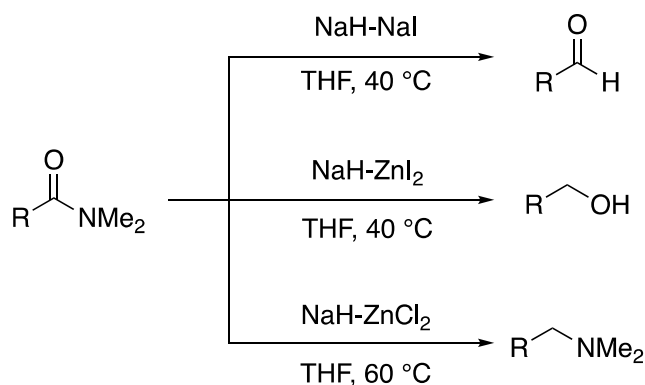


CONTROLLED REDUCTION OF CARBOXAMIDES TO ALDEHYDES, ALCOHOLS OR AMINES

Derek Y. Ong and Shunsuke Chiba

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

Our group recently reported a concise protocol to use sodium hydride (NaH) as a hydride donor by its solvothermal treatment with dissolving metal halides in THF, that enabled unprecedented reductive transformations such as hydrodeacylation of α -quaternary benzyl cyanides[1] and hydrodehalogenation of haloarenes[2]. Herein, we present controlled reduction of carboxamides to aldehydes, alcohols, or amines. Selective synthesis of aldehydes was achieved using the NaH-NaI system through single hydride reduction of carboxamides[3]. Double hydride reduction was established using combination of NaH and zinc halides (ZnX_2)[4], in which the selectivity for the formation of alcohols or amines is dictated by the halides on ZnX_2 ; the NaH- ZnI_2 system delivers alcohols and the NaH- $ZnCl_2$ system gives amines. The mechanistic investigation revealed that different zinc hydride species are formed and responsible for the observed selectivity.



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