

^{13}C MAGNETIC RESONANCE OF SOME CIS AND TRANS SUBSTITUTED
ETHYLENE PHOSPHINES

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Spin-spin coupling between ^{13}C and ^{31}P in mainly saturated compounds have been reported in the literature (1-7). A recent paper on heteroaromatic phosphine derivatives (8) prompts us to report some preliminary results on cis and trans substituted ethylene phosphines.

The ^{13}C spectra were obtained on a VARIAN XL-100-15 spectrometer operating at 25.2 MHz. Field/frequency lock was established via the deuterium resonance of C_6D_6 used as a solvent (ca. 50 % v/v). Chemical shifts are reported in ppm downfield from TMS. Single scan proton noise decoupled (9) spectra were obtained with 12 mm sample tubes at sweep widths of 10 and 20 Hz/cm. 2 Hz/cm spectra were run with the aid of a C-1024 CAT.

Signals assignable to the OC_2H_5 , $\text{N}(\text{CH}_3)_2$ and $t\text{-C}_4\text{H}_9$ carbons were identified from known substituent effects (1,10,7). Lines due to olefinic and aromatic carbons partially overlapped. The aromatic carbons $\gamma\delta$ and ϵ were assigned with the aid of intensity arguments. However, no distinction between C_δ and C_ϵ could be made.

Continuous wave proton decoupling experiments enabled the assignment of carbons α , β and ω . Irradiation of the aromatic protons left the signals from aromatic carbons unchanged, whereas the olefinic carbons were not completely decoupled (Fig. 1-b). These experiments are consistent with the previous assignment of carbons γ , δ and ϵ and unambiguously identify C_ω . Distinction between C_α and C_β was made in the same manner by consecutively irradiating the olefinic protons whose chemical shifts are known from previous studies (11) (Fig. 1-c,d).

The results are listed in table 1. The same trends are observed in the chemical shifts of $^{13}\text{C}_{\alpha,\beta}$ and $^1\text{H}_{A,B}$ which suggests that local charge density and not magnetic anisotropy effects dominate the shielding. A comparison with corresponding olefins (12,13) shows that phosphorus substitution ($\Delta\delta > 0$) deshields

- Table 1 -

$\begin{array}{c} (\text{CH}_3\text{CH}_2\text{O})_2\text{P} \\ \gamma \quad \beta \quad \alpha \\ \text{C} = \text{C} \\ \text{B}^{\text{H}} \quad \alpha \quad \beta \quad \text{H}_A \\ \text{C}(\text{CH}_3)_3 \\ \gamma \quad \delta \end{array} \quad \underline{1a}$						$\begin{array}{c} [(\text{CH}_3)_2\text{N}]_2\text{P} \\ \beta \quad \gamma \quad \delta \\ \text{C} = \text{C} \\ \text{B}^{\text{H}} \quad \alpha \quad \beta \quad \text{H}_A \\ \text{C}(\text{CH}_3)_3 \\ \gamma \quad \delta \end{array} \quad \underline{1b}$				
	δ	$\Delta\delta$	$n_{\text{J}_{\text{C-P}}}$ (n)	$^2\text{J}_{\text{P-H}_B}$	$^3\text{J}_{\text{P-H}_A}$	δ	$\Delta\delta$	$n_{\text{J}_{\text{C-P}}}$ (n)	$^2\text{J}_{\text{P-H}_B}$	$^3\text{J}_{\text{P-H}_A}$
$\text{C}_\alpha(\text{H}_B)$	131.1	+20.8	29.2 (1)	-0.2		127.1	+16.8	11.4 (1)	+0.2	
$\text{C}_\beta(\text{H}_A)$	155	+ 4.7	19.8 (2)		+23.7	151.9	+ 1.6	21 (2)		+24.9
C_γ	35.6		1.4 (3)			35.3		1.4 (3)		
C_δ	31.3		9.9 (4)			30.9		8.4 (4)		
$\text{C}_{\beta'}$	61.3		10.8 (2)			40.7		15.6 (2)		
$\text{C}_{\gamma'}$	17.3		5.3 (3)							
$\begin{array}{c} (\text{CH}_3\text{CH}_2\text{O})_2\text{P} \\ \gamma \quad \beta \quad \alpha \\ \text{C} = \text{C} \\ \text{B}^{\text{H}} \quad \alpha \quad \beta \quad \text{H}_A \\ \text{C}_6\text{H}_5 \\ \gamma \quad \delta \quad \epsilon \quad \zeta \end{array} \quad \underline{2a}$						$\begin{array}{c} [(\text{CH}_3)_2\text{N}]_2\text{P} \\ \beta \quad \gamma \quad \delta \\ \text{C} = \text{C} \\ \text{B}^{\text{H}} \quad \alpha \quad \beta \quad \text{H}_A \\ \text{C}_6\text{H}_5 \\ \gamma \quad \delta \quad \epsilon \quad \zeta \end{array} \quad \underline{2b}$				
	δ	$\Delta\delta$	$n_{\text{J}_{\text{C-P}}}$ (n)	$^2\text{J}_{\text{P-H}_B}$	$^3\text{J}_{\text{P-H}_A}$	δ	$\Delta\delta$	$n_{\text{J}_{\text{C-P}}}$ (n)	$^2\text{J}_{\text{P-H}_B}$	$^3\text{J}_{\text{P-H}_A}$
$\text{C}_\alpha(\text{H}_B)$	131.6	+17.4	24.3 (1)	+13.4		129.9	+15.7	1.1 ₅ (1)	+21.1	
$\text{C}_\beta(\text{H}_A)$	141.9	+ 4.2	33 (2)		+11.8	139	+ 1.3	20.2 (2)		+6.9
C_γ	136.9	- 1.4	10.5 (3)			138	- 0.2	5.6 (3)		
$\text{C}_\delta, \text{C}_\epsilon$	{ 127.2 128.7	{ - 1.7 - 0.2				{ 126.7 128.7	{ - 2.2 - 0.2	1.8 1.0 ₄		(4,5)
C_ζ	128.7	+ 1.5				127.8	+ 0.6	1.4 (6)		
$\text{C}_{\beta'}$	62		9.8 (2)			41.5		15 (2)		
$\text{C}_{\gamma'}$	17.5		5.0 (3)							

δ in ppm down field from TMS (50 % v/v C_6D_6)

$\Delta\delta$: phosphorus substitution effect (differences between δ in the phosphorus substituted compounds and in the parent olefins)

J in Hz

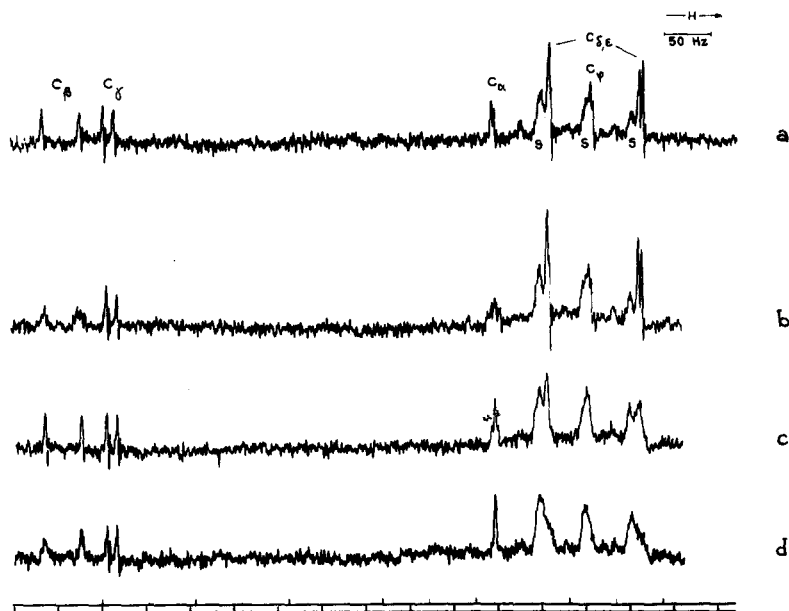


Figure 1

Low-field portion of the ^{13}C spectrum of $\text{trans } [(\text{CH}_3)_2\text{N}]_2\text{P-CH=CH-C}_6\text{H}_5$ under different double resonance conditions :

- | | |
|--|--------------------------------|
| (a) proton noise decoupled | - decoupler offset = 45 503 Hz |
| (b-d) CW proton decoupled | |
| (b) aromatic protons irradiated | - decoupler offset = 45 531 Hz |
| (c) H_A olefinic proton irradiated | - decoupler offset = 45 492 Hz |
| (d) H_B olefinic proton irradiated | - decoupler offset = 45 461 Hz |
- S : bands arising from the solvent C_6D_6

both ethylenic carbons (inductive and mesomeric effects).

To our knowledge, the given coupling constants $J(C-P)$ are the first values reported for ethylene phosphines. However only the magnitudes $|J(C-P)|$ are reported. Previous results for the aromatic and heteroaromatic phosphines gave $|^1J(C-P)| < |^2J(C-P)|$ (14,8). The same relationship was observed in the ethylene phosphines except for 1a. No simple correlation between $|^1J(C-P)|$ and $^2J(P-H)$ is evident although $|^2J(C-P)|$ and $^3J(P-H)$ seem to vary in the same manner.

Identical values of $^3J(P-H)$ in the two cis derivatives studied suggest a highly favoured conformation (11) in accordance with the results obtained for $|^2J(C-P)|$. On the other hand, the quite different values for $^3J(P-H)$ in the trans substituted compounds indicate rapid interconversion between different conformers. Equally different values for $|J(C-P)|$ might be an indication of a dependence of these coupling constants on conformation. This is being verified by variable temperature experiments.

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