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Studies on the Wittig Reaction (V) Trans Stereoselectivity in the Reaction of Benzylidene Alkyl Diphenylphosphorane and Aldehydes

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Studies on the Wittig Reaction (V) Trans Stereoselectivity in the Reaction of Benzylidene Alkyl Diphenylphosphorane and Aldehydes

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In previous papers, we reported the E-selectivity in the Wittig reaction of phosphorus ylid of the general formula $\text{Ph}_2\text{R}'\text{CH}_2\text{P}=\text{CHR}$ (R=alkenyl; R'=H, alkenyl) and aldehydes. This continuing research for the stereochemistry of diphenylphosphorane in the title reaction of $\text{Ph}_2\text{R}'\text{CH}_2\text{P}=\text{CHR}$ and $\text{R}''\text{CHO}$, where R=Ph, R'=H, Ph and R''=Ph, p-substituted phenyl, has led to the similar results. However, the E-selectivity is dependent on the ylid structure, reaction condition and the nature of the substituents on the aromatic ring. Generally the effect is stronger with benzyl diphenylphosphorane (R=H), the proportion of E olefin is produced in a larger quantity in salt-free condition than in the salt-containing medium, and the aromatic aldehyde bearing an electronwithdrawing group on the ring gives a higher E/Z ratio. Moreover, we also found that the logarithms of the E/Z ratio of the substituted stilbene products are linear with the σ constant of the substituents of the aromatic aldehydes: $\log E/Z = a\sigma + b$

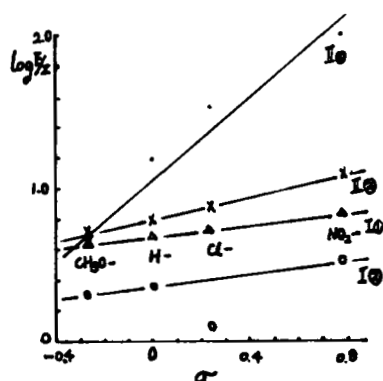


Figure I. Plot of $\log E/Z$ vs. σ constant for the reaction of p-R-CHO and $\text{PhR}'\text{CHP}=\text{CHPh}$ (R=CHO, H, Cl, NO_2)

	II_0	II_1	I_0	I_1
base	t-BuOK	BuLi	t-BuOK	BuLi
R'	Ph	Ph	H	H
a	1.27	0.38	0.19	0.22
b	1.09	0.78	0.69	0.34

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