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α-THIOCARBONYL-STABILIZED PHOSPHORANES: STRUCTURE AND ALKYLATION REACTION OF ALKOXYTHIOCARBONYLMETHYLENETRIPHENYLPHOSPHORANES

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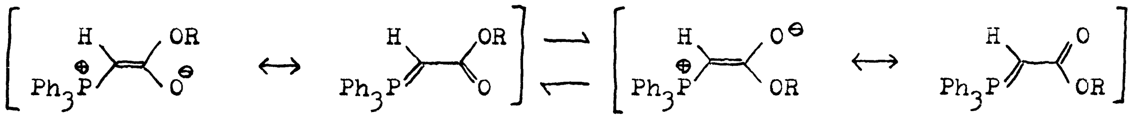
NMR spectra of alkoxythiocarbonylmethylenetriphenylphosphoranes (II; R=Me, Et, i-Pr) show existence of cis and trans isomers. Alkylation of II took place exclusively at sulfur in quantitative yields. The effects of solvents and alkylating reagents on the products ratio (III_{cis}/III_{trans})were also studied.

The NMR spectra of carbonyl-stabilized phosphoranes have been widely studied in recent years.[1)] It is well known that NMR spectra of alkoxycarbonyl-stabilized ylides(I) show to be a mixture of cis and trans isomers:

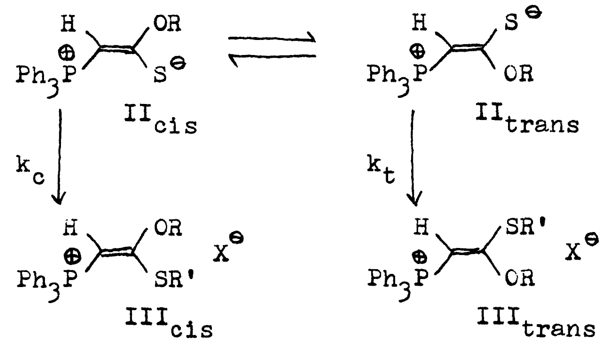


I_{cis} I_{trans}

In this communication we will report on the structure and alkylation reaction of some new alkoxythiocarbonylmethylenetriphenylphosphoranes(II).[2)]

It is known that alkoxycarbonylmethylenephosphorane undergoes alkylation with alkyl halides to afford normal C-alkylation product,[3)]whereas alkylation with triethyloxonium tetrafluoroborate yields C-alkylation product.[4)] Contrary to these results, alkylation of II with various alkylating reagents took place exclusively at sulfur very easily at room temperature to give salts III(cis and trans).

The stereochemistry of the products were assigned on the assumption that the protons of the R group cis to the phosphorous are shielded by the phenyl rings and appear at higher field than the R trans to the phosphorous. NMR data for II and III are given in Table 1.



When we put $K=II_{cis}/II_{trans}$ and $\kappa=III_{cis}/III_{trans}$, cis and trans alkylation rate constants, k_c and k_t, are expressed as follows;

$$k_c=k(\kappa/K)(1+K)/(1+\kappa) \qquad k_t=k(1+K)/(1+\kappa) \qquad k_c/k_t=\kappa/K$$

where k is a rate constant for II(cis + trans).

Table 2 shows the effect of solvents and R on K for I and II.

The variable temperature NMR study for I(R=Me) shows the methyl protons which appear as a singlet above the coalescence temperature (Tc=35±3 °C for I(R=Me)), and an unsymmetrical doublet at lower temperature.5) The NMR spectra of II at 34.5 °C gave clean peaks of two groups corresponding to cis and trans isomers (Table 1). This result indicates that Tc for II may be higher than Tc for I. But, the rotation for II is not restricted, because II came to equilibrium fairly rapidly in any solvent(Tables 2 and 4), and while the reaction proceeded with R'X no change of K was observed.

It is clear that $P^{\oplus}/O^{\ominus}$ or $P^{\oplus}/S^{\ominus}$ attraction is maximized in I_{cis} or II_{cis}. As is shown in Table 2 (see Table 4 and Figure 1 also), both I and II show similar properties: large R and increasing solvent polarity favor a relatively high population of trans. The regular variation of K for I and II may be interpreted as a result of steric inhibition by R to solvation. Smaller K value for II than for I seems to show the higher solvent aggregation around thiocarbonyl than that around carbonyl. This result cleanly reflects the higher mesomeric character for thiocarbonyl than carbonyl group.6)

The effects of solvents and alkylating reagents on K, κ and k_c/k_t were studied in detail for IIa. The results are collected in Tables 3, 4 and Figures 1, 2. Table 3 shows that large R' favors a high population of III_{trans}. Thus the formation of III_{trans} seems to be a lower energy path than that of III_{cis} formation. This result agrees well with the fact that the value of k_c/k_t increases with the increase of ε (Table 4 and Figure 2). Steric hindrance caused by Ph_3P and R' groups favors k_t

Table 1. NMR data for II and III. δppm from internal TMS in $CDCl_3$ at 34.5 °C. J(Hz) values are in parentheses.

		IIa(R=Me)		IIb(R=Et)		IIc(R=i-Pr)	
		cis	trans	cis	trans	cis	trans
II	H	4.32(26.0)	4.64(26.0)	4.35(26.0)	4.68(25.5)	4.33(26.0)	4.68(25.9)
	R	3.83	3.53	4.42 q (7.9) 1.30 t	4.23 q (7.9) 0.67 t	(6.5) 1.27 d	5.52 sep (6.5) 0.72 d
III	H	5.36(10.8)	5.11(13.6)	5.30(10.9)	5.04(13.9)	5.28(10.5)	4.98(15.0)
	SMe	2.27	2.83	2.29	2.83	2.25	2.88
	R	4.33	3.60	4.62 q (7.9) 1.51 t	4.05 q (7.8) 0.73 t	5.41 sep (6.5) 1.52 d	4.78 sep (6.5) 0.87 d

Table 2. Cis/trans ratios for I^* and II^{**} in various solvents

Solvent(ε)	I(R=Me)	II(R=Me)	I(R=Et)	II(R=Et)	I(R=i-Pr)	II(R=i-Pr)
PhH(2.27)	cis	3.5	5.9	2.1	2.9	1.8
CD_3CN(37.5)	5	1.9	2.3	1.2	1.3	0.82
CD_3NO_2(38.6)	4.0	2.1	2.4	1.2	1.4	0.56
$CDCl_3$(4.7)	4.6	0.82	1.8	0.67	1.0	0.26

* Taken from ref 1a. Recorded at -10~0 °C. ** Recorded at 34.5 °C.

Table 3. Alkylation of IIa with various alkylating reagents(R'X) at 34.5 °C in $CDCl_3$

R'X	κ	k_c/k_t
MeI	0.82	1.00
MeBr	0.51	0.62
$MeOSO_2Ph$	0.32	0.39
EtI	0.50	0.61
$PhCH_2Br$	0.22	0.27
$PhCH_2OSO_2Ph$	0.23	0.28
$PhCOCH_2Br$	0.22	0.27

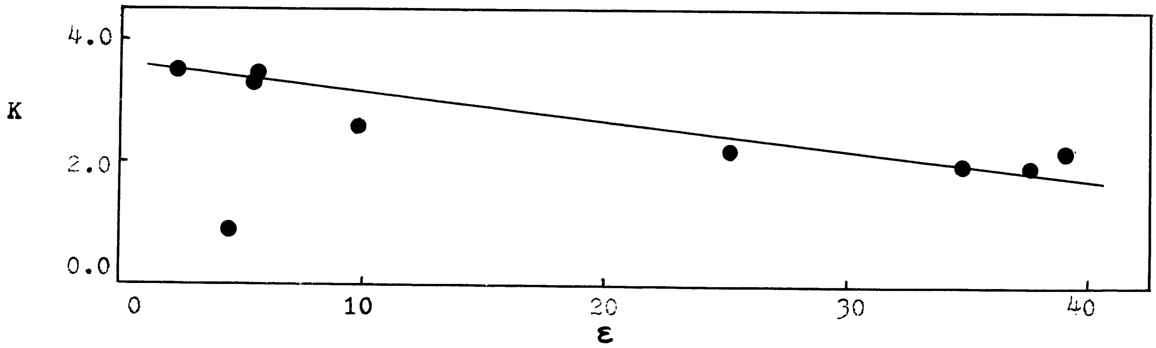


Figure 1. The relation between ε and K

Table 4. Methylation with methyl iodide.
Effect of solvents on cis/trans ratios, K and κ for IIa.

Solvent	ε	K	κ	k_c/k_t
PhH	2.27	3.5	0.93	0.27
PhBr	5.4	3.38	1.00	0.35
PhCl	5.62	3.54	1.43	0.40
$o\text{-}C_6H_4Cl_2$	9.93	2.63	1.15	0.44
PhCN	25.2	2.21	1.29	0.58
$PhNO_2$	34.8	1.97	1.38	0.70

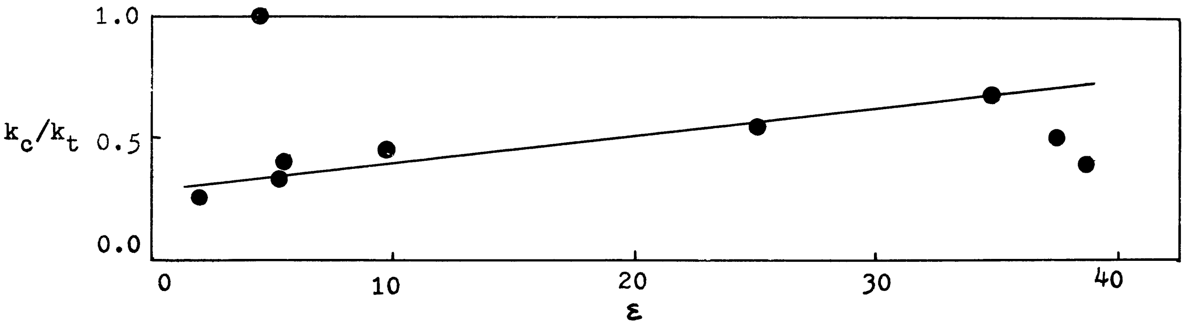


Figure 2. The relation between ε and k_c/k_t

over k_c. Contrary to this, solvent aggregation around the thiocarbonyl may be unfavorable to k_t due to desolvation on the reaction path.$^{6)}$ Deviation of $CDCl_3$ from the line may be explained by strong hydrogen bond$^{1a)}$ with II_{trans}. It is not easy to explain the deviation in CD_3CN and CD_3NO_2(Figure 2), small solvent molecule comes close to the intermediates for II_{cis} and II_{trans}, and so only steric factor may govern the reaction courses. Thus we concluded that K and k_c/k_t for II are governed by $P^{\oplus}$ and $S^{\ominus}$ dipole interaction and solvation of thiocarbonyl group.

Studies on other α-thicarbonyl ylides are now in progress.

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6) Recently C-N rotational barriers in dimethylacetamide(A) and thioamide(B) have been investigated[R. C. Neuman and V. Jones, J. Org. Chem., 39, 929(1974)]. A has smaller Ea than that for B in polar and non polar solvents, and dipolar association with DMSO(a polar solvent) has a much greater effect on the dipolar character of B than that of A. This system [$>N-C\overset{\displaystyle /\!\!/X}{\scriptstyle \backslash}$ $\longleftrightarrow$ $>\overset{\oplus}{N}=C\overset{\displaystyle /X^{\ominus}}{\scriptstyle \backslash}$ (X=O, S)] seems to show a good correlation to our systems I and II.

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