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YLIDE STRUCTURE. II. ROTATIONAL DYNAMICS OF METHOXYCARBONYL-METHYLENETRIPHENYLPHOSPHORANES BY NMR.[1]

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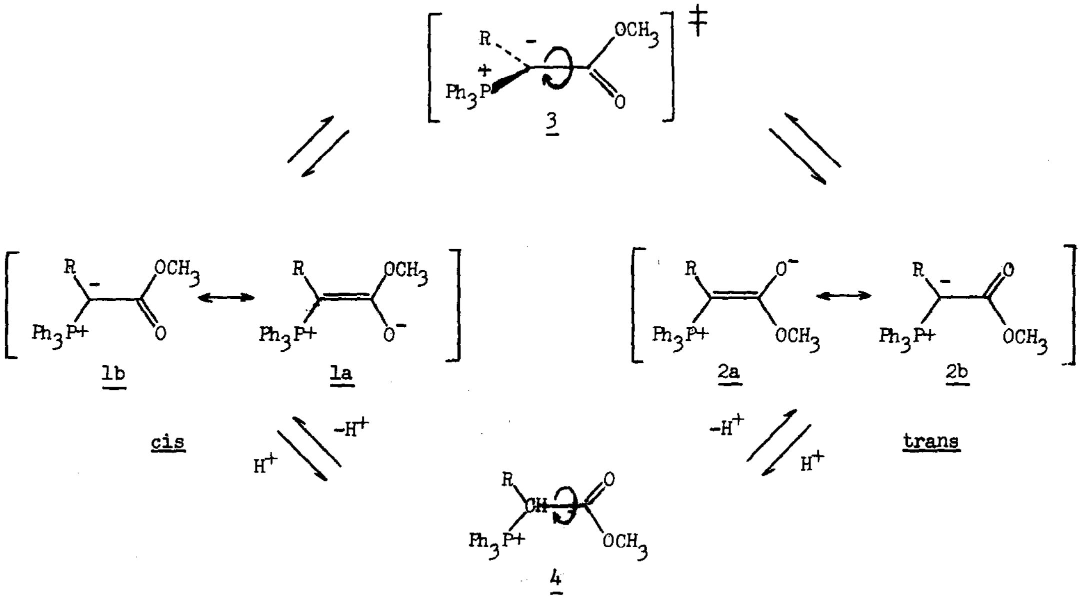
Hindered internal rotation in molecular systems is conveniently appraised by variable temperature NMR. Several laboratories have employed this technique to study the dynamics of selected phosphorus[3] and sulfur[4] ylides stabilized by alpha-carbonyl. Only recently has it been recognized that a second temperature dependent process, reversible proton exchange, operates simultaneously with the hindered rotation.[3cd,4b,5] Exclusion of acid traces not only precludes the acid-base reaction but significantly raises the energy barrier to rotation.[5]



We have measured the variable temperature spectra of a series of methoxycarbonyl phosphoranes in deuterochloroform under acid free conditions as indicated in Table I. Coalescence temperatures in the absence of trace quantities of DCl found in commercial $CDCl_3$ are roughly 30° higher for rotation through transition state *3* than by way of the intermediate phosphonium salt *4*. The overall response of the *pure rotation process* to substituent effects is clearly delineated both with respect to conformational preference in the ground state (rotamer population) and to ease of rotation (T_c).

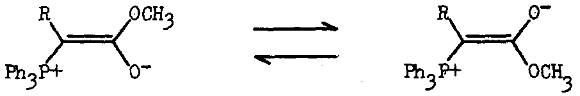
Assignment of rotamer populations is based on the chemical shift of the methyl ester absorption which appears as a rotation averaged singlet at temperatures above the coalescence temperature (T_c) and an unsymmetrical doublet at lower temperatures. The downfield band (τ 6.26-6.40) attributable to *cis* rotamer *1* correlates with the value for simple methyl esters (τ 6.2-6.4). The NMR spectra of stereochemically defined salts derived by O-alkylation of cyclic and acyclic triphenyl phosphoranes allow confident assignment of the upfield absorption (τ 6.64-6.87) to the O-methyl of *trans*-2.[6]

Conformer ratios demonstrate that phosphorane stereochemistry is sensitive to substituent steric bulk at carbanion carbon. The thermodynamic rotamer balance shifts from *cis*-preferred to *trans* preferred in the order: R = H, $CH_3 \sim C_2H_5$, *n*-Pr ~ *n*-Pent, *i*-Bu, *i*-Pr. ($\Delta G_{cis/trans}$) varies regularly from -0.93 to +0.58 kcal/mole; Table I). The steric order reverses itself for aromatic substituents. In every case the *cis* rotamer is favored by 2:1 over the *trans*. A stereoelectrostatic effect can be invoked to account for the observed ratio.

While the isomer ratio mirrors the free energy difference between equilibrium concentrations of rotamers, the coalescence temperature reflects diminished importance of carbon-carbon double bond character as depicted by resonance structures *1b* and *2b* and/or unfavorable ground state steric interactions which may be relieved by twisting through transition state *3*. Except for one case (R = *i*-Pr) the coalescence temperatures are consistent with electron release in the order: alkyl > H > aryl.[3b] The corresponding decrease in double bond character is further verified by the observed gradations in the aryl series. The divergence of the iso-propyl derivative is probably due to ground state steric destabilization which lowers T_c relative to the other alkyl ylides. Steric interference for this compound is strongly evidenced in its low temperature rotamer ratio.

TABLE I

Variable Temperature Proton NMR Spectra of Phosphorane O-CH_3 Protons Under Acid-Free Conditions.[a]



R	Coalescence Temperature ($T_c \pm 3°C$)	Low Temperature isomer ratio: *cis/trans*[b]	Chemical Shift (τ)	ΔG ($\pm$ 0.03kcal/mole)
H	35	82 18	6.38 6.64	-0.93
CH_3	68	50 50	6.38 6.83	0.00
C_2H_5	62	47 53	6.32 6.82	+0.09
n-Pr	58	43 57	6.38 6.87	+0.19
n-Pent	60	43 57	6.34 6.84	+0.19
i-Bu	65	36 64	6.38 6.87	+0.38
i-Pr	36	28 72	6.35 6.86	+0.58
p-$(CH_3)_2NC_6H_4$	-17	78 22	6.34 6.76	-0.64
p-$CH_3OC_6H_4$	-19	81 19	6.37 6.76	-0.73
C_6H_5	-48	79 21	6.34 6.75	-0.59
p-BrC_6H_4	-59	80 20	6.31 6.70	-0.59
p-$NO_2C_6H_4$	<-65	- -	- -	- -

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a. All spectra were taken in $CDCl_3$ in the presence of basic aluminum oxide.[5] New compounds gave satisfactory analyses. Internal standard: TMS.

b. Isomer ratios are accurate to ± 3%.

For the methyl and ethyl derivatives with equal mean lifetimes in the cis and trans conformations, first order rate constants of 60 sec^{-1}(68°) and 67 sec^{-1}(62°) are obtained with the expression $k_1 = \pi \Delta \nu / \sqrt{2}$.[7] Application of the Eyring equation with the usual assumptions furnishes $\Delta G^{\pm}$ values of 18.4 ± 0.5 and 17.1 ± 0.5 kcal/mole respectively. Similar modest activation barriers for rotation around suitably substituted carbon-carbon double bonds have been reported recently.[8] These findings suggest that in the absence of acid catalyzed proton exchange, non-aryl substituted carboethoxyphosphoranes can most accurately be described by enolate structures 1a and 2a with minor but important contributions from canonical forms 1b and 2b and perhaps 5: $(C_6H_5)_3P{=}CR{-}CO_2CH_3$.[9] The relative importance of 1b/2b and 5 has yet to be determined. Ylides of this type have conventionally been pictured with carbon-phosphorus $p\pi$-$d\pi$ bonding as in the latter. Aryl substituted ylides stabilized by an ester moiety are best represented by similar structures in addition to those with carbanion delocalization expressed in the aryl ring.

Solvent effects and kinetics for the rotation process shall be presented in the full discussion.

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