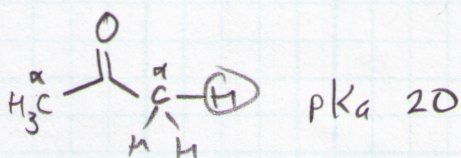
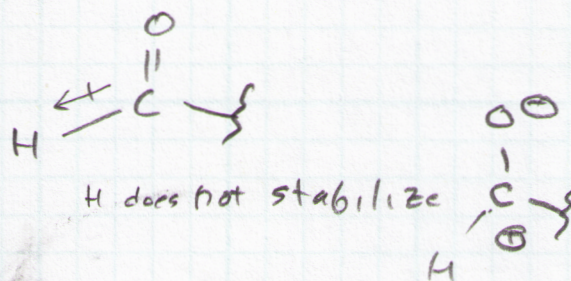
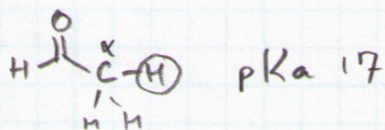
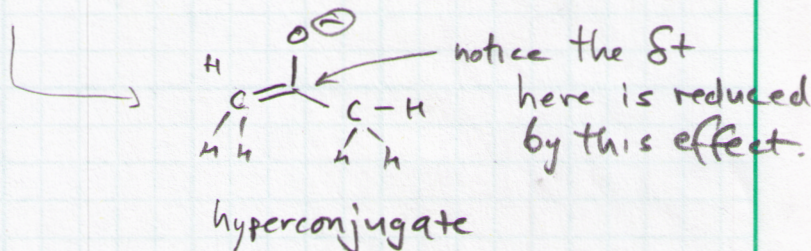


ENOLS ENOLATES and ALDOL CONDENSATION

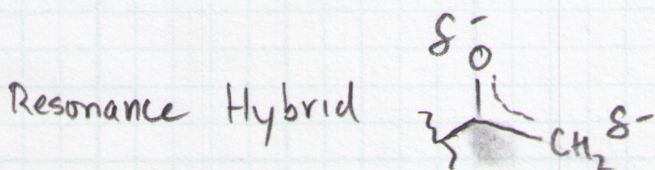
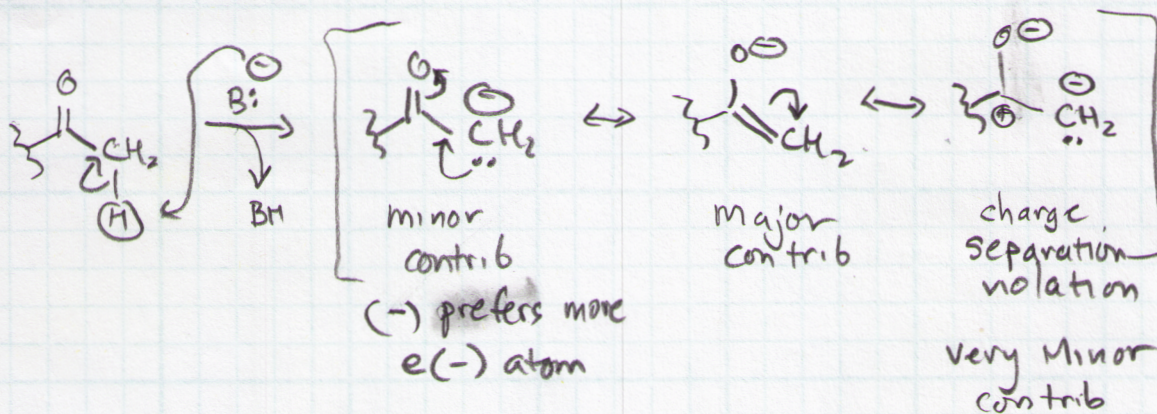


∴ deprotonation of acidic proton (α-H) of aldehyde occurs at greater rate over ketone deprotonation

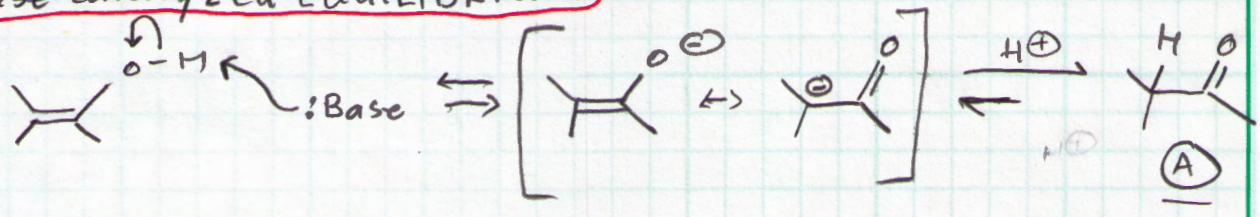
recall hyperconjugation donates e⁻ toward carbonyl C.



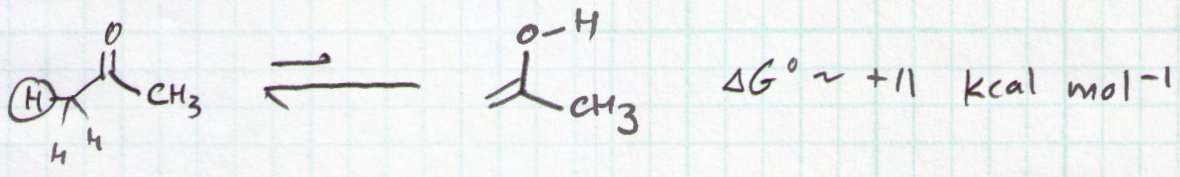
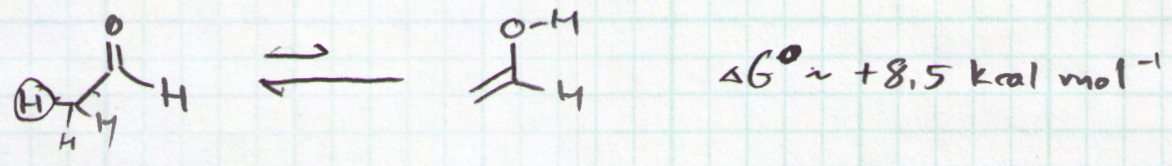
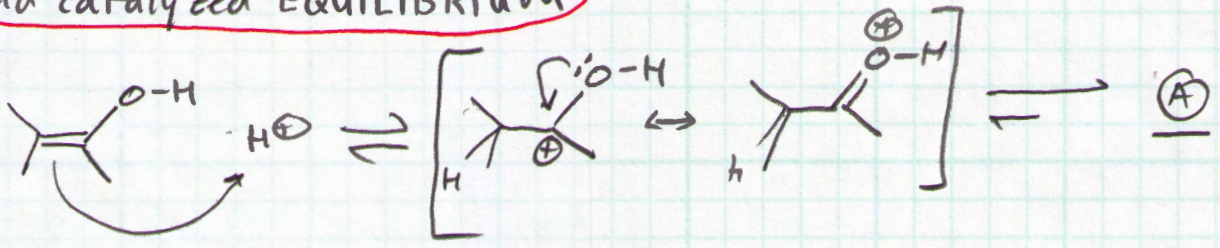
Deprotonation is stabilized by resonance



keto-enol tautomerization (H-transfer is not internal)
Base catalyzed EQUILIBRIUM

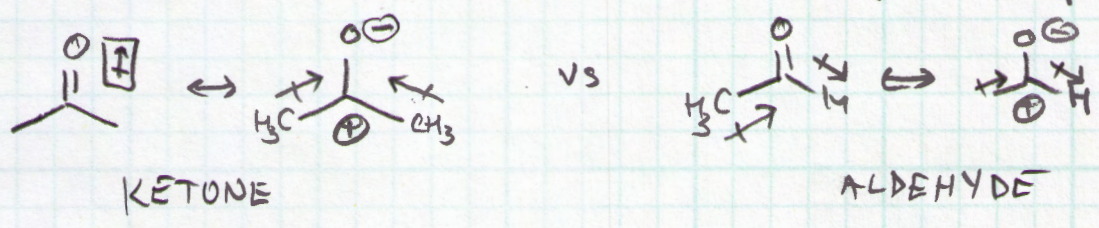


Acid catalyzed EQUILIBRIUM



Which (H) is more acidic? Evaluate stability of conj bases!

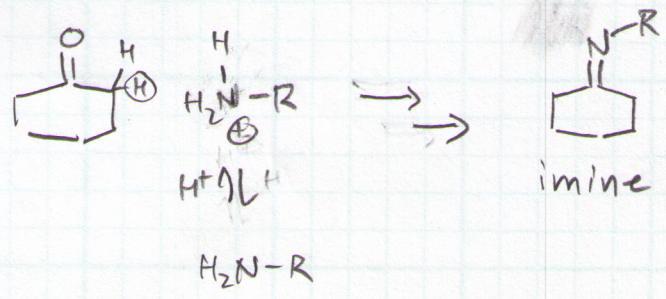
* ketone $\text{C}=\text{O}$ is more stable than aldehyde $\text{C}=\text{O}-\text{H}$. WHY?



KETONE

ALDEHYDE

We know

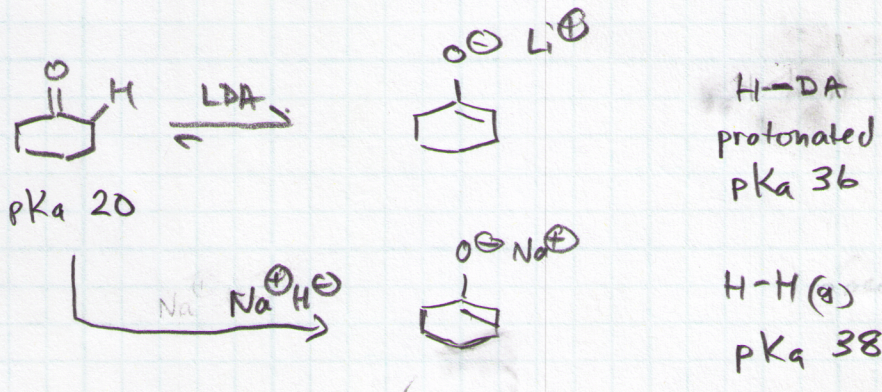
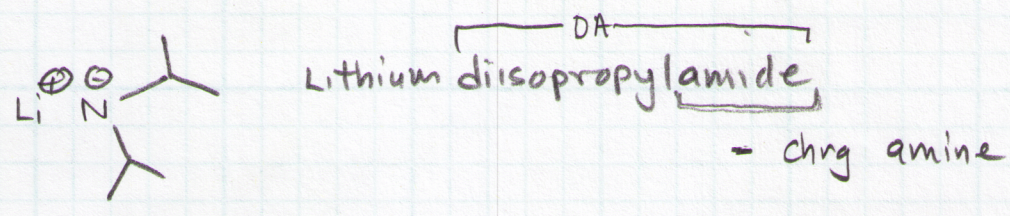


if R-NH- small base is used to remove α -H THEN COMPETITION

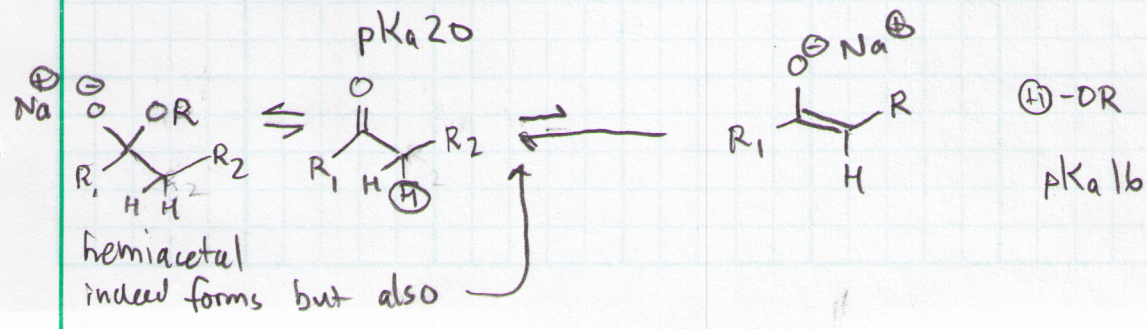
CC(=O)CC \rightleftharpoons CC(=O)CC

(Need a base whose conjug acid has higher pKa than α -H of ketone)

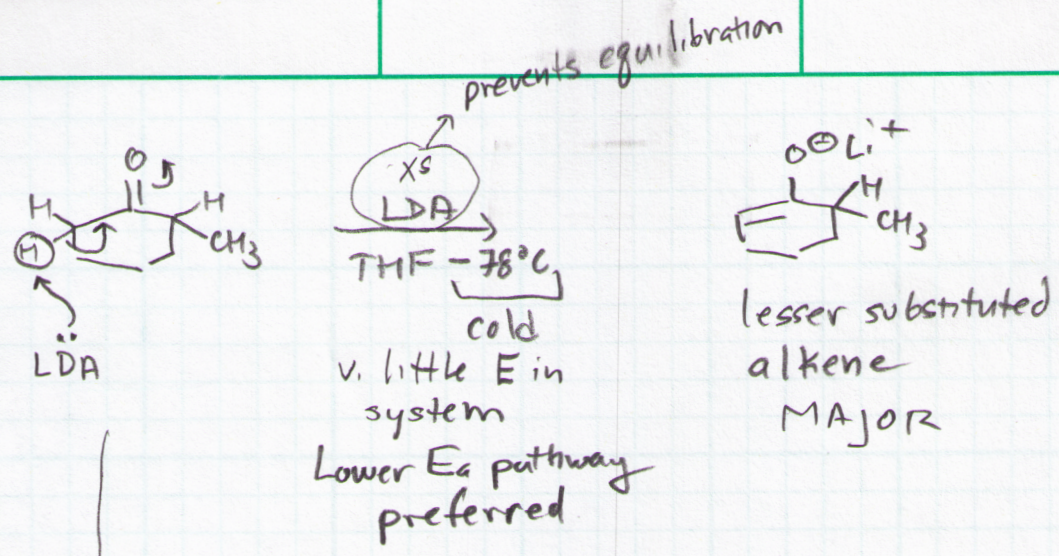
Need bulkier base that's not nucleophilic or non-nucleophilic base



often ROH/RO⁻Na⁺ mixtures are used

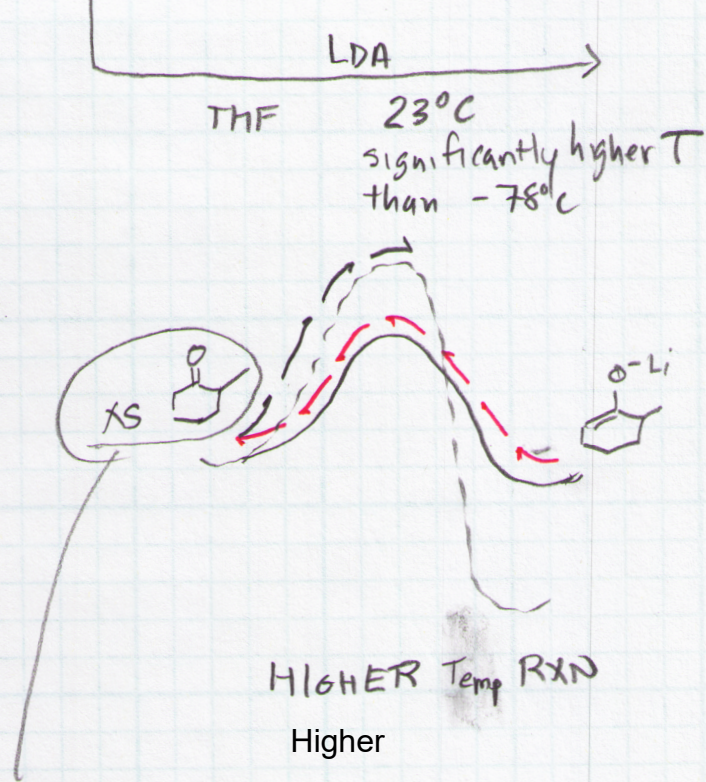


NOTE pKa values - equil lies to left



XS ketone - promotes equilibration

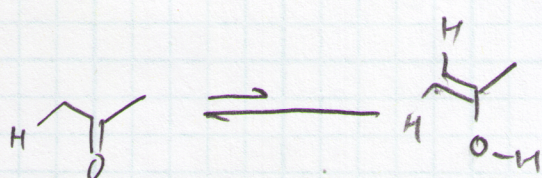
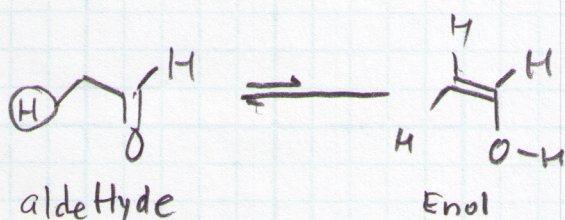
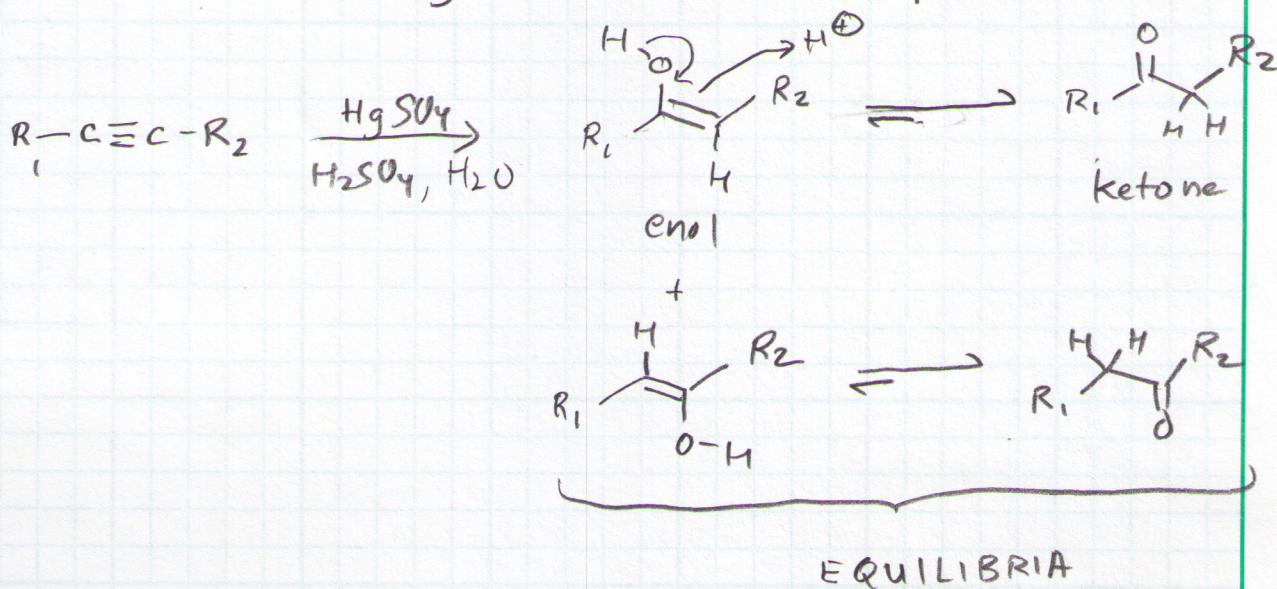
XS Means 1.5 equiv



Maintains EQUILIBRIUM w/ KINETIC ENOLATE, When kinetic enolate returns to ketone, then it can pass over higher E_a and go to the thermodynamic product.

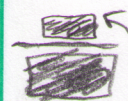
Keto-enol Equilibrium

You learned the following rxns in earlier chapters



$$K_{eq} = 6 \times 10^{-7} = \frac{[\text{Enol}]}{[\text{ald}]}$$

$$K_{eq} = 5 \times 10^{-9} = \frac{[\text{Enol}]}{[\text{Ket}]}$$

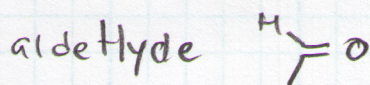


rel. compare size



Both K_{eq} values are small ($10^{-\#}$) indicating the $C=O$ cpds are more stable than the corresponding enols.

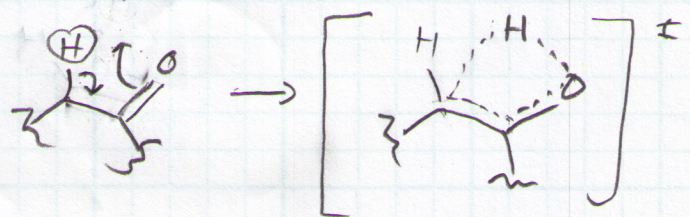
But 10^{-7} aldehyde vs 10^{-9} ketone suggests the aldehyde dissociates more to its enol than does the ketone. ∴ Ketone $C=O$ is more stable than



Keto-enol tautomerization occurs intermolecularly
 not intramolecularly
 within the same molecule

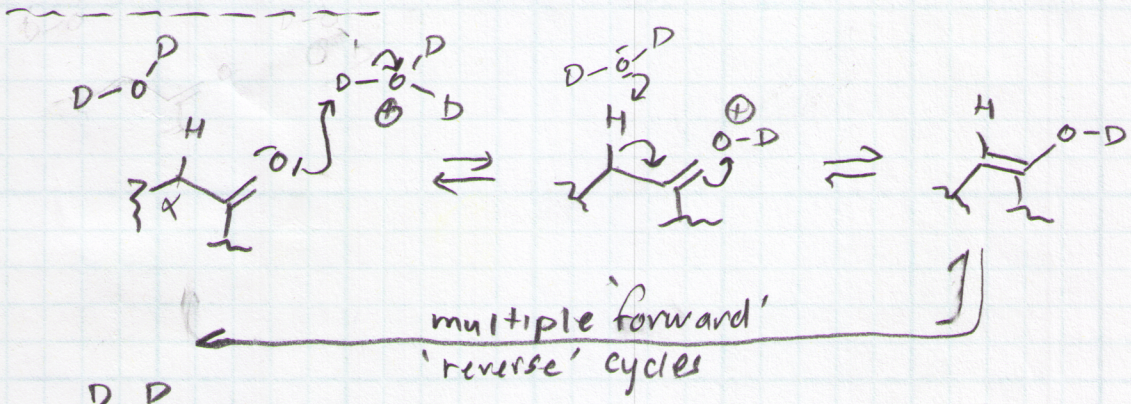
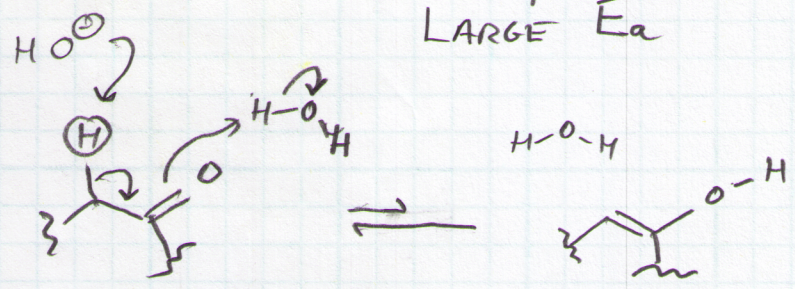
intermolecularly
 ↓
 exchanges with external proton source

Intramolecular is HIGH E



4-membered ring
 TS intermediate
 Highly strained
 LARGE E_a

THEORETICAL CALC.
 53 kcal mol⁻¹ barrier
 req. 500°C to overcome



complete exchange of H by D from D₂O/D₃O⁺