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

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

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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 CX₃CHO by PM3 and *ab initio* methods in STO-3G, 3-21G, 6-31G*, MP2/6-31G* basis set and also DFT method (B3LYP).

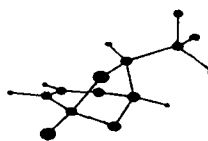
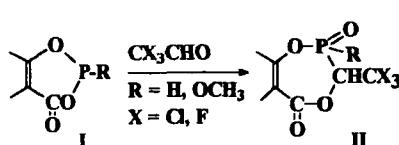


Fig. 1.

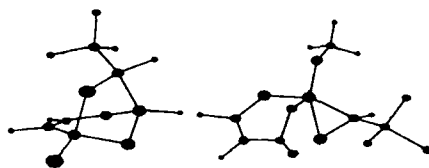


Fig. 2.

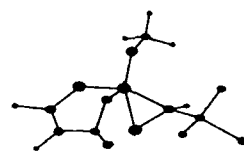


Fig. 3.

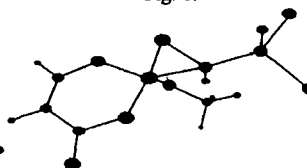


Fig. 4.

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.