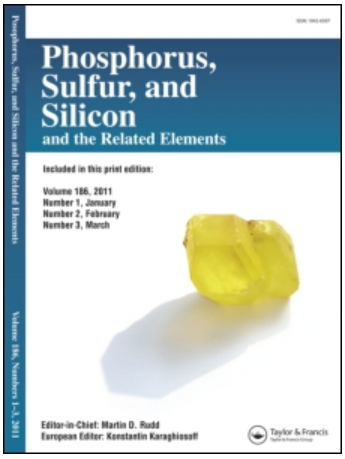

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Yu. A. Veits[a]; E. G. Neganova[a]; A. A. Rorisenko[a]; V. L. Foss[a]; I. F. Lutsenko[a]
[a] Lomonosov Moscow State University, Moscow, USSR

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REVERSIBLE PHOSPHAALKENE FORMATION FROM IMINODIPHOSPHINES

Yu.A.VEITS, E.G.NEGANOVA, A.A.BORISENKO, V.L.FOSS, and I.F.LUTSENKO
Lomonosov Moscow State University, Lenin Hills,
Moscow 117234, USSR

Addition of various nucleophiles to phosphaalkenes is considered to be irreversible. As an example, the quantitative formation of iminodiphosphine III from phosphinous amide and phosphaalkene was recently reported (1). We found that the reaction (1) is reversible

$$\underset{\text{I}}{R^1P{=}CR^2R^3} + \underset{\text{II}}{R^4R^5PNHR^6} \rightleftharpoons \underset{\text{III}}{R^1(R^2R^3CH)P\text{-}P(=NR^6)R^4R^5} \qquad (1)$$

The equilibrium is shifted completely to the right, when $R^1=(Me_3Si)_2N$, $R^2=H$, $R^3=R^6=Me_3Si$, $R^4=Me_3SiCH_2$, $R^5=Et_2N$; and to the left, when $R^1=(Me_3Si)_2N$, $R^2=H$, R^3Et_3Si, $R^4=R^5=i\text{-}Pr$, $R^6=Ph$ or $t\text{-}Bu$. When the substituents R^1-R^5 are the same as in the latter case and $R^6=Me_3Si$, equilibrium ratio may be observed by ^{31}P NMR. Very strong temperature dependence of the equilibrium was observed (the content of phosphaalkene increases from 6.5% at 20°C to 30% at 85°C; after cooling an initial equilibrium ratio is recovered). Thus, as stated in (2), phosphaalkenes may be produced via pyrolysis of iminodiphosphines.

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