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YLIDE STRUCTURE. V.[1] MEDIUM EFFECTS ON PHOSPHORANE ROTATIONAL EQUILIBRIA: STERIC INHIBITION TO SOLVATION.

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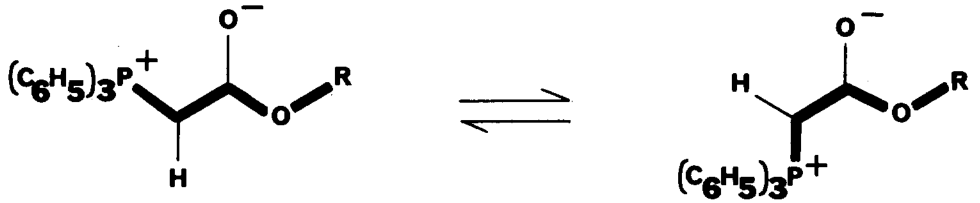
Considerable insight into ylide structure has been provided by monitoring the nmr sensitive internal rotation about carbons *alpha* and *beta* to phosphorus in carbonyl stabilized phosphoranes. Ester substituted systems rotate readily,[2] while keto derivatives exist on the nmr time scale as static conformers with oxygen usually *cis* to phosphorus.[3] The aldehyde analog, formylmethylenetriphenylphosphorane, mimics the latter in its motional behavior.[1,3b,4] A few sulfur ylides have likewise been examined for rotation by variable temperature nmr.[5]

In the overwhelming number of cases studied, deuterochloroform has been utilized as solvent presumably because of its ready availablility and convenient solubility properties. We should like to report that a profound solvent effect obtains for the equilibrium associated with the hindered internal rotation process, and that chloroform occupys a unique position in the spectrum of solvents employed. In addition the low energy conformation within the ylide ester group has been defined in agreement with conclusions reached by employment of other techniques.

The variable temperature nmr spectra of compounds **1**, with substituent variation in the ester moiety,[6] were measured in $CDCl_3$. Remarkably the rotamer ratio ($K_{\underline{cis}/\underline{trans}}$) inverts from strongly *cis* preferred to *trans* preferred as the volume occupied by R increases. Progressive alignment of the bulky groups $-P(C_6H_5)_3$ and -OR on the same side of the partial double bond is indicated for three series of phosphoranes in Table I.

The unusual dependence of ylide stereochemistry on the size of R occurs in other solvent systems as well (Table II). In polar as well as nonpolar media there is an inverse relationship between the size of R and $K_{\underline{cis}/\underline{trans}}$. In addition, for a given R, as the polarity of the solvent matrix increases, the equilibrium shifts in the direction of the *trans* rotamer. An exception to the smooth response of $K_{\underline{cis}/\underline{trans}}$ to solvent polarity obtains for $CDCl_3$. *Trans*-1 is stabilized more effectively by deuterochloroform (D = 4.70) than by acetonitrile (D = 37.5) and nitromethane (D = 38.6). The chlorocarbon solvent evidently associates with negative oxygen by a hydrogen bonding interaction. Addition of a more traditional hydrogen-bonding component to the solution, in this case an alcohol, enhances the *cis*-*trans* conversion to an even greater extent. The Lewis acid, LiBr, furnishes the polar extreme, even the methyl ester ylide preferring the *trans* conformation. Isomer ratios of nonidentical charge-separated rotamers obtained in chloroform must consequently be interpreted with caution. The ability of chloroform to participate in hydrogen-bonding in other systems has not gone unnoticed.[7]

In sum, either separately or in unison, large R and increasing solvent aggregation about the ester carbonyl favor a relatively high population of *trans*-1. The regular variation of $K_{cis/trans}$ found for ylides **1** can be reasonably interpreted as a result of steric inhibition to solvation. The R dependence thus requires a *syn* relationship between carbonyl oxygen and R as the dominant low energy geometry within the ester moiety.[8]



cis-W **trans-S**

When two bulky groups (e.g. $-P(C_6H_5)_3$ and R) occupy the wings of the W, as in *cis*-**W**, negative oxygen is protected from the solvent medium. So long as little energy is gained by solvation, crowding effects between alkoxy and triphenylphosphorus groups can be avoided, while P^+/O^- attraction is maximized in the W conformation. The latter features are overwhelmed, however, by strong medium-solute association. The *trans*-**S** rotamer then competes favorably as the low energy equilibrium partner.[9,10]

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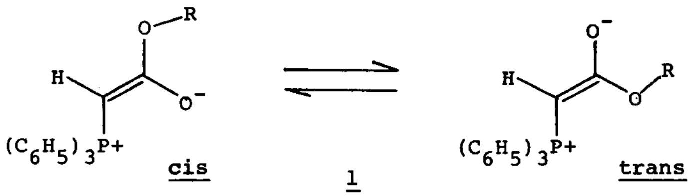

TABLE I:[a,b] Cis/Trans Ratios for Phosphorane 1 in $CDCl_3$.

R	$K_{cis/trans}$	R	$K_{cis/trans}$	R	$K_{cis/trans}$
CH_3	4.6	CH_3	4.6	CH_3	4.6
CH_2CH_3	1.8	CH_2CH_3	1.8	$CH_2C_6H_5$	2.1
$CH(CH_3)_2$	1.0	$CH_2C(CH_3)_3$	0.88	$CH(C_6H_5)_2$	0.84
$C(CH_3)_3$	0.50				

TABLE II:[a,b] Cis/Trans Ratios for Phosphorane 1 in Various Solvents.

Solvent (D,E_t)[c]	CH_3	CH_2CH_3	$CH(CH_3)_2$	$C(CH_3)_3$
CCl_4 (2.23,32.5)	cis only	6.2	2.6	2.1
C_6H_6 (2.27,34.5)	cis only	5.9	2.9	1.8
CD_3CN (37.5,46.0)	~5	2.3	1.3	0.57
CD_3NO_2 (38.6,46.3)	4.0	2.4	1.4	0.62
$CDCl_3$ (4.70,39.1)	4.6	1.8	1.0	0.50
$CDCl_3/CH_3OH$[d] (5:1)	1.9	0.83	0.37	0.11
$CDCl_3/LiBr$[e]	0.74	0.57	0.32	0.14

a) All nmr spectra were taken in the presence of basic Al_2O_3 from -10 to 0° at concentrations from 0.2-0.7M. No significant dependence of $K_{cis/trans}$ upon concentration occurs over this range.

b) Each low temperature spectrum was integrated a minimum of ten times.

c) C. Reichardt, Ang. Chem., Int. Edn., 4, 36 (1965).

d) tert-Butyl alcohol was utilized for R = CH_3.

e) A few mg of anhydrous LiBr were introduced into the nmr tube, the latter was shaken and the spectrum was recorded as usual.

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