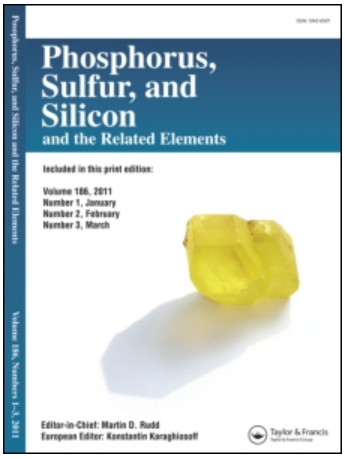


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Quantum-Chemical Investigation of Reaction Mechanism of 2-R-4-Oxo-5,6-Benzo-1,3,2-Dioxaphosphorinanes with Chloral and Fluoral

Roza M. Aminova[a]; Grigory A. Shamov[a]; Vladimir B. Mushkin[a]; Vladimir F. Mironov[b]; Alexander I. Konovalov[b]; Albert V. Aganov[a]
[a] Kazan State University, Kazan, Russia [b] A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia

To cite this Article Aminova, Roza M. , Shamov, Grigory A. , Mushkin, Vladimir B. , Mironov, Vladimir F. , Konovalov, Alexander I. and Aganov, Albert V.(1999) 'Quantum-Chemical Investigation of Reaction Mechanism of 2-R-4-Oxo-5,6-Benzo-1,3,2-Dioxaphosphorinanes with Chloral and Fluoral', Phosphorus, Sulfur, and Silicon and the Related Elements, 147: 1, 265
To link to this Article: DOI: 10.1080/10426509908053613
URL: http://dx.doi.org/10.1080/10426509908053613

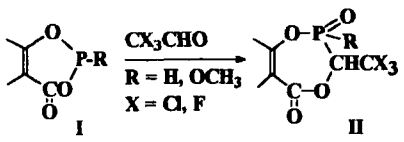
Phosphorus, Sulfur and Silicon, 1999, Vol. 147, pp. 265-265
Reprints available directly from the publisher
Photocopying permitted by license only

Quantum-Chemical Investigation of Reaction Mechanism of 2-R-4-Oxo-5,6-Benzo-1,3,2-Dioxaphosphorinanes with Chloral and Fluoral

ROZA M. AMINOVA[a], GRIGORY A. SHAMOV[a], VLADIMIR B. MUSHKIN[a], VLADIMIR F. MIRONOV[b], ALEXANDER I. KONOVALOV[b] and ALBERT V. AGANOV[a]

[a]*Kazan State University, Kazan, 420008, Russia and* [b]*A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, 420088, Russia*

Reaction of 2-R-4-oxo-5,6-benzo-1,3,2-dioxaphosphorinanes I with chloral leading to formation of seven-membered heterocycles - 1,4,2-dioxaphosphepines is characterized by the high degree of stereoselectivity. We investigated the model reactions of 2-R-4-oxo-1,3,2-dioxaphosphorin-5-enes with CX_3CHO by PM3 and *ab initio* methods in STO-3G, 3-21G, 6-31G*, MP2/6-31G* basis set and also DFT method (B3LYP).



I II

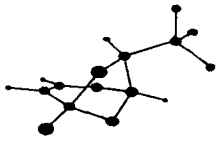


Fig. 1.

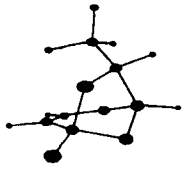


Fig. 2.

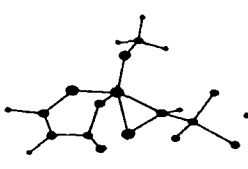


Fig. 3.

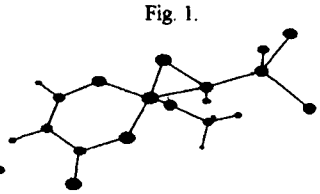


Fig. 4.

The calculations of electronic and spatial structures of the reagents, products and transition states have been carried out. Two types of transition states has been determined on the potential energy surface. One of the pathways of the reaction on the potential energy surface leading to formation of seven-membered heterocycles with required molecule configuration can be characterized as a consistent asynchronous [3+2] cycloaddition. Corresponding transition states are shown on fig. 1, 2. Alternative pathway includes the formation of three-membered phosphorane heterocycle intermediates pictured on fig. 3, 4. It should be noticed that the last intermediates have been obtained only for polarized basis sets on all heavy atoms. The intermediate shown on fig. 3 is most stable.