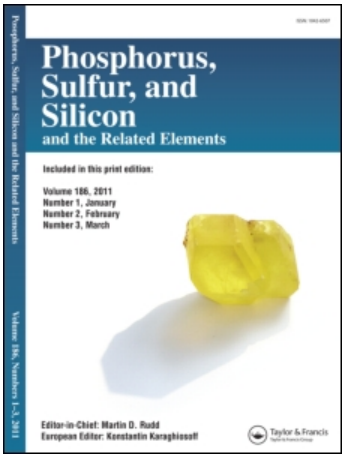

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Kinetics and Mechanism of the Pudovik Reaction in the Series of Shiff Bases. Addition of Dialkylphosphites to Substituted N-Alkyl(Aryl)Benzylideneamines

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To cite this Article Sobanov, A. A. , Zolotukhin, A. V. , Galkin, V. I. , Galkina, I. V. and Cherkasov, R. A.(1999) 'Kinetics and Mechanism of the Pudovik Reaction in the Series of Shiff Bases. Addition of Dialkylphosphites to Substituted N-Alkyl(Aryl)Benzylideneamines', Phosphorus, Sulfur, and Silicon and the Related Elements, 147: 1, 71
To link to this Article: DOI: 10.1080/10426509908053516
URL: http://dx.doi.org/10.1080/10426509908053516

Phosphorus, Sulfur and Silicon, 1999, Vol. 147, pp. 71-71
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Kinetics and Mechanism of the Pudovik Reaction in the Series of Shiff Bases. Addition of Dialkylphosphites to Substituted N-Alkyl(Aryl)Benzylideneamines

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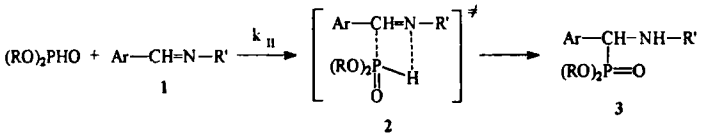
Kinetic and preparative investigation of the reaction of addition of dialkylphosphites to a series of Shiff bases of the type Ar-CH=N-R (R = Alk, Ar') (**1**) is investigated. On the basis of kinetic data obtained (Table) the nucleophilic addition mechanism is suggested.

Table. Rate constants and activation parameters of the reaction of $(MeO)_2PHO$ with X-C_6H_4-CH=N-Pr-i (*i*-propanol, 25 °C)

№	R	k_{II}, l/ mole·sec	$\Delta H^{\neq}$, kcal/mole	$-\Delta S^{\neq}$, e.u.
1	n-$(CH_3)_2N$	$(5,85+/-0,67)\cdot10^{-4}$	12,29	32,01
2	n-CH_3O	$(1,34+/-0,01)\cdot10^{-3}$	15,86	18,37
3	n-H	$(1,11+/-0,01)\cdot10^{-2}$	10,55	32,00
4	n-Cl	$(1,20+/-0,15)\cdot10^{-2}$	7,67	41,49
5	n-F	$(1,27+/-0,02)\cdot10^{-2}$	6,22	46,25
6	m-NO_2	$(2,77+/-0,10)\cdot10^{-2}$	1,11	61,86

Significant negative values of activation entropy (Table) indicate that the reaction proceeds through the four-membered cyclic transition state **2**, where the imine nitrogen atom plays the role of insert base:



1 **2** **3**

A wide series of aminophosphonates **3** is obtained and characterized.

The work is realized under financial support of Russian Fond of Fundamental Investigations (grant N 96-03-32864a)