

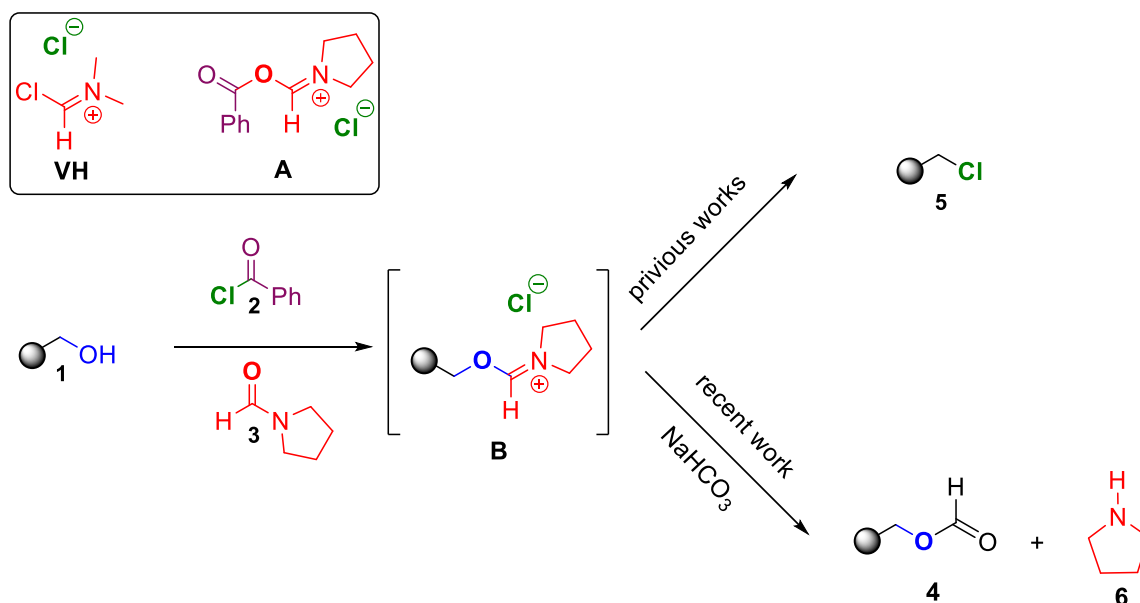
EFFICIENT FORMYLATION OF ALCOHOLS VIA A VILSMEIER-HAACK TYPE INTERMEDIATE

MSc. Thuyen Do, Prof. Dr. Peter Huy

Rostock University, Institute of Chemistry, Albert-Einstein-Strasse 3a, 18059 Rostock/D
thuyen.do@uni-rostock.de

The Vilsmeier-Haack reagent **VH** plays an important role and is commonly employed in organic synthesis for the formylation of arenes and as a promotor for C-Cl bond formation.^[1-3] This amidate and derivatives thereof are typically generated by the reaction of an amide with highly electrophilic reagents, such as phosphorus oxychloride (POCl₃),^[4] triphenylphosphine and NBS,^[5] and gaseous sulfuryl fluoride (SO₂F₂).^[6] However, there are several limitations due to the toxicity of these agents.

Our group has discovered that certain amides like **3** catalyze the transformation of alcohols **1** into alkyl chlorides **5** as Lewis bases by means of *in situ* generated Vilsmeier-Haack type intermediates like **A**.^[7] Based on this finding, we wish to report a novel method for the formylation of alcohols under mild conditions in enhanced sustainability.^[8] Noteworthy, this protocol is also applicable to highly reactive benzylic and allylic substrates, which readily react further to the respective chloro alkanes, by means of anion exchange.



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