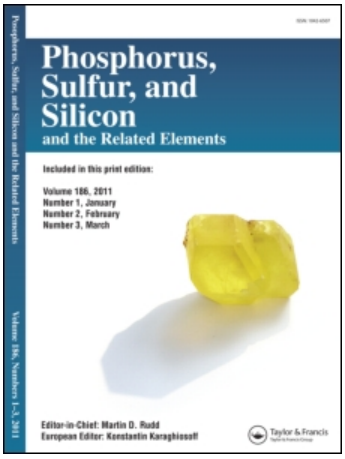


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Dynamic Stereochemistry of Phosphaalkenes

M. I. Povolotskii[a]; V. V. Negrebetskii[a]; V. D. Romanenko[a]; L. S. Kachkovskaya[a]; L. N. Markovsky[a]
[a] Institute of Organic Chemistry of the Ukrainian Academy of Sciences, Kiev, USSR

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

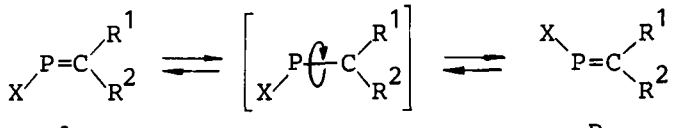
URL: http://dx.doi.org/10.1080/10426509008040850

Phosphorus, Sulfur, and Silicon, 1990, Vols. 51/52, p. 319
Reprints available directly from the publisher
Photocopying permitted by license only

DYNAMIC STEREOCHEMISTRY OF PHOSPHAALKENES

M.I.POVOLOTSKII, V.V.NEGREBETSKII, V.D.ROMANENKO, L.S.KACHKOVSKAYA, and L.N.MARKOVSKY
Institute of Organic Chemistry of the Ukrainian Academy of Sciences, Murmanskaya Str. 5, Kiev, USSR

The degenerative Z,E-isomerization at the P=C bond in phosphaalkenes 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.



A B

I: $R^1=R^2=Me_3Si$; X = Me_2N, i-Pr_2N, N, t-Bu_2N

II: R^1, R^2 = Me_2N, Et_2N; X = H, t-Bu_2P, Me_3Si

The following activation parameters were found for bis(trimethylsilyl)-substituted phosphaalkenes: $\Delta H^{\neq}$ = 59.9 ÷ 96.3 kJ·mol^{-1}; $\Delta S^{\neq}$ = -46.5 ÷ 17.5 J·mol^{-1} K^{-1}; $\Delta G^{\neq}_{303}$ = = 66.6 ÷ 103.1 kJ·mol^{-1}. The linear dependence of the free energy of activation ($\Delta G^{\neq}$) on the chemical shift of the sp^2-hybridized carbon atom in these compounds indicates that the exchange A⇄B occurs by the rotation mechanism ($\Delta G^{\neq}_{303}$ = 0.46δ^{13}C + 11 kJ·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: $\Delta H^{\neq}$ = 53.6 ÷ 73.7 kJ·mol^{-1}; $\Delta S^{\neq}$ = -20.1 ÷ 44.4 J·mol^{-1}K^{-1}; $\Delta G^{\neq}_{303}$ = 64.5÷80.8 kJ·mol^{-1} ($G^{\neq}$ < 40 kJ·mol^{-1} for X = Me_3Si).

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