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# $C^{13}$ NMR SPECTRA OF ORGANOPHOSPHORUS COMPOUNDS; DETERMINATION OF SUBSTITUENT CONSTANTS FOR PHOSPHORUS CONTAINING GROUPS

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Systematic investigations of carbon shieldings in organophosphorus compounds are conspicuously absent from the literature of NMR spectroscopy. Despite recent advances in organophosphorus chemistry, the electronic structures of these compounds are not well understood and little quantitative data on the electron attracting or donating ability of phosphorus substituents are available.[1] The demonstrations of empirical correlations between carbon shielding and electronic distributions in molecules[2,3] prompted us to obtain and analyze the $C^{13}$ NMR spectra of selected organophosphorus compounds. We wish to report the $C^{13}$ chemical shifts of para carbons in $C_6H_5PZ_n$ structures and the derivation of substituent constants ($\sigma_p$, $\sigma_p^+$) for the $-PZ_n$ groups from this data.

Spiesecke and Schneider have shown that the general trend of para carbon shieldings ($\delta_p$) in monosubstituted benzenes is consistent with that expected from changes in $\pi$-electron density at the para carbon atom; a near linear correlation with Hammett substituent constants ($\sigma_p$) was obtained.[3] Although these authors explicitly state that the scatter of individual datum is sufficiently great that the usefulness of the correlation is limited, a statistical analysis of their data revealed that the root-mean-square of the $\sigma_p$-deviations about the curve resulting from a least squares fit was only

0.16. The largest deviation for a single $\sigma_p$ value was 0.26, the range of values studied being -0.83 to +0.778. Such deviations, though by no means trivial, are not so large as to preclude the approximation of $\sigma_p$ constants by this method. For substituents (e.g. $-PZ_n$) for which only a very few reactivity constants are available in the literature, approximate values can be derived from $\delta_p$. These values should possess sufficient validity to serve as useful guidelines until determinations of substituent constants by conventional methods are made.

The determination of $\sigma_p$ values by chemical methods has been reported for only four $-PZ_n$ groups: $-PO_3H^-$ (+0.17),[4] $-PO_3^=$ (-0.16),[4] $-PO_2H^-$ (+0.14)[5] and $-P(O)(OC_2H_5)_2$ (+0.60).[6] Unfortunately, the limited solubility in basic solution of the acids necessary for the determination of $\sigma_p$ for the first three groups prevented $C^{13}$ NMR studies. However, the spectrum of $C_6H_5P(O)(OC_2H_5)_2$ was obtained; $\delta_p$ indicated a $\sigma_p$ value of +0.55 (Table I) which is in good agreement with the reported[6] value (+0.60). $\delta_p$ were measured for nine additional compounds and, with the exception of dimethyl phenyl phosphate, proved to be less than the shielding in benzene indicating $\pi$-electron densities at the <u>para</u> carbon to be $\leq 1$ and $\sigma_p$ to be $\geq 0$. These results indicate these substituents to be moderate to weak electron attractors in accord with expectation.[1] $\sigma_p$ constants calculated from $\delta_p$ for all compounds investigated are given in Table I.

Although $\sigma_p$ constants have been determined chemically for only one of the ten substituent groups investigated, $\sigma_p^+$ values have been measured recently for two of these groups; a competitive free radical bromination procedure was employed.[1b] An attempt to correlate the data of Spiesecke and Schneider with $\sigma_p^+$ values was undertaken and resulted in a least squares fit at least as good as that for the $\sigma_p$ constants, although the relationship proved to be non-linear. $\sigma_p^+$ values obtained from $\delta_p$ for the ten organophos-

### TABLE I.

*Para* Carbon Shieldings and Chemical Reactivity Parameters for $C_6H_5PZ_n$[a]

| $-PZ_n$ | *Para* Carbon Shielding[b] | $\sigma_p$ | $\sigma_p^+$ |
|---|---|---|---|
| $-P(C_6H_5)_2$ | -5.9 | 0.68 | 0.70 |
| $-PCl_2$ | -4.9 | 0.61 | 0.62 |
| $-P(O)(OC_2H_5)_2$ | -4.0 | 0.55 | 0.54 |
| $-P(O)(C_6H_5)_2$ | -3.8 | 0.53 | 0.52 |
| $-P(Cl)C_6H_5$ | -2.5 | 0.44 | 0.40 |
| $-P(O)Cl_2$ | -2.3 | 0.43 | 0.38 |
| $-P(S)Cl_2$ | -1.8 | 0.39 | 0.33 |
| $-P(OC_2H_5)_2$ | -1.0 | 0.33 | 0.24 |
| $-P(OC_2H_5)(C_6H_5)$ | -0.9 | 0.32 | 0.23 |
| $-OP(O)(OCH_3)_2$ | +2.8 | 0.04 | -0.21 |

[a] The spectra of triphenylphosphine and the oxide were determined on solutions in $CS_2$ and acetone, respectively; all other spectra were determined on neat samples.

[b] In p.p.m. from benzene.

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phorus groups are also given in Table I. The spectrometrically obtained values for $-P(O)(OC_2H_5)_2$ (+0.54) and $-P(O)(C_6H_5)_2$ (+0.52) agree reasonably well with the chemically determined values (+0.62 and +0.49).[1b] In the absence of independent confirmation, $\sigma_p$ and $\sigma_p^+$ values for the $-PZ_n$ groups of Table I must be used cautiously and considered to be only approximate. However, it must be pointed out that the inherent chemical sensitivity of certain of these groups may prevent the determination of substituent constants by chemical reactivity studies. In these cases, spectrometric methods may represent the only feasible approaches to these determinations.

$C^{13}$ NMR studies of selectively deuterated analogs are in progress in order to provide unambiguous assignments of the *ortho* and *meta* $C^{13}$NMR signals.

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