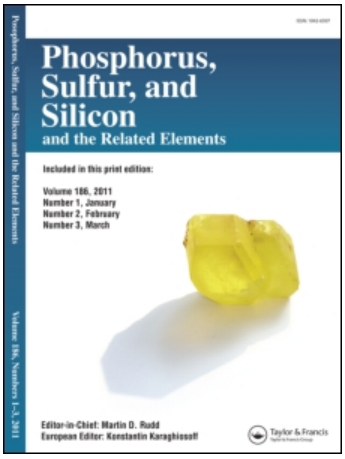

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On the Reactivity of Diazadiphosphetidine Derivatives Towards Electrophilic Agents, a Mndo Study

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ON THE REACTIVITY OF DIAZADIPHOSPHETIDINE DERIVATIVES TOWARDS ELECTROPHILIC AGENTS, A MNDO STUDY.

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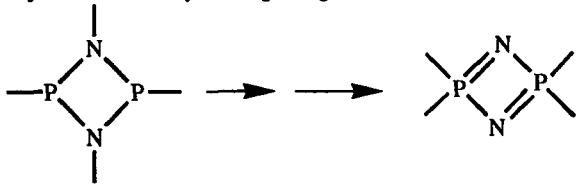
The utilization of $\sigma^3\lambda^3$ diazadiphosphetidine as precursor of the potentially usefull cyclodiphosphazenes

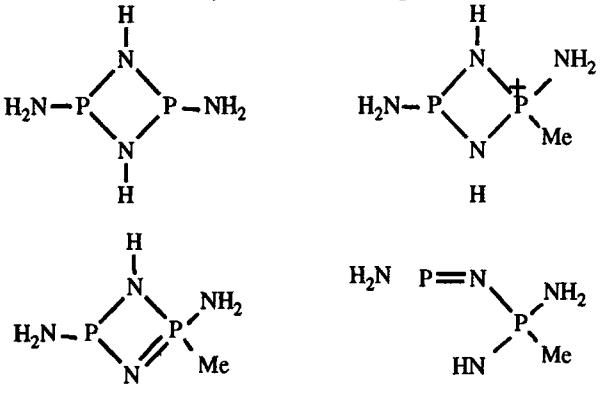


has shown some interestings facts on the reactivity of the intermediates

a) The monoinsaturated diazadiphosphetines are relatively unstable and undergo an electrocyclic ring opening reaction, even at low temperature.

a) the PIII atom in the monocationic and monoinsaturated derivatives show a lack of the phosphine character.

The AB INITIO study of some simple models



has shown that the open molecule is energetically more stable than the monoinsaturated one, and this cyclic system has an intracyclic

P-N bond too long for a real single bond. that could explain the opening experimentally observed. On the other hand, both monocationic and monoinsaturated models have HOMO's located too low in energy, and that can explain the lack of phosphine character.

Nevertheless, all models show HOMO's located essentially on the intracyclic atoms while experimentally the phosphorus atoms are the reactive centers.

In order to gain further understanding on this reactivity, we have performed a serie of semi empirical calculations, using more realistics models, that means substituted diazadiphosphetidines, in order to see the effect of the substituents on the electronic distribution. MNDO calculations show the same results.

We have performed then,the simulation of an electrophilic atack (by H+) on the intracyclic P and intracyclic N atoms. In all cases, the proton atack is less energetically demanding by the more sterically protected side, and the addition is made on the Nitogen atom, showing an important energetic barrier. The study of the molecular orbitals shows that the interaction of the electrophile with the amino substituents is responsible of these observations.

The addition on the phosphorus atom is more energetically demanding, but the it is made without energetic barrier. One can think that only the polarizability of the phosphorus atom is responsible of the reactivity experimentally observed, making the atack to the phosphorus atom kinetically more favoured.

These observations are the same independently of the electrophilic agent and the the substituents.

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