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Reactivity of Triazaphospholes and Phosphenium Kations with Diazadienes and α Diketones

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

In order to emphasize this difference of nucleophilicity between $\underline{3}$ and diketones we tried to increase the electrophility of phosphorus. That prompted us

to prepare
$$\begin{array}{c|c} Ph & N \\ N - N_R \end{array}$$
 $\begin{array}{c} P^+ \\ N - N_R \end{array}$ $\begin{array}{c} A^- & A^-$

The reactions involved lead us to classify the reactants in terms of the HSAB theory. Diazadiènes $\underline{3}$ 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 $\underline{2}$ leading to a cation $\underbrace{\stackrel{N}{N}}_{N} \stackrel{+}{P} \stackrel{N}{\underset{N}{\longrightarrow}}_{N}$ while in presence of $\underline{2}$ α diketones react with $R"-\zeta=0$

AlCl₄ (or AlCl₃) and displace Cl yielding
$$\begin{array}{c} R'' - C = 0 \\ Ph - N - N \\ N - N - N \\ Me \end{array}$$
 AlCl₃

Futhermore $\underline{2}$ is more electrophilic than neutral dicoordinated $\underline{1}$ towards the diazadiene.

Other kinds of conjugated dienes have been studied.