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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>

Mechanism of Formation of Ribonucleoside Cyclic 2',3'-Phosphates in the Reaction of Appropriate 3',5'-Phos-Phorothioates with Epoxides

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To cite this Article Okruszek, A. , Guga, P. and Stbc, Wojciech J.(1990) 'Mechanism of Formation of Ribonucleoside Cyclic 2',3'-Phosphates in the Reaction of Appropriate 3',5'-Phos-Phorothioates with Epoxides', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 51: 1, 373

To link to this Article: DOI: 10.1080/10426509008040900

URL: <http://dx.doi.org/10.1080/10426509008040900>

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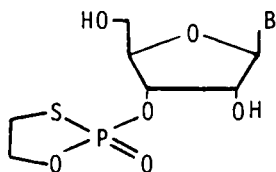
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MECHANISM OF FORMATION OF RIBONUCLEOSIDE CYCLIC 2',3'- -PHOSPHATES IN THE REACTION OF APPROPRIATE 3',5'-PHOS- PHOROTHIOATES WITH EPOXIDES

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It has been recently demonstrated in our laboratory (1) that ribonucleoside cyclic 3',5'-phosphorothioates react with epoxides to give as a major product corresponding cyclic 2',3'-phosphates. We now report the results of our stereochemical studies of this reaction. We have found that the diastereomerically pure (Sp) 3',5'-cUMPS when treated with styrene [^{18}O]-oxide in ethanol gives the same isotopomer of 2',3'-[^{18}O]cUMP as that obtained from the reaction of endo-2',3'-cUMPS with styrene [^{18}O]-oxide. This result strongly supports our previous assumption that reaction of 3',5'-cNMPs with epoxides proceeds *via* 3'-oxathiaphosphorylated intermediate (1) which is formed with inversion and decomposes to 2',3'-cNMP with retention of configuration at phosphorus atom.



1

The participation of 1 in the reaction mechanism was further confirmed by its independent synthesis and decomposition into cyclic 2',3'-phosphate.

(1) A.Okruszek, P.Guga, W.J.Stec,
J.Chem.Soc.,Chem.Comm., **1985**, 1225