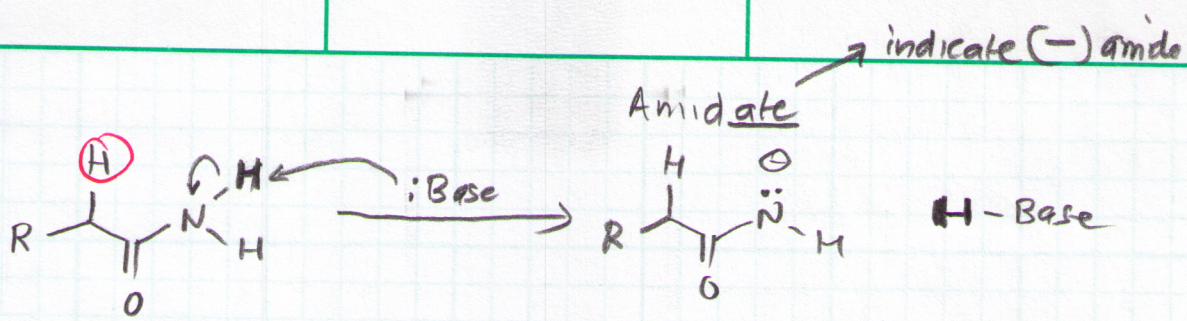
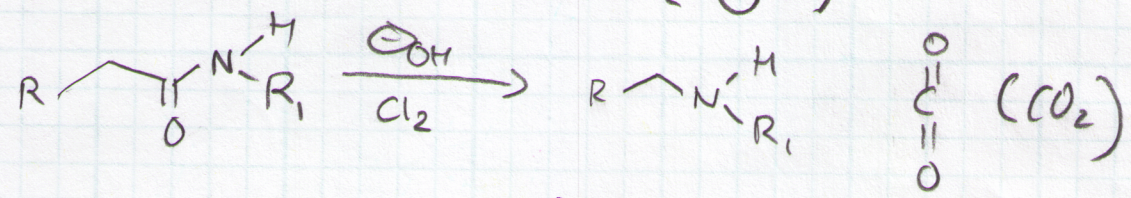


which has a lower pKa **(H)** or **H**?

Evaluate the rel. stability of the conj bases!

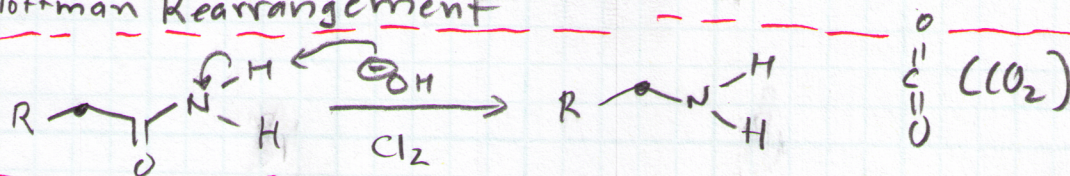
why?

Knowing that an amide N with two acidic H can be removed and thus can become nucleophilic via its amidate, the following transformation can occur via a haloamide ($\text{R}-\overset{\text{O}}{\parallel}-\overset{\ominus}{\text{N}}-\text{X}$)

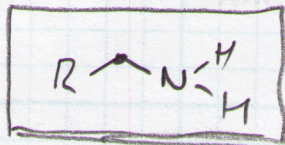
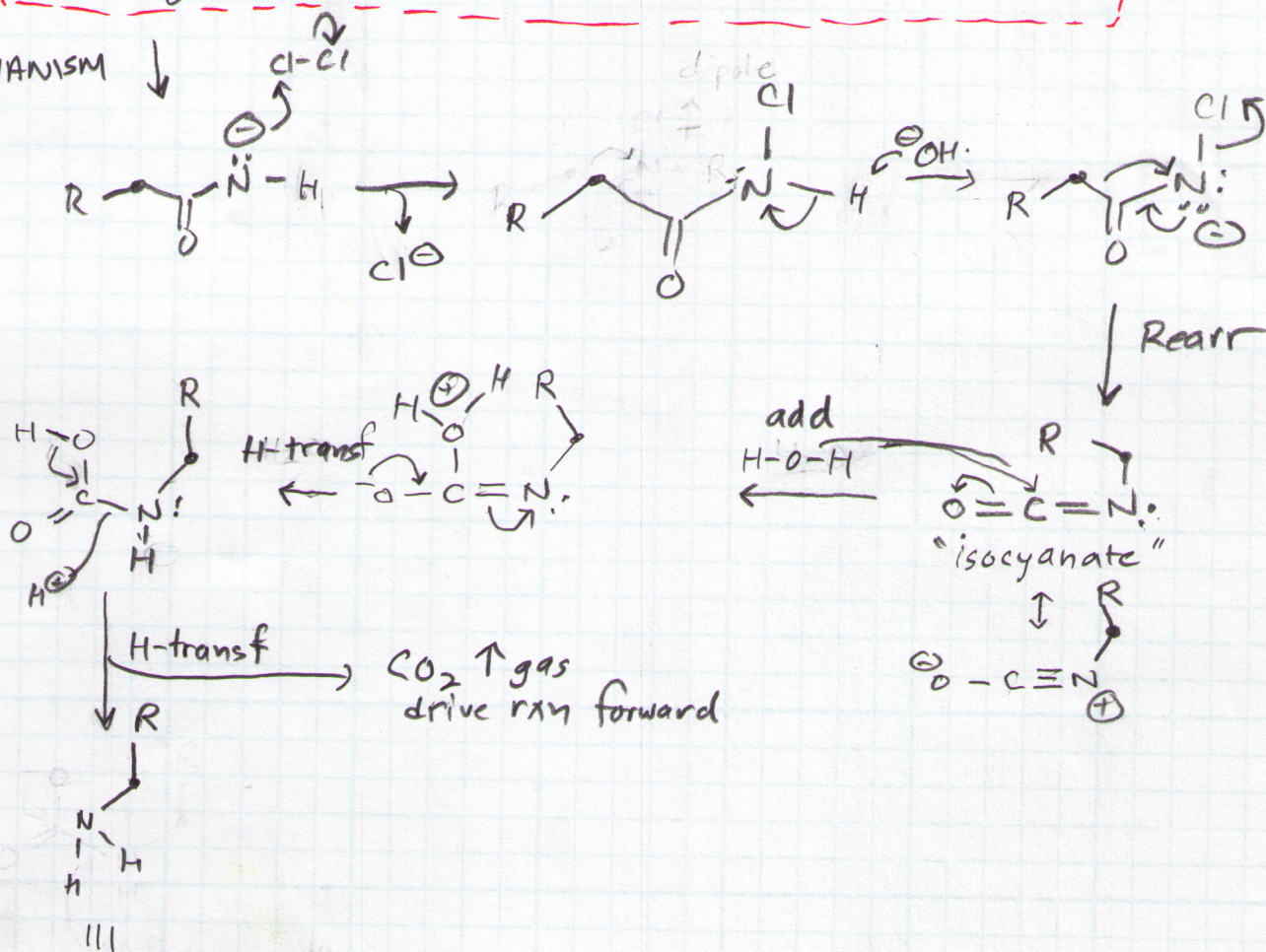


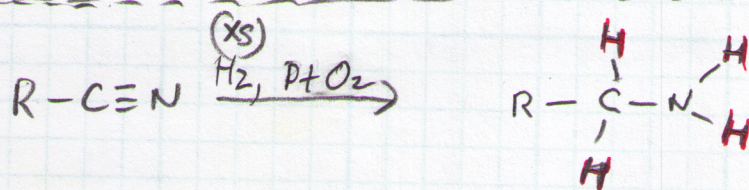
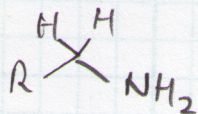
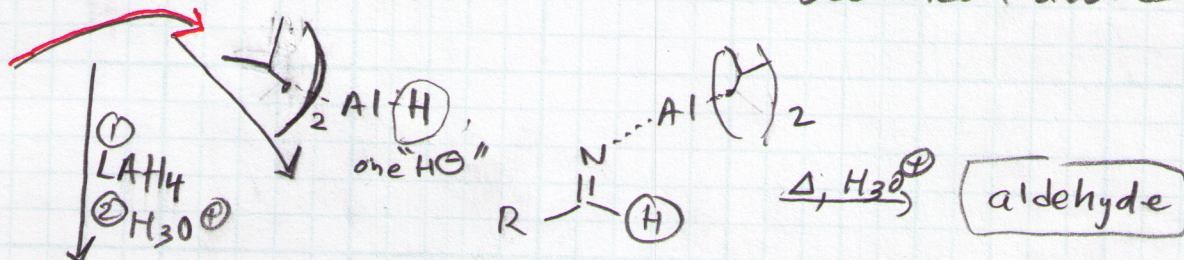
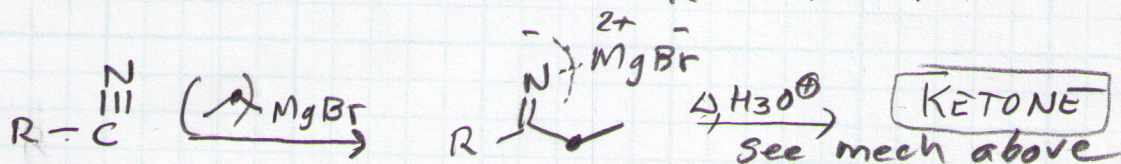
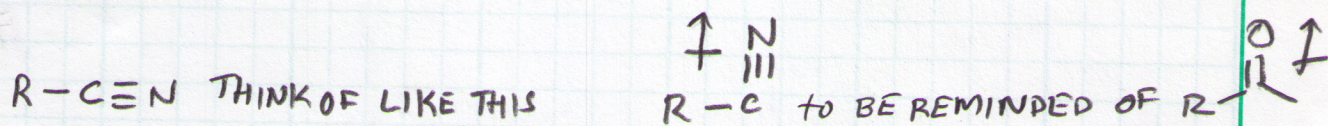
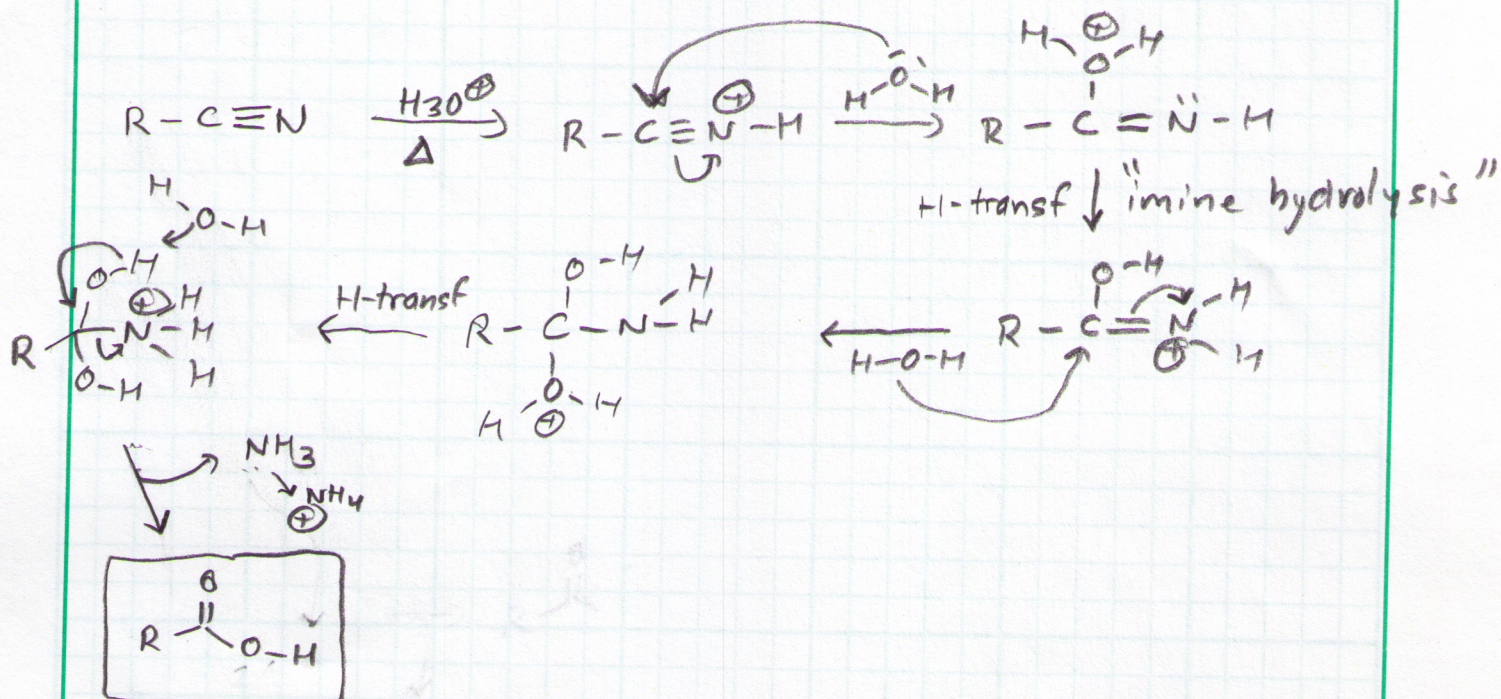
Mechanism (Hoffman Rearr)

Hoffman Rearrangement

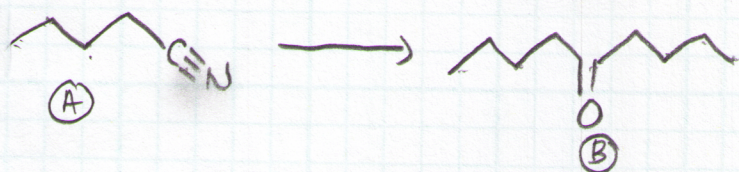


MECHANISM





diisobutyl aluminium hydride



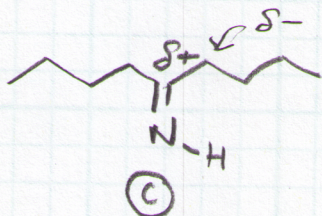
How would you start?

① Count carbons!

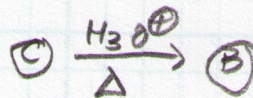
(A) = C₅ (B) = C₈

$\therefore$ need to add 4 C's to (A)

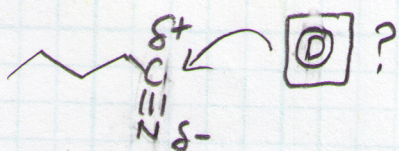
② The intermediate that (B) can come from that contains an N instead of O is



Think forward too!

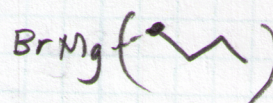
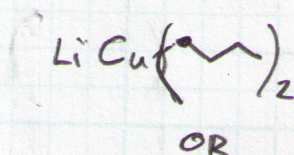


③ We know (C) can come from (A), but what is needed to rxn w/ (A)?

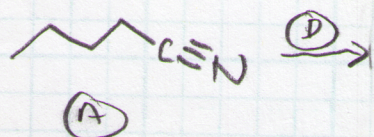


Drawn oddly to help

(D) is like this, and it could come from

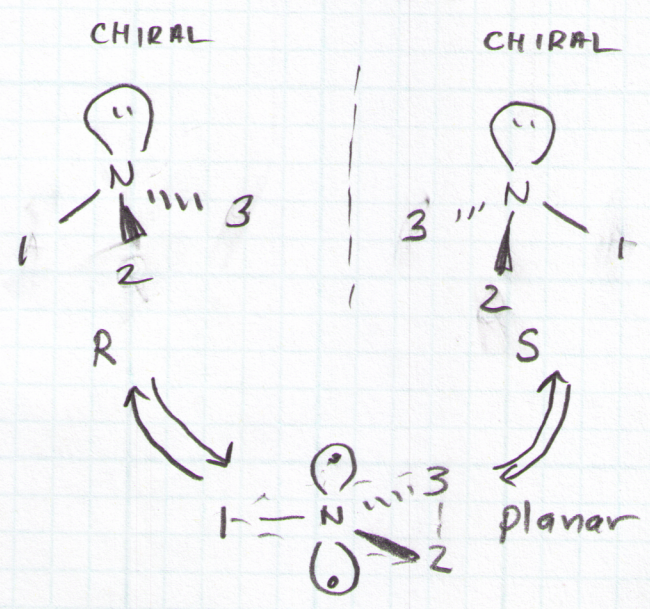


NOW YOU COMPLETE THE FORWARD RXN



Amines

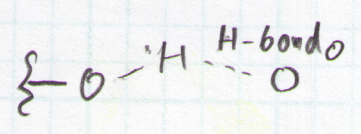
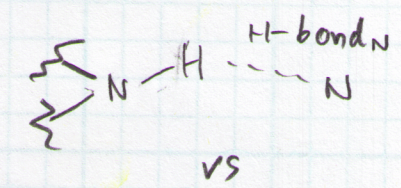
orbitals
tetrahedral
 sp^3



pyramidal
geometry of N
and its 3 substituents

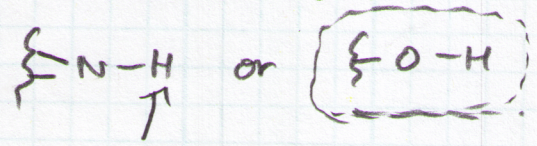
low E barrier

NOT optically active on
the spectrometer time scale



which is stronger H-bond_N
or
H-bond_O ?

Think in terms of acidity
which is more acidic?



Smaller δ^+
because N share
 e^- with H better
 $\downarrow \delta^+$

