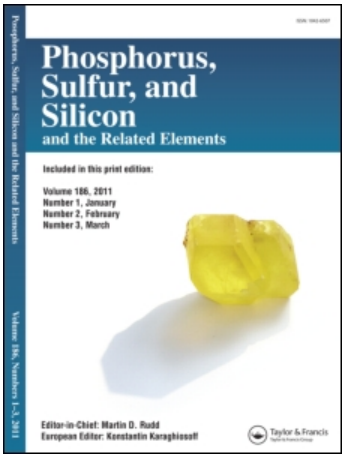

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Studies on the Wittig Reaction (V) Trans Stereoselectivity in the Reaction of Benzylidene Alkyl Diphenylphosphorane and Aldehydes

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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 $Ph_2R'CH_2P{=}CHR$ (R=alkenyl; R'=H,alkenyl) and aldehydes. This continuing research for the stereochemistry of diphenylphosphorane in the title reaction of $Ph_2R'CH_2P{=}CHR$ and R"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: $\log E/Z = a\sigma + b$

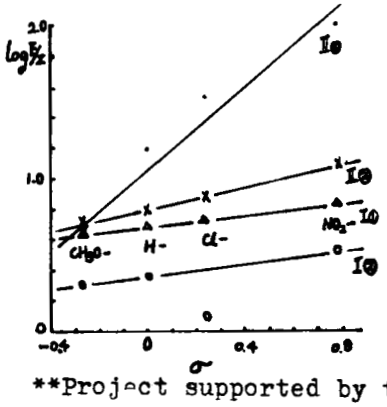

Figure I. Plot of log E/Z vs. σ constant for the reaction of p-R-C_6H_4CHO and $PhR'CH_2P{=}CHPh$(R=CH_3O, H, Cl, NO_2)

	II◎	II◉	I◎	I◉
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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