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YLIDE STRUCTURE IV.[1] FORMYLMETHYLENETRIPHENYLPHOSPHORANE

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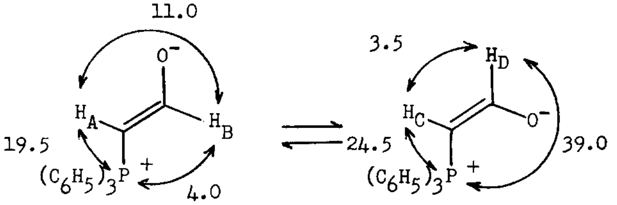
Carboalkoxyphosphoranes show hindered internal rotation[3] while ketophosphoranes do not.[1] A compound which bridges the behavior of the keto and ester functionalities is formylmethylenetriphenylphosphorane[4] (1).



trans 1 cis

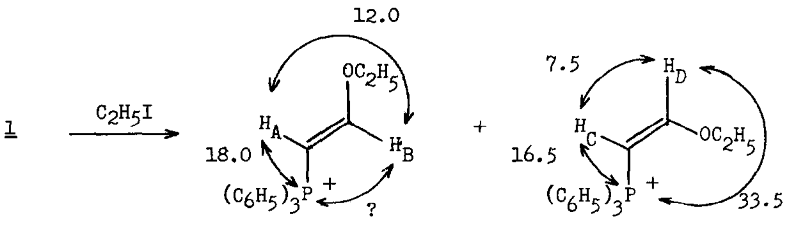
H_X	$\tau(-12^o)$
A	5.81
B	1.72
C	6.30
D	1.08

(Coupling constants in Hz)

At -12° ($CDCl_3$) two rotamers can be observed by nmr with a cis/trans ratio of 53/47 corresponding to a free energy difference of ΔG(cis-trans) = 0.063 kcal/mole. Of the two aldehydic band sets, the upfield quartet (τ=1.72) is assigned to proton H_B cis to phosphorus.[1,3] Chemical shift values for protons H_A, H_C and H_D and the appropriate H-H and P-H coupling constants are indicated above. The validity of the assignments is confirmed by deuterium exchange, spin-spin decoupling and O-alkylation.

Introduction of D_2O to a chloroform solution of phosphorane 1 causes immediate exchange of hydrogen alpha to phosphorus. The proton resonances at τ5.81 (H_A) and 6.30 (H_C) disappear while the quartets at τ1.08 and 1.72 collapse to doublets corresponding to phosphorus hydrogen coupling. Similarly rf irradiation (-12°) of protons H_A or H_C converts the quartets at τ1.72 and 1.08 respectively to doublets with the expected splitting. In accord with the well-known relationship of cis and trans coupling constants on a carbon-carbon double bond, $J_{AB} > J_{CD}$ and $J_{PD} > J_{PB}$.

An analogous nmr analysis obtains for the O-ethylation products 2 and 3 derived by treatment of 1 with ethyl iodide. Chemical shifts (τ) and J values are shown.



H_X	τ
A	3.39
B	ca. 3
C	4.30
D	1.76

2 (20%) 3 (80%)

Although the ratio of cis/trans salt in the product mixture (4:1) is not a simple function of the concentration of ylide 1 rotamers, the preparation of 2 and 3 clearly reflects the existence of such an equilibrium.

As the temperature of formylphosphorane 1 in $CDCl_3$[5] is raised, both the $H_{A,C}$ and $H_{B,D}$ multiplets broaden and merge at 80° to a broad unsymmetrical doublet and singlet respectively. At this temperature the solution has blackened, evidencing decomposition; spectroscopic reversibility is achieved, however, upon cooling. A first order rate constant of 85 sec^{-1} (80°) corresponds to a rotation barrier of $\Delta G^{\pm}$ = 17.6 kcal ± 0.5 kcal/mole.[6]

The above observations are noteworthy in several respects. Formyl ylide 1 would appear best described by the enolate formulation 1. However it exists in two conformational forms interconvertible by passage over an energy barrier of the same magnitude as that for a pair of related ester stabilized ylides 4 and 5 (R_1=CH_3,CH_2CH_3; R_2=OCH_3; 17-18 kcal/mole[3]).

4 5

This stands in sharp contrast to the static behavior of a selection of ketophosphoranes 5 (R_1 = H, CN,$COCH_3$,Cl,I;R_2=alkyl,C_6H_5) in which oxygen is exclusively cis to phosphorus.[1,7] The near 1:1 ratio of cis and trans conformers of ylide 1 indicates either that P^+/O^- attraction is negligible or that the latter is just compensated by a steric interaction between the two moieties.

The ^{31}P spectrum of ylide 1 exhibits two resonances at -15 and -19 ppm (relative to 85% H_3PO_4) in an approximate 1:1 ratio. The latter band is assignable to trans-1. β-Carbonyl triphenylphosphoranes and related salts regularly absorb in the same region ($\delta^{31}P$ = -16.9 to -22 ppm).[8] On the other hand both static and equilibrating oxyphosphoranes reveal phosphorus to be considerably shielded relative to these values ($\delta^{31}P$ = -10.8 to +49.5 ppm).[9] The implication obtains that there is little interaction of consequence between the oppositely charged $^{+}P/O^{-}$ moieties in β-ketophosphoranes. In view of the apparent importance of similar attractive forces in the phosphonium betaine intermediates of the Wittig reaction,[10] such an observation is surprising.

The divergent stereochemical behavior of formyl ylide 1 and acylmethylenetriphenylphosphorane[1] (5, R_1 = H, R_2 = CH_3), implies that steric effects play a dominant role in rigidifying ketophosphoranes in a single conformation. The steric rationale for ylide geometry has been suggested previously[7b,8a,11] as has attraction between the positive heteroatom and negative oxygen.[11] Several investigators have pictured β-carbonyl ylides with oxygen cis to phosphorus with neither supporting evidence nor comment as to the forces involved.[8b,11,12] We are investigating this point further.

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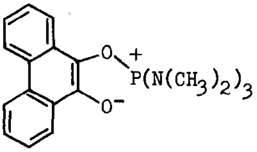
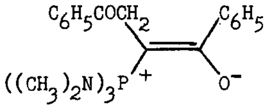


6 ($\delta^{31}P$ = -38.5 ppm)



7 ($\delta^{31}P$ = -63.2 ppm)

The spatial contiguity of O^- and P^+ in compound 6, negative oxygen providing a diamagnetic environment, could account for this difference. Rapid equilibration cannot be ruled out entirely, however, even though 6 has been represented as the open dipolar ion.

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