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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>

Homolytical Reaction Peculiarities of Phosphororganic Compounds

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To cite this Article Rakhimov, A. I. , Ozerov, A. A. , Litinskij, A. O. , Rysin, S. L. and Buzinova, O. P.(1990) 'Homolytical Reaction Peculiarities of Phosphororganic Compounds', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 51: 1, 256

To link to this Article: DOI: 10.1080/10426509008040790

URL: <http://dx.doi.org/10.1080/10426509008040790>

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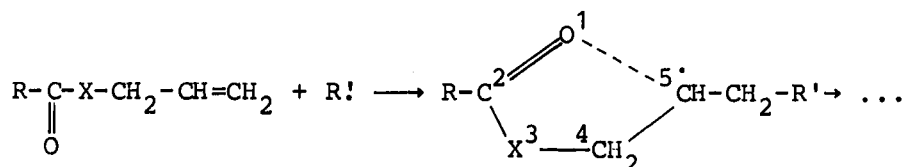
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HOMOLYTICAL REACTION PECULIARITIES OF PHOSPHORORGANIC COMPOUNDS

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The influence of the transient cyclic radical structure on the reactivity of unsaturated compounds in the processes of homolytical phosphorylation, and allyl and vinylphosphonates in the processes of homolytical perfluoroalkylation is shown by the MINDO/3 method of quantum chemistry computations. The addition of allyl derivatives of amides and esters of carbonic, aminocarbonic and carbaminoacids to phosphocentric radicals yields five-membered cyclic radical structures with NH- and O-heteroatoms in the cycle:



Delocalization of the spin density of nonpaired electron on the atoms of the cycle and bonding of O¹ and C⁵ atoms depend on the heteroatom X nature. X, spin density in % on the atoms O¹, C², X³, C⁴, C⁵, the order of bond (Wiberg index) O¹ - C⁵ are presented:

NH, 14.9, 2.3, 1.5, 1.6, 58.4, 0.181;

O, 13.2, 0.8, 2.0, 2.7, 63.3, 0.125.

The high stability of five-membered cyclic radical structures makes the transmission of radical chain difficult and decreases the reaction velocity in the case of N-allylamides of carbonic, carbamino and aminoacids (X = NH) more then for the corresponding allyl esters (X = O), which is in accordance with the results of kinetic analysis.