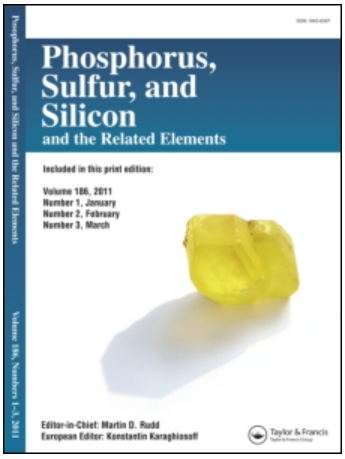

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Reactivity of Triazaphospholes and Phosphenium Kations with Diazadienes and α Diketones

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Reactivity of Triazaphospholes and Phosphenium Kations with Diazadienes and α Diketones

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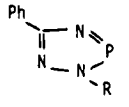
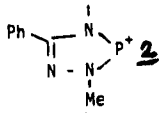
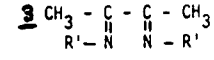
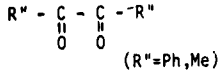
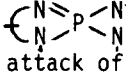
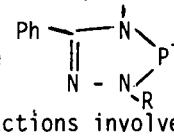

1


2

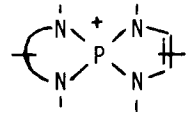
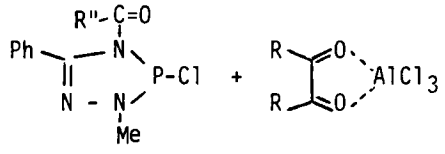

3


(R"=Ph,Me)

We previously reported that 1 (R = Ph, Me) reacts faster with 3 (R'= Ph, nPr) than the α diketones, leading mainly to spirocompounds  . The first step of the reaction of diazadiene with 1 involves an attack of the nitrogen atom lone pair on phosphorus.

In order to emphasize this difference of nucleophilicity between 3 and diketones we tried to increase the electrophility of phosphorus. That prompted us to prepare  A^- (A^- = $AlCl_4^-$, $CF_3SO_3^-$)

The reactions involved lead us to classify the reactants in terms of the HSAB theory. Diazadiènes 3 are softer bases than the α diketones studied. $AlCl_3$ is an acid harder than the phosphenium.

In fact diazadiène reacts exothermically with the phosphenium 2 leading to a cation  while in presence of 2 α diketones react with $AlCl_4^-$ (or $AlCl_3$) and displace Cl^- yielding 

Futhermore 2 is more electrophilic than neutral dicoordinated 1 towards the diazadiene.

Other kinds of conjugated dienes have been studied.