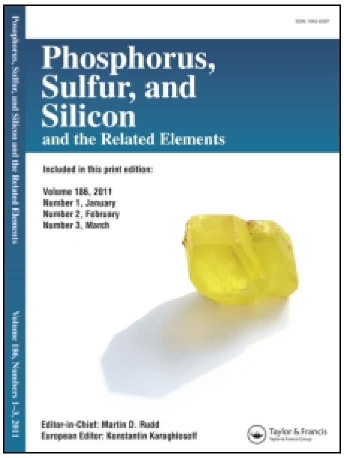

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Theoretical Aspects of Cycloaddition Reactions of Phosphorylnitrile Oxides to Unsaturated Compounds

Alexander I. Kurdjukov[a]; Valeriy A. Pavlov[a]
[a] Dept. of Organic Chemistry, Kazan State Technological University, Kazan, Russia

To cite this Article Kurdjukov, Alexander I. and Pavlov, Valeriy A.(1996) 'Theoretical Aspects of Cycloaddition Reactions of Phosphorylnitrile Oxides to Unsaturated Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 111: 1, 39

To link to this Article: DOI: 10.1080/10426509608054668
URL: http://dx.doi.org/10.1080/10426509608054668

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 39
Reprints available directly from the publisher
Photocopying permitted by license only

THEORETICAL ASPECTS OF CYCLOADDITION REACTIONS OF PHOSPHORYLNITRILE OXIDES TO UNSATURATED COMPOUNDS.

Alexander I. **KURDJUKOV**, Valeriy A. **PAVLOV**
Dept. of Organic Chemistry, Kazan State Technological University, K. Marx St. 68,
Kazan 420015, Russia

Abstract. Ab initio (4-31G*) and semiempirical (MNDO, AM1) quantum-chemical calculations of phosphorus-functionalized and non-phosphorylated nitrile oxides have been done. In approximation of general multielectronic perturbation theory, all nitrile oxides, including trifluoroacetonitrile oxide and dialkoxyphosphorylnitrile oxides, by type of orbital interactions qualify as electron-donor dipoles.

The following based on a comparison of energies and structure of pπ-bondying and pπ-antibondying orbitals of phosphorylnitrile oxides and the most characteristic non-phosphorylated nitrile oxides and an evaluation in approximation of the general multielectronic perturbation theory [1] the contributions of orbital interactions of frontal molecular orbitals (FMO's) into the stabilization energy (Est) of transition state of reaction systems of "nitrile oxide - dipolarophile" type conclusions have been made.

(Dialkoxyphosphoryl)nitrile oxides, despite the lowering energy of HOMO as compared with benzonitrile oxide by approximately 1.75 eV, should be classified with electron-donating agents in which the interactions with participation of LUMO under condition of dissimilerity of HOMO constitution on reaction centres of dipolarophile can influence regioselectivity of cycloaddition. In the competition of electronic and steric interactions determining are the last. (Dialkoxyphosphoryl)nitrile oxides both for character of orbital interactions and for chemical properties are close to trifluoroacetonitrile oxide.

The electron-donating property of phosphorylnitrile oxides is the consequence of the inertness of phosphoryl moiety rather, then its influence. This follows from the fact that the separation of phosphoryl group and nitrile oxide fragment by methylene link in dimethoxyphosphorylacetonitrile oxide has a little influence on changing the character of FMO's [2] and chemical properties of nitrile oxides [3,4].

It is represented correct to speak about differentiation of all nitrile oxides in cycloaddition reactions on a degree of electron-donation.

Calculated energy of orbital interactions "HOMO of nitrile oxide - LUMO of dipolarophile" and Est for the given systems that react by "head to tail" type are somewhat less than those for the systems reacting by "head to head" type. It testifies about high sensitivity of cycloaddition reactions to steric hindrances. As in the case of reaction of (diisopropoxyphosphoryl)nitrile oxide with isopropylpropiolate (which under the electronic characteristics is analogue of methylpropiolate, but stericaly is more loaded) is observed formation the only 5-substituted cycloadducts, while the reaction with methylpropiolate results to formation 4- and 5-substituted cycloadducts [3].

In (*bis*aminophosphoryl)nitrile oxides HOMO and adjacent to it molecular orbital are formed unshared electronic pairs of amino groups. Therefore, in view of marked above electron-donating character of all nitrile oxides, should be expected strong secondary-orbital interactions for potential reaction systems and low activity of (*bis*aminophosphoryl)nitrile oxides in reactions [2+3]-cycloaddition.

References

[1] Klopman G. // J.Am.Chem.Soc., 90, 223 (1968)
[2] Kurdjukov A.I., Pavlov V.A., Gorin B.I., Moskva V.V. // Zh.Obshch.Khim., 64, 1388 (1994).
[3] Pavlov V.A., Kurdjukov A.I., Aristova N.V., Gorin B.I., Zjablikova T.A., Moskva V.V. // Zh.Obshch.Khim., 64, 1373 (1994).
[4] Tsuge O., Kanemasa S., Suga H., Nakagawa N.//Bull.Chem.Soc.Japan., 60, 2463 (1987).