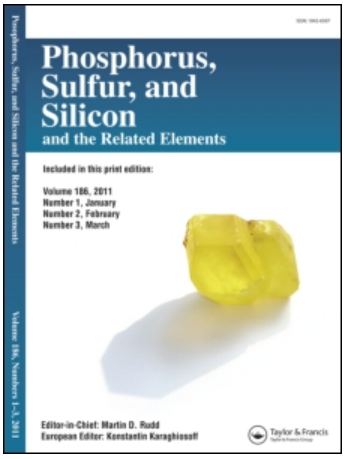

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Scope and Limitation for the Reaction of α,β-Unsaturated Carbonyl Compounds with Phosphorus Nucleophiles by Determination of the Half-Wave Potential

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SCOPE AND LIMITATION FOR THE REACTION OF α,β-UNSATURATED CARBONYL COMPOUNDS WITH PHOSPHORUS NUCLEOPHILES BY DETERMINATION OF THE HALF-WAVE POTENTIAL

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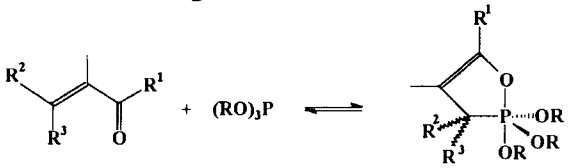
During the formation of oxaphospholenes the phosphorus in the reagent gets oxidised and the double bond in the enones gets reduced.



The polarographic $E_{1/2}$ potential of the enones have been measured in nonprotic solvents and it was found that not only their reducibility but also the production of the oxaphospholene can be predicted from these $E_{1/2}$ values. We found that when the $E_{1/2}$ of enone was lower than -1600 mV the reaction did occur with trimethyl phosphite, while no reaction could be observed with enones having higher $E_{1/2}$ values. In case of using a better nucleophile like triethyl phosphite the border of $E_{1/2}$ value lies at -1710 mV, while the triphenyl phosphite of a weaker nucleophilic character does not react even with the enone having the $E_{1/2}$ at -1294 mV.

reaction occurs with trimethyl phosphite

R^1	R^2	R^3	$E_{1/2}$(mV)
Ph	Ph	H	-1464
Ph	$4NO_2Ph$	H	-1294
Ph	4ClPh	H	-1403
Ph	4MeOPh	H	-1525
$4NO_2Ph$	Ph	H	-1320
4ClPh	Ph	H	-1403
4MeOPh	Ph	H	-1540

no reaction

R^1	R^2	R^3	$E_{1/2}$(mV)
Ph	$4Me_2NPh$	H	-1770
Me	Ph	H	-1692
Me	Ph	Me	-1878
$(CH_2)_3$		H	-2124
$(CH_2)_2$		H	-2184
Me	Me	H	-2300

Moreover, a linear correlation was observed between the $E_{1/2}$ values of the enones and the equilibrium constants of the reaction