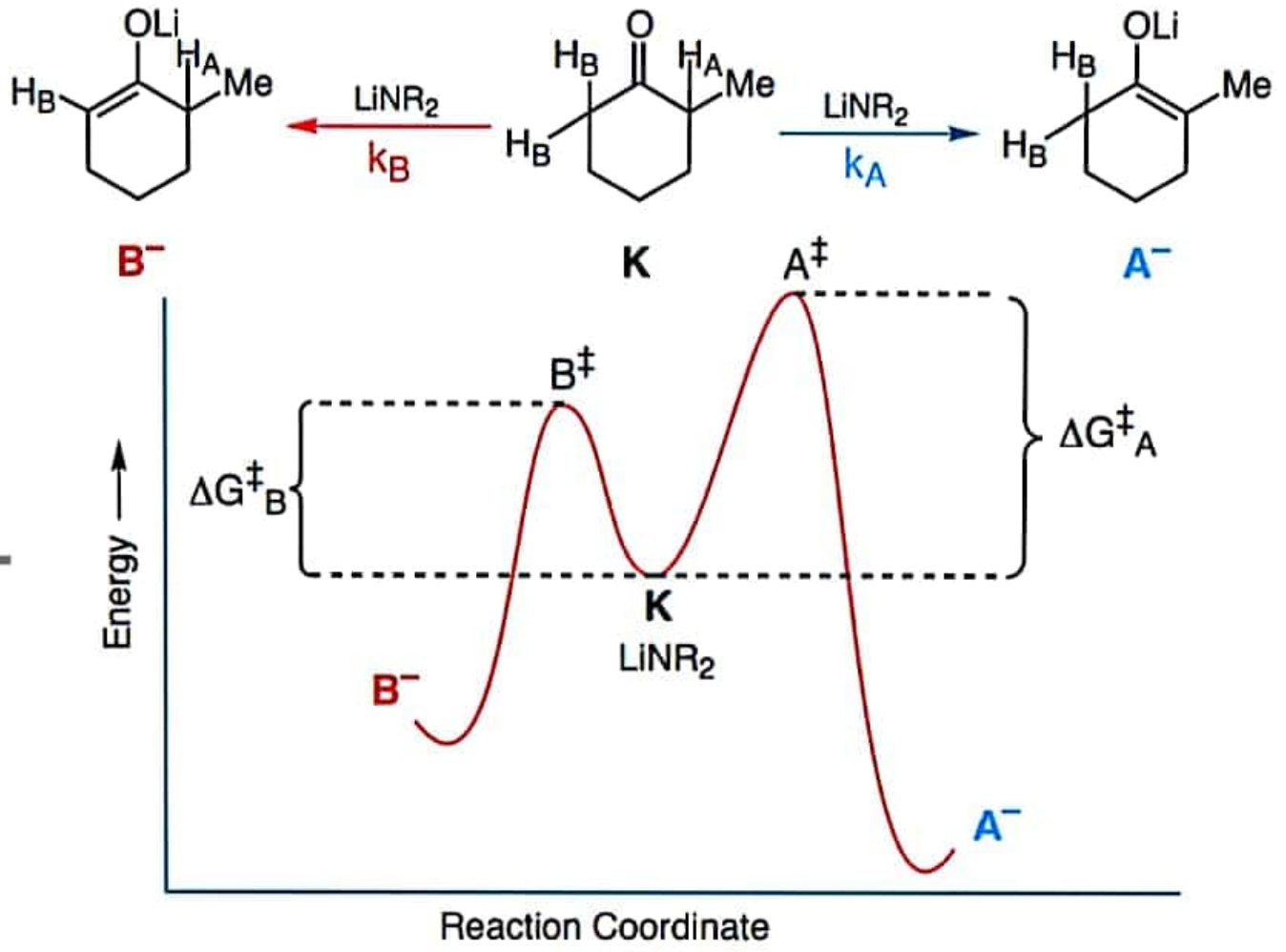
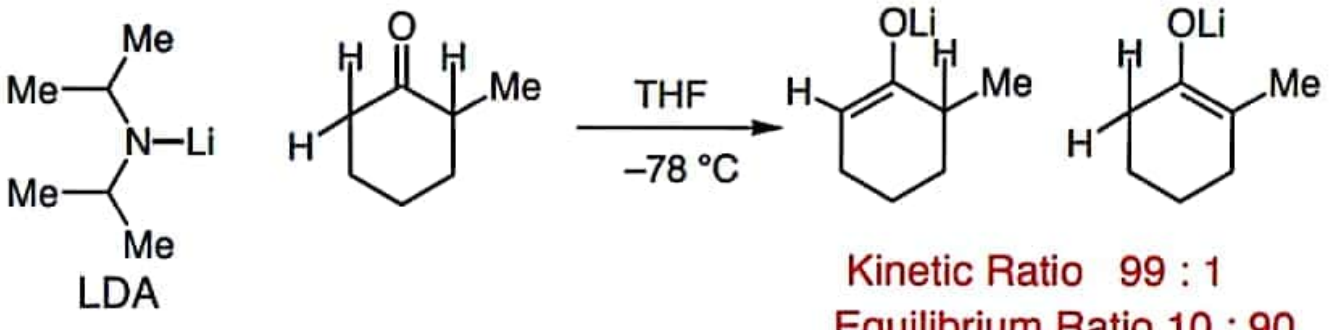
Kinetic Acidity: Rates of proton removal

Consider enolization of the illustrated ketone under non-equilibrating conditions:



Kinetic acidity refers to the rate of proton removal. e.g. k_A vs k_B. For example, in reading the above energy diagram you would say that H_A has a lower kinetic acidity than H_B. As such, the structure of the base (hindered vs unhindered) employed plays a role in determining the magnitude of k_A and k_B. For the case shown above, $\Delta G^‡_A$ will increase more than $\Delta G^‡_B$ as the base becomes more hindered since the proton H_A resides in a more sterically hindered environment. The example shown below shows the high level of selectivity which may be achieved with the sterically hindered base lithium diisopropylamide (LDA).



Kinetic Ratio 99 : 1
Equilibrium Ratio 10 : 90