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AN ABNORMALLY LOW P-N-C-H COUPLING CONSTANT

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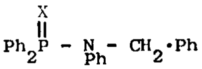
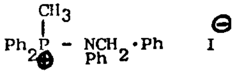
The nuclear magnetic resonance spectra of a number of aminophosphines of the type $R_2P\text{-}NR^1R^2$ have been studied and values of $J_{P-N-C-H}$ are normally between 8-19 Hz$^{(1)}$. During the course of some other work we have prepared an aminophosphine with a $J_{P-N-C-H}$ value which is both abnormally low and temperature dependent.

In o-xylene solution at 20° N-phenylbenzylaminodiphenylphosphine ($PhCH_2NPh\cdot PPh_2$) (1) (m.p. 113-114°, prepared from diphenylchlorophosphine and lithium N-benzylanilide in ether at -50°) has a doublet at τ 5.40, $J_{P-N-C-H}$ = 1.4 Hz. The value of $J_{P-N-C-H}$ for the aminophosphine (I) was shown to be temperature dependent, varying from 1.4 Hz at +20° to 2.8 Hz at +100° in o-xylene solution. That a coupling constant rather than a chemical shift was being observed was confirmed by spectra at both 60 mHz and 100 mHz. Spin decoupling throughout the aromatic proton region failed to effect the observed coupling in any way.$^{(2)}$ The values of $J_{P-N-C-H}$ for the aminophosphine oxide (2a) (9.5 Hz at +25°), τ 5.39 ($CDCl_3$), the aminophosphine sulphide (2b) (7.6 Hz at +23°), τ 5.45 ($CDCl_3$), and the methiodide (3) (8.0 Hz at +23°), τ 5.26 ($CDCl_3$) are not abnormal, nor are they temperature dependent within the limits of accuracy of our measurements. Dibenzylaminodiphenylphosphine (4) (m.p. 79-80°) showed a doublet at τ 5.88, $J_{P-N-C-H}$ = 9.2 Hz ($CDCl_3$) and its oxide, m.p. 130-131°, showed a doublet at τ 5.95, $J_{P-N-C-H}$ = 10.0 Hz ($CDCl_3$).



$Ph_2\overset{X}{\overset{\|}{P}} - \underset{Ph}{N} - CH_2\cdot Ph$

2 (a) X = O
(b) X = S



$Ph_2\overset{CH_3}{\overset{|}{\overset{\oplus}{P}}} - \underset{Ph}{N}CH_2\cdot Ph \quad \overset{\ominus}{I}$

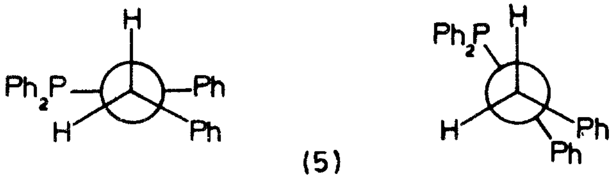
(3)

$Ph_2P - N(CH_2Ph)_2$

(4)

Application of Mislow's rules$^{(3)}$ shows that the benzylic hydrogens in (1) are enantiotopic and hence magnetically equivalent in achiral solvents. Restricted rotation about the P-N bond appears to be irrelevant and the variation in coupling is much greater than would be expected from conjugation effects.$^{(4)}$ The results are best explained by conformer population effects.

Space filling models suggest considerable crowding in (1) and if nitrogen inversion is rapid, the conformations (5) appear to be most favourable. The magnitude of phosphorus-



(5)

hydrogen coupling has been shown to vary with dihedral angle in a number of systems.(5) We suggest that conformer populations in (1) are such that the average dihedral angle leads to the value of $J_{P-N-C-H}$ observed. This explanation is supported by the small variation of $J_{P-N-C-H}$ with temperature since changes in conformer population with temperature are usually small.(6) The "normal" value of $J_{P-N-C-H}$ for the diphenylaminophosphine (4) also supports this explanation.

The absence of similar effects in the phosphine oxide (2a), sulphide (2b) and methiodide (3) is possibly due to differences in hybridisation from the aminophosphine (1). The direct dependence of coupling constants on changes in hybridisation is well known(7) and the different spatial effects of p^3 phosphorus in (1) and sp^3 phosphorus in (2) and (3) probably influence the steric interactions during rotation about the N-C bond.

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