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

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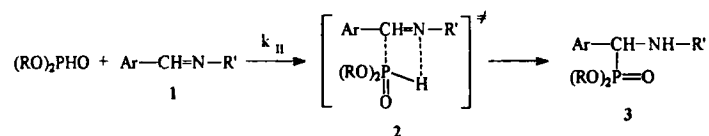
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Kinetic and preparative investigation of the reaction of addition of dialkylphosphites to a series of Schiff bases of the type Ar-CH=N-R ($\text{R} = \text{Alk, Ar}'$) (1) is investigated. On the basis of kinetic data obtained (Table) the nucleophilic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

Table. Rate constants and activation parameters of the reaction of $(\text{MeO})_2\text{PHO}$ with $\text{X-C}_6\text{H}_4\text{-CH=N-Pr-i}$ (*i*-propanol, 25 °C)

No	R	k_{11} , l/mole·sec	ΔH^\ddagger , kcal/mole	$-\Delta S^\ddagger$, e.u.
1	$\text{n-(CH}_3)_2\text{N}$	$(5,85 \pm 0,67) \cdot 10^{-4}$	12,29	32,01
2	$\text{n-CH}_3\text{O}$	$(1,34 \pm 0,01) \cdot 10^{-3}$	15,86	18,37
3	n-H	$(1,11 \pm 0,01) \cdot 10^{-2}$	10,55	32,00
4	n-Cl	$(1,20 \pm 0,15) \cdot 10^{-2}$	7,67	41,49
5	n-F	$(1,27 \pm 0,02) \cdot 10^{-2}$	6,22	46,25
6	m-NO_2	$(2,77 \pm 0,10) \cdot 10^{-2}$	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:



A wide series of aminophosphonates 3 is obtained and characterized.

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