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YLIDE STRUCTURE. III.[1] CONFORMATIONAL IMMOBILITY OF CIS-KETOTRIPHENYLPHOSPHORANES.

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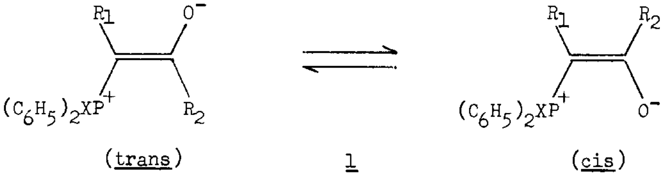
We have previously shown that a wide variety of ester stabilized phosphoranes (1, $R_2 = OCH_3$, $X = C_6H_5$) are best described by equilibrating forms 1(trans) and 1(cis).[1]



Trace quantities of a proton acid provide an alternative lower energy pathway between the configurational rotamers as a result of an extremely facile transylidation process.[3] We should like to report that while ketophosphoranes 1 (a-i), Table I, likewise experience rapid proton exchange, they evidence no other dynamic behavior in the nmr. Furthermore ylides 1 (a-i) are uniform in exhibiting cis stereochemistry.

Both in the presence and absence of acid, compounds 1 (a-e) have unaltered nmr chemical shifts and multiplicities for R_2 from -20 to +85°,[4] the temperature range in which transylidation is arrested. Additionally, the sharp methyl doublet of acyl phosphorane 1a is unchanged to 180°.[5] A similar result obtains after a 132° (chlorobenzene) solution of 1a is quenched in liquid nitrogen and the spectrum recorded at -60°. That the temperature invariant pmr spectrum of ketophosphoranes

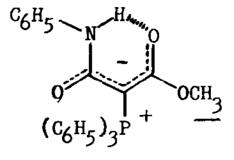
1 (a-e) is due to the presence of a single isomer, the cis rotamer, is suggested by the chemical shift values of R_2. Each correlates well with the value for the corresponding methyl ketone, a valid approximation if R_2 is trans to phosphorus. Were the alkyl moiety R_2 cis to the $(C_6H_5)_3P$ grouping, considerable shielding by the phenyl rings would be expected.[1] Confirmation of the stereochemical assignment is provided by model systems 2, 3 and 4.

TABLE I

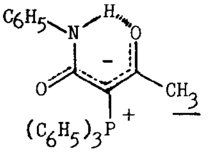
Proton NMR Spectra of Alkyl Carbonyl Substituents in Phosphorane 1. ($CDCl_3$)

1	X	R_1	R_2	R_2,τ (J_{PCH})	model ($CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}R_2$)
a	C_6H_5	H	CH_3	7.90 (d,2.0 Hz)	7.91[a]
b	C_6H_5	H	$CHCHC_6H_5$	ca3.0 (d,J_{HH}=15 Hz)	2.52 (d) 3.30 (d)[a]
c	C_6H_5	H	$CH_2CH_2C_6H_5$	7.15 (octet)	7.26, 7.47 (m)[a]
d	C_6H_5	H	$CH_2C_6H_5$	6.41 (d,2.0 Hz)	6.30[$(C_6H_5CH_2)_2CO$][b]
e	C_6H_5	H	$CH(C_6H_5)_2$	5.01 (d,2.0 Hz)	4.92[a]
f	C_6H_5	CN	CH_3	7.66 (d,2.0 Hz)	7.91[a]
g	C_6H_5	$COCH_3$	CH_3	7.78 (d,2.0 Hz)	7.91[a]
h	CH_3	H	CH_3	7.94 (d,2.0 Hz)	7.91[a]
i	CH_3	CN	CH_3	7.72 (d,2.0 Hz)	7.91[a]

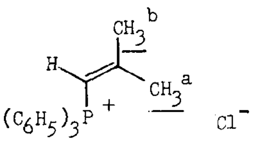
a) F.A. Bovey, "NMR Data Tables for Organic Compounds," Vol. 1, Interscience Publishers, New York, 1967. b) H.A. Szymanski and R.E. Yelin, "NMR Bond Handbook," IFI/Plenum, New York, 1968.



2



3



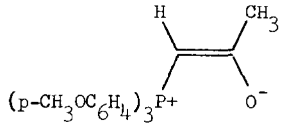
4

CH_3(τ): 6.78 8.54 a. 8.24
b. 7.69

Phosphorane 2, obtained by C-carbamoylation of the ester ylide 1 (R_1 = H, R_2 = OCH_3, X = C_6H_5), shows a single shielded methyl in the nmr at τ6.78, providing assurance that hydrogen bonding (NH,τ-1.44) affords methoxy cis to phosphorus.[1,6] Likewise the methyl of adduct 3[7] is observed as a single sharp resonance at τ8.54 (NH, τ-2.96). The geometrically related vinyl phosphonium salt 4[8] possesses both a shielded and a deshielded methyl (Δδ = 33Hz). A methyl group β and cis to the triphenyl phosphorus functionality thus experiences a diamagnetic shift of 30-40 Hz as compared to methyl situated trans. This is somewhat larger but comparable to observations in the ester series[1] ($\Delta\delta$ = 14-31Hz). Thus ketophosphoranes 1 (a-e) do not evidence hindered internal rotation at nmr temperatures and can confidently be assigned cis stereochemistry. Furthermore it is clear that phosphorus ketoylides possess highly developed enolate character (1(cis)), structures such as $(C_6H_5)_3P{=}CH\text{-}COCH_3$ and $(C_6H_5)_3\overset{+}{P}\text{-}\bar{C}H\text{-}COCH_3$ playing a minor role in the overall resonance hybrid.

These stereochemical and electron distribution findings for ketophosphoranes in solution are in accord with X-ray diffraction measurements on two related compounds,[9] and infrared[10] and ^{31}P data.[10,11]

Considering the relatively low barrier to rotation for ester stabilized ylides,[1] it became of interest to determine its magnitude in the keto series. Our approach has been to modify the electronic and steric character of the system by substitution in order to provoke a rotation response.[12] Compounds 1(f,g) possess powerful electron withdrawing groups at carbanion carbon, each of which might be expected to reduce the indicated carbon-carbon double bond character. Models indicate substantial reduction of steric interaction between cis methyl and the triphenylphosphorus residue upon replacement of P-phenyl for P-methyl (1h). Phosphorane 1i employs a complimentary combination of the steric and resonance features. Finally the trianisyl derivative 5 was prepared in order to reduce the importance of possible coulombic interaction between phosphorus and oxygen.[13] In no case was more than a single isomer observed at all temperatures accessible to the nmr method. Acyl methyl chemical shifts are without exception consistent with the cis-relationship between phosphorus and oxygen.



τ_{CH_3} = 7.96

5

Further studies are underway in order to discern the nature of the energy barrier between cis and trans rotamers of ketophosphoranes and the factors responsible for its shape.

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