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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>

Phosphorylation as a Method of Stabilization of Thermodynamically Unstable Isomers of A-Amino Ketones

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To cite this Article Balitsky, Y. V. , Pipko, S. E. , Kolodka, T. V. and Kovalenko, A. L.(1990) 'Phosphorylation as a Method of Stabilization of Thermodynamically Unstable Isomers of A-Amino Ketones', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 51: 1, 282

To link to this Article: DOI: 10.1080/10426509008040816

URL: <http://dx.doi.org/10.1080/10426509008040816>

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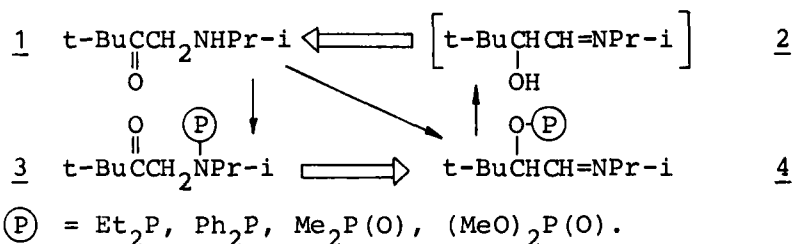
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PHOSPHORYLATION AS A METHOD OF STABILIZATION OF THERMODYNAMICALLY UNSTABLE ISOMERS OF α -AMINO KETONES

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α -hydroxy imines 2 are unstable compounds which irreversibly isomerize into thermodynamically more stable α -amino ketones 1, usually at the moment of formation. We have found the principles of stabilization of both isomeric forms, for example, by regioselective phosphorylation of the ambident substrate 1.



Depending on the structure of the phosphorylating reagent and the reaction conditions (kinetic or thermodynamical control) the interaction leads to the products of N- or O-phosphorylation. As a rule, phosphorotropic isomers 3, 4 are stable enough to be isolated and identified. In contrast to prototropic isomer 1, N-phosphorylated amino ketones 3 on heating at 120-160°C transform into thermodynamically more stable O-derivatives by [1,4]-(N→O)-migration of the phosphorus-containing group. The thermal isomerization is accelerated in the presence of acids. The mild hydrolysis of both O- and N-phosphorylated compounds 3, 4 leads to the α -amino ketone 1 in accordance with the equilibrium of prototropic isomers, completely shifted to the side of N-H form 1.