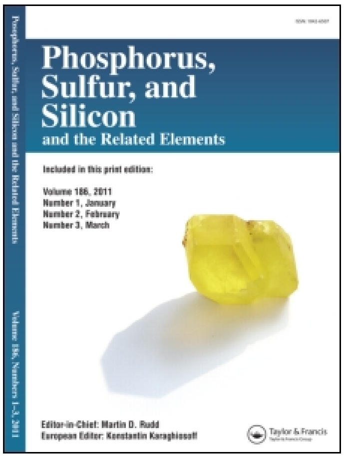

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Development of a New Approaches to the Synthesis of Polyfunctional Phosphorylated Cyclopropanes

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To cite this Article Pavlov, V. , Gazizova, V. , Shamov, G. , Moskva, V. , Winsel, H. , De Meijere, A. , Baird, M. and Kulinkovich, O.(1999) 'The Development of a New Approaches to the Synthesis of Polyfunctional Phosphorylated Cyclopropanes', Phosphorus, Sulfur, and Silicon and the Related Elements, 147: 1, 311

To link to this Article: DOI: 10.1080/10426509908053636

URL: http://dx.doi.org/10.1080/10426509908053636

Phosphorus, Sulfur and Silicon, 1999, Vol. 147, pp. 311-311
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Gordon and Breach Science Publishers imprint.
Printed in Malaysia

The Development of a New Approaches to the Synthesis of Polyfunctional Phosphorylated Cyclopropanes

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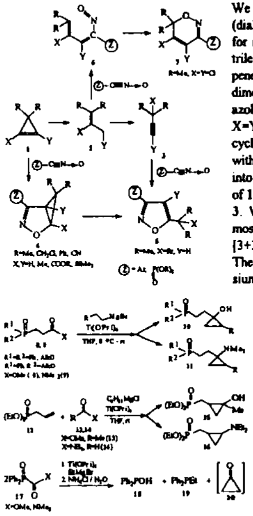
The report presents the study of cycloaddition reactions of phosphorylnitrile oxides to dipolarophiles of cyclopropene series and development of a new methods for synthesis of cyclopropanols and cyclopropylamines bearing phosphoryl moiety.



We have reported [1] about synthesis of highly reactive (dialkoxyphosphoryl)nitrile oxides - valuable reagents for indirect phosphorylation. While the reactions of nitrile oxides with a number of functionalised cyclopropenes 1 lead to bicyclic adducts 4, 1-bromo-3,3-dimethylcyclopropene (1; X=Br, Y=H) leads to an isoxazole 5 and 1,2-dichloro-3,3-dimethylcyclopropene (1; X=Y=Cl) leads to an oxazine 7. Direct [3+2]-cycloaddition of nitrile oxides to 1-bromocyclopropenes with further transformation of bicycle (4; X=Br, Y=H) into isoxazole 5 are more preferable than ring-opening of 1 to vinylcarbene 2 and then rearrangement to alkyne 3. When X=Y=Cl intermediate vinylcarbene 2 is the most stable and it leads to its stepwise unusual formal [3+3]-cycloaddition forming oxazine 7.

The reaction of alkanecarboxylates with alkylmagnesium bromide and titanium isopropoxide is a convenient way for the preparation of corresponding cyclopropanols [2]. This reaction and its modification for carboxylic amides we applied for synthesis of phosphorylated cyclopropanols 10 and cyclopropylamines 11 from phosphorylpropionates 8 or -amides 9. The attempt to synthesize cyclopropanes 15 and 16, when phosphoryl moiety and cyclopropane ring are linked by one methylene unit, using the above procedure was failed, because of acidity of methylene bridge protons in phosphorylacetate. Herein we extended a new synthetic method [3] for desired products 15, 16 by utilizing Ti-mediated coupling of phosphoryl-substituted olefins 12 with carboxylic esters 13 or amides 14. Influence of adjacent carbonyl group and intramolecular coordination of titanium with phosphoryl oxygen in phosphorylformiate 17 lead to cleavage of P-C bond.

This research was supported by the International Association INTAS (grant 94-0428).

References

[1] V.A. Pavlov, A.I. Kurdjukov, N.V. Aristova, et al, *Zh.Obshch.Khim.*, **64,** 1373 (1994).
[2] O.V. Kulinkovich, S.V. Sviridov, D.A. Vasilevski, *Synthesis*, 234 (1991).
[3] J. Lee, Y.G. Kim, J.G. Bae, J.K. Cha, *J. Org. Chem.*, **61,** 4878 (1996).