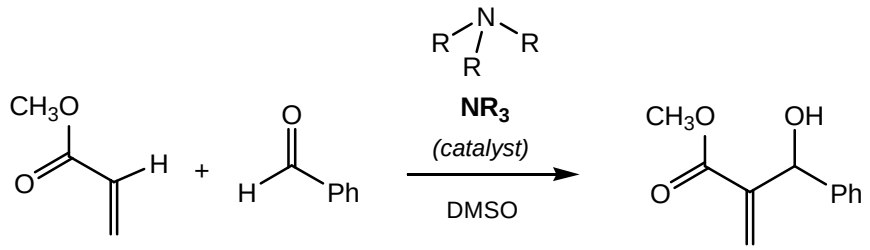
Section Question 5

This problem requires that you have looked at Exam 1, Problem 2 from 2006.

For the Baylis-Hillman reaction,

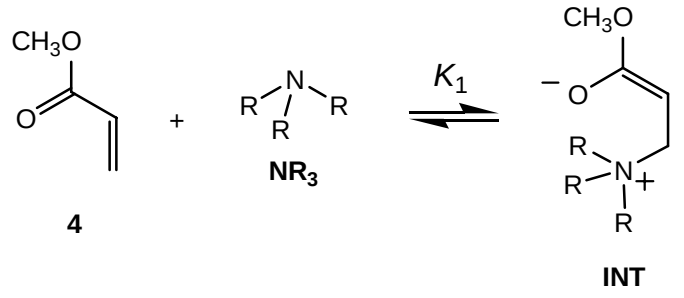


4 **PhCHO** **5**

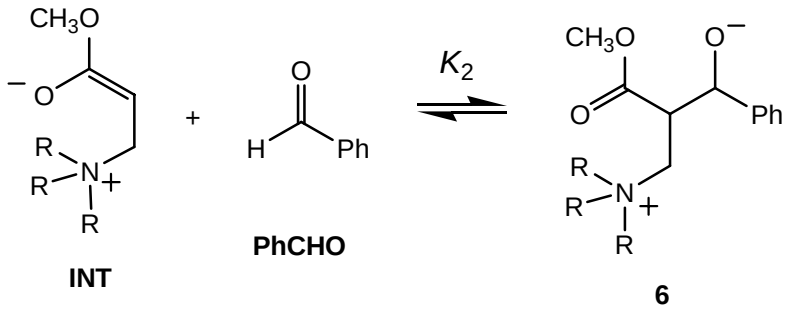
Price et al. evaluated an instantaneous rate expression

$$rate = -\frac{\partial[\mathbf{4}]}{\partial t} = k[\mathbf{4}][\mathbf{PhCHO}]^2[\mathbf{NR_3}]$$

by the method of initial rates. In the exam, you assumed an intermediate **6** that could be synthesized and isolated. Setting up a pre-equilibrium, however, makes it unnecessary to assume that [**6**] can be known, and only requires that we express $[\mathbf{6}]_{eq}$ in terms of other known concentrations. Mechanistically, we might get from **4** to **6** in two steps:



4 **INT**



INT **PhCHO** **6**

a) Using the pre-equilibrium assumption, write an expression for $[\mathbf{6}]_{eq}$.

b) In the exam, you concluded that it would be possible to write a single, combined rate expression

$$rate = -\frac{\partial[\mathbf{4}]}{\partial t} = -\frac{\partial[\mathbf{6}]}{\partial t} = k_1[\mathbf{6}][\mathbf{NR_3}] + k_2[\mathbf{6}][\mathbf{PhCHO}]$$

that described two simultaneous mechanisms with different rate constants k_1 and k_2. In reality, Price et al. concluded that one of the two mechanisms predominated. Based on your answer to (a), which one?