl coupling constant. Therefore the marked changes of J_{PCH} shown by the salts in Table 1 must be due to the substituent X. The geminal coupling constant increases in the order:

$$J_{PCH_2OH} < J_{PCH_2OCH_3} < J_{PCH_2Cl} = J_{PCH_2Br} < J_{PCH_2I}$$

The trend is clearly for the coupling constant to increase as the electronegativity of X decreases. Evidence will be presented later in this paper that these coupling constants are negative. The methylene resonance of the hydroxymethylphosphonium salt (IV, X = OH) in deuterochloroform solution appears as a singlet but in trifluoroacetic acid solution it is a closely spaced doublet with J_{PCH} = 1.5 c/sec. (The change in coupling constant and chemical shift for α protons in trifluoroacetic acid as compared with deuterochloroform has been discussed by Griffin and Gordon.)(5)

We have also examined the spectra of several salts of the general structure (V) in which the phosphorus atom bears a methyl group as well as a substituted methyl group.



V

The hybridisation changes at the methyl carbon atom in the methylphosphine series(3) have been shown to be small and we therefore expect the P-Me coupling to reflect hybridisation changes that occur at the phosphorus atom. The parameters of these spectra are given in Table 2.

TABLE 2.

Coupling Constants and Chemical Shifts for the Aliphatic Protons of the 9-Phosphafluorene Salts (V).

Salt	Solvent	PCH_2X ppm.	J_{PCH_2X} c/sec.	CH_3 ppm.	J_{PCH_3} c/sec.
Va, X = OH, Hal = Br^-	$CDCl_3$	4.74	0	7.15	15.4
	CF_3CO_2H	4.82	1.1	7.50	15.0
Vb, X = OMe, Hal = Cl^-	$CDCl_3$	4.40	4.4	7.05	15.6
	CF_3CO_2H	5.31	4.8	7.57	15.0
Vc, X = Cl, Hal = Cl^-	$CDCl_3$	4.07	8.0	6.81	15.6
	CF_3CO_2H	5.44	7.4	7.41	14.9
Ve, X = I, Hal = I^-	CF_3CO_2H	5.94	8.4	7.32	14.8
Vf, X = H, Hal = I^-	CF_3CO_2H			7.55	15.0
Vg, X = CH_3, Hal = I^-	CF_3CO_2H			7.55	14.7

Like the corresponding triphenylphosphonium salts the size of the methylene coupling constants increase as the electronegativity of X decreases. In contrast the methyl PCH coupling constants of the salts (Va-e) do not change and in trifluoroacetic acid the constants are, within experimental error, the same as those shown by the dimethylphosphonium salt (Vf) and the methylethylphosphonium salt (Vg). These results indicate that there is little or no increase in the s character of the bonding orbitals of the phosphorus atom. We accept that the phosphorus bonding orbital to the methyl carbon atom will not experience exactly the same change as the phosphorus bonding orbital to the methylene carbon atom.

However the absence of any changes for the former would imply that the changes in the latter are quite small and that the low PCH coupling constants are due mainly to rehybridisation at the methylene carbon atom.

Several workers(6, 7) have indicated that the s orbital of an atom tends to concentrate in the hybrid orbitals that are directed to the less electronegative atoms, and it has been found(8) that halogen and oxygen atoms bonded to a methyl group cause the geminal coupling constant to decrease (in fact, a positive shift for a negative constant) When two electronegative groups are bonded to a methylene group we would expect an even larger proportion of s character to be directed into the bonding orbitals of carbon which point to hydrogen and a corresponding larger decrease in the geminal coupling constant. A positively charged phosphorus atom (bonded to the methylene group) will act as an electronegative group as well as a probe for detecting hybridisation changes on the carbon atom. Thus for the grouping $\overset{+}{P}\text{-}CH_2\text{-}X$ we would predict that so long as there are no hybridisation changes for the phosphorus atom, J_{HCH} and J_{PCH} will show fairly large positive shifts. Our results confirm this prediction for J_{PCH}.

The parallel changes in J_{HCH} and J_{PCH} give further confirmation that the geminal coupling for phosphonium salts is negative. Further the trend for the low coupling constant of the salts (IV) and (V) to decrease with rising electronegativity of X indicates that these coupling constants also have a negative sign.

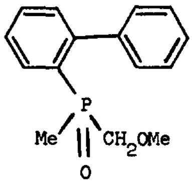
Similar effects on the size of the coupling constant would be expected to occur for phosphine oxides and phosphine sulphides.(2) The spectra of the phosphine oxides (VI) and (VII)(9) (see Table 3) confirm this; the oxides exhibit high P-methyl geminal coupling and low $P\text{-}CH_2X$ coupling.

TABLE 3.

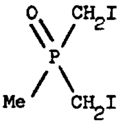
Coupling Constants and Chemical Shifts for the Aliphatic Protons of the Phosphine Oxides.

Oxide	Solvent	CH_2X ppm.	J_{PCH_2X} c/sec.	CH_3 ppm.	$J_{P\text{-}CH_3}$ c/sec.
VI	$CDCl_3$	6.4	5.3	8.55	13.4
VII(9)	$CDCl_3$	6.59	7	8.08	13

It is also apparent that the phosphine oxides are most unlikely to have contributing phosphorane forms as a cause for the low coupling constants.(1)



VI



VII

The preparation and characterisation of the new compounds will be reported later as part of another programme.(10) The NMR spectra were obtained using a Perkin-Elmer R10 spectrometer with TMS as an internal reference and the coupling constants were determined from spectra expanded to 1 c/sec. per unit.

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