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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>

Dynamic Stereochemistry of Phosphaalkenes

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To cite this Article Povolotskii, M. I. , Negrebetskii, V. V. , Romanenko, V. D. , Kachkovskaya, L. S. and Markovsky, L. N.(1990) 'Dynamic Stereochemistry of Phosphaalkenes', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 51: 1, 319

To link to this Article: DOI: 10.1080/10426509008040850

URL: <http://dx.doi.org/10.1080/10426509008040850>

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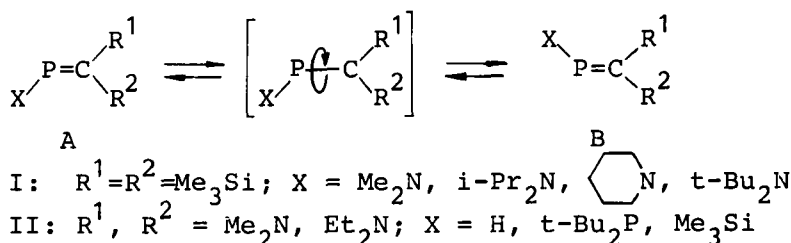
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DYNAMIC STEREOCHEMISTRY OF PHOSPHAALKENES

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The degenerative Z,E-isomerization at the P=C bond in phosphaaalkenes I and II has been studied by dynamic NMR spectroscopy. The complete bandshape analysis was used to evaluate the activation parameters for intramolecular dynamic process.



The following activation parameters were found for bis(trimethylsilyl)-substituted phosphaaalkenes: $\Delta H^\ddagger = 59.9 \div 96.3$ $\text{kJ}\cdot\text{mol}^{-1}$; $\Delta S^\ddagger = -46.5 \div 17.5$ $\text{J}\cdot\text{mol}^{-1} \text{K}^{-1}$; $\Delta G_{303}^\ddagger = 66.6 \div 103.1$ $\text{kJ}\cdot\text{mol}^{-1}$. The linear dependence of the free energy of activation (ΔG^\ddagger) on the chemical shift of the sp^2 -hybridized carbon atom in these compounds indicates that the exchange $\text{A} \rightleftharpoons \text{B}$ occurs by the rotation mechanism ($\Delta G_{303}^\ddagger = 0.46\delta^{13}\text{C} + 11$ $\text{kJ}\cdot\text{mol}^{-1}$).

Replacement of electrone-withdrawing Me_3Si -groups by electrone-releasing Alk_2N -groups leads to the reversed P=C bond polarity, but it does not influence the mechanism of degenerative Z,E-isomerization. Activation parameters of intramolecular exchange process in bis(dialkylamino)-methylenephosphines are listed below: $\Delta H^\ddagger = 53.6 \div 73.7$ $\text{kJ}\cdot\text{mol}^{-1}$; $\Delta S^\ddagger = -20.1 \div 44.4$ $\text{J}\cdot\text{mol}^{-1} \text{K}^{-1}$; $\Delta G_{303}^\ddagger = 64.5 \div 80.8$ $\text{kJ}\cdot\text{mol}^{-1}$ ($G^\ddagger < 40$ $\text{kJ}\cdot\text{mol}^{-1}$ for X = Me_3Si).

1. M.I. Povolotskii, V.V. Negrebetskii, Zh. Obshch. Khim. 58, 231 (1988).