

Today

Other Reactions  
16.11-16.13, 16.15

Next Class

Reactions at the  $\alpha$ -Carbon  
17.1-17.3, 17.6

Test 3 on Chap 16 Postponed until 4/22

Additional Zoom Office Hours:

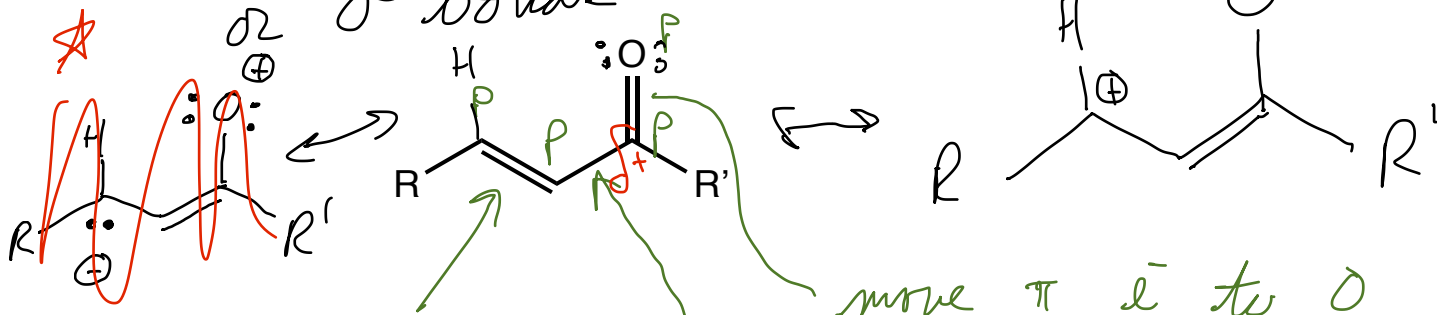
Today 11:15 – 11:45, 12:30 – 1:00, and 4:30 – 5:00

Tomorrow 9:30 – 10:30

$\alpha,\beta$ -unsaturated carbonyls: introduction resonance contributors Section 16.15, 16.16

just move  $\pi$  bonds and lp  $e^-$ 's not atoms

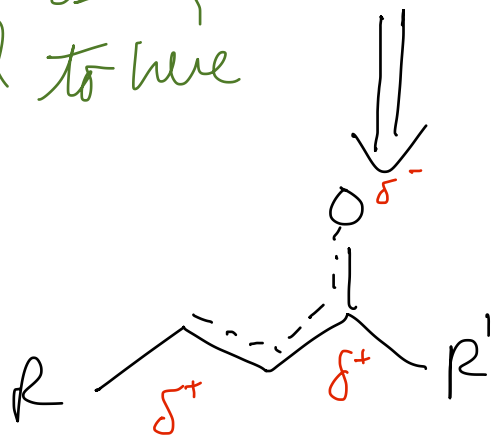
$\sigma$  bonds



move this  $\pi$  bond to here

move  $\pi$   $e^-$  to O

$$FC_2 = 4 - 5 = -1$$



\* too much going wrong with this drawing

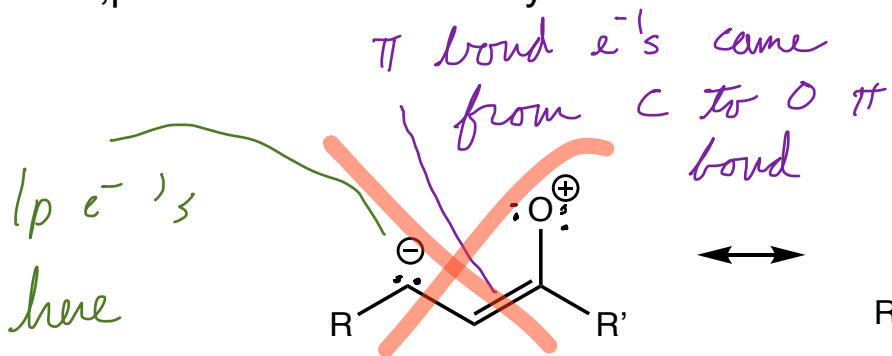
"wrong" charges  
O atom with an incomplete octet

The  $\beta$ -C of an  $\alpha,\beta$ -unsaturated carbonyl is electrophilic

$\alpha,\beta$ -unsaturated carbonyls

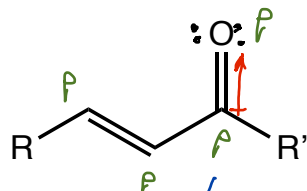
4 p orbitals in a row

Resonance



unreasonable & unimportant resonance contributor

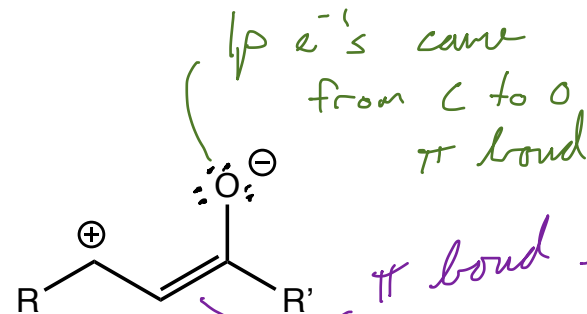
breaks **three** Lewis structure rules:  
 O has an incomplete octet  
 unnecessary charge separation exists  
 more electronegative atom is (+)  
 while the less electronegative atom is (-)



good & important resonance contributor

follows all Lewis structure rules

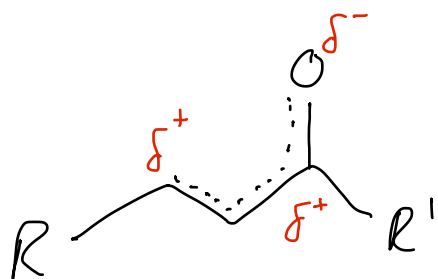
one electrophilic C?



reasonable & important resonance contributor

breaks two Lewis structure rules:  
 C has an incomplete octet  
 unnecessary charge separation exists

$\pi$  bond  $e^-$ 's came from the original C to C  $\pi$  bond



no, two electrophilic C's because of the extended  $\pi$  system

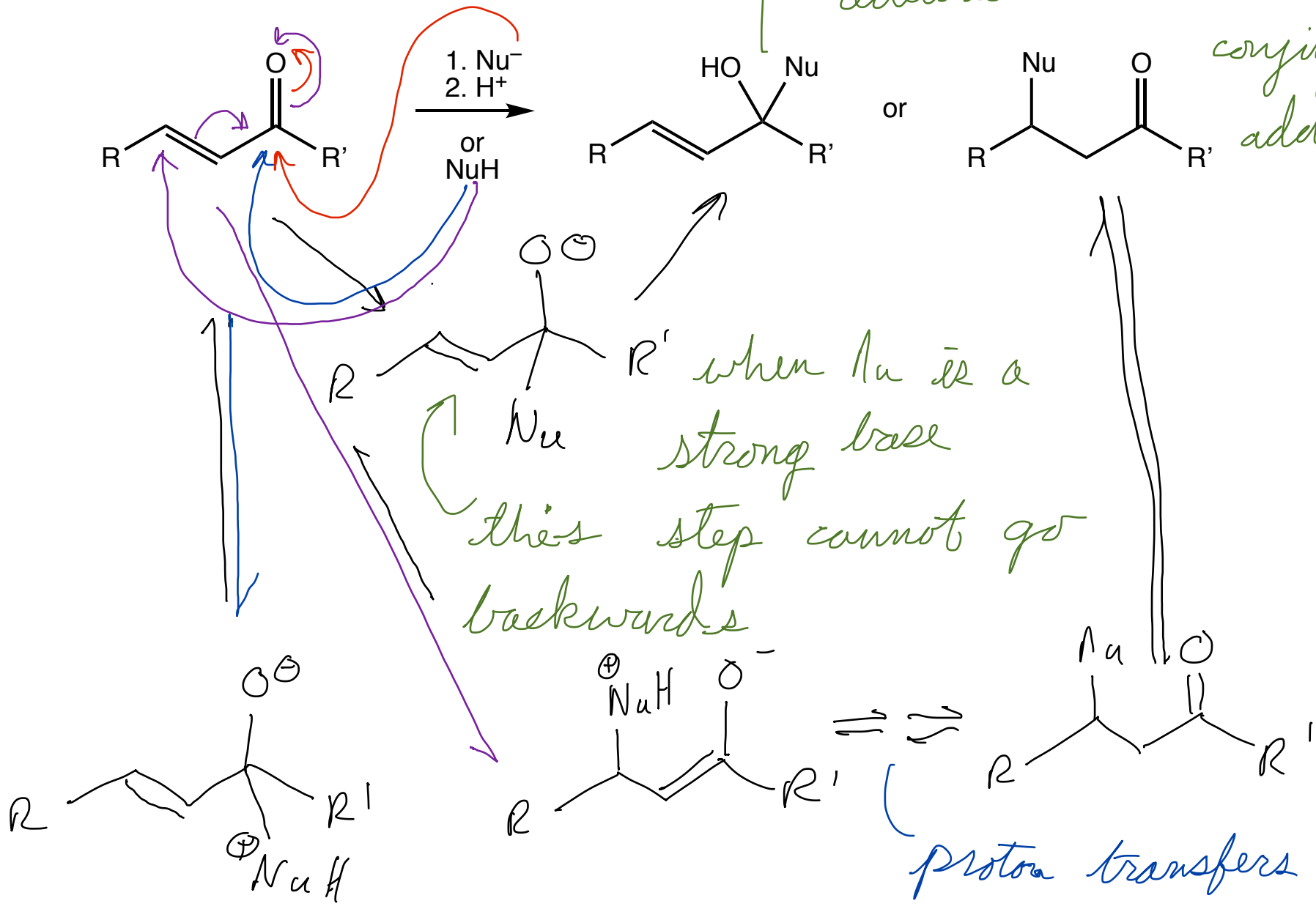
MO theory is a lot of work so sometimes we use the kludge called resonance

$\alpha,\beta$ -unsaturated carbonyls: kinetic vs thermodynamic control

Section 16.15, 16.16

nucleophilic addition

conjugate addition



weak bases can be released from the  $\text{C}=\text{O}$ 's C.

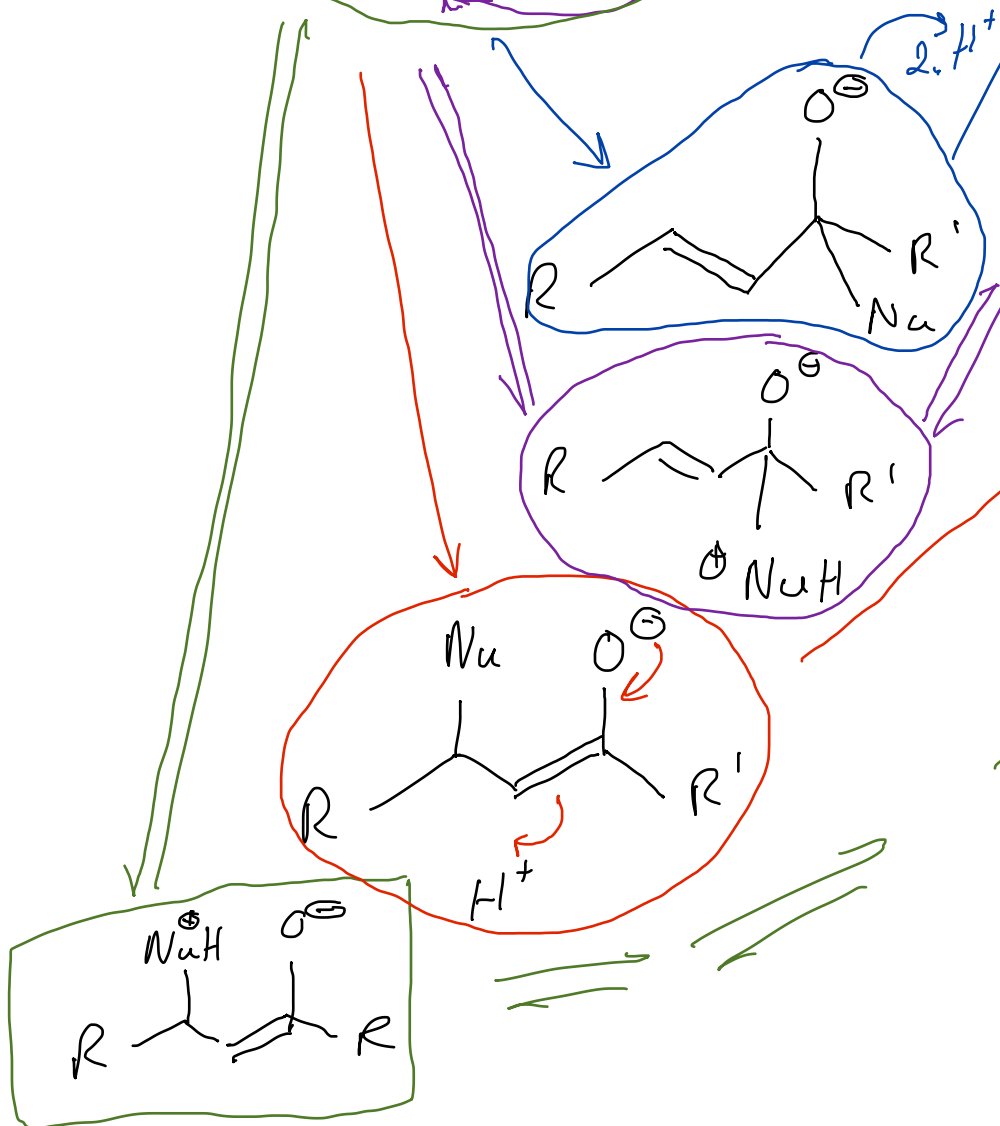
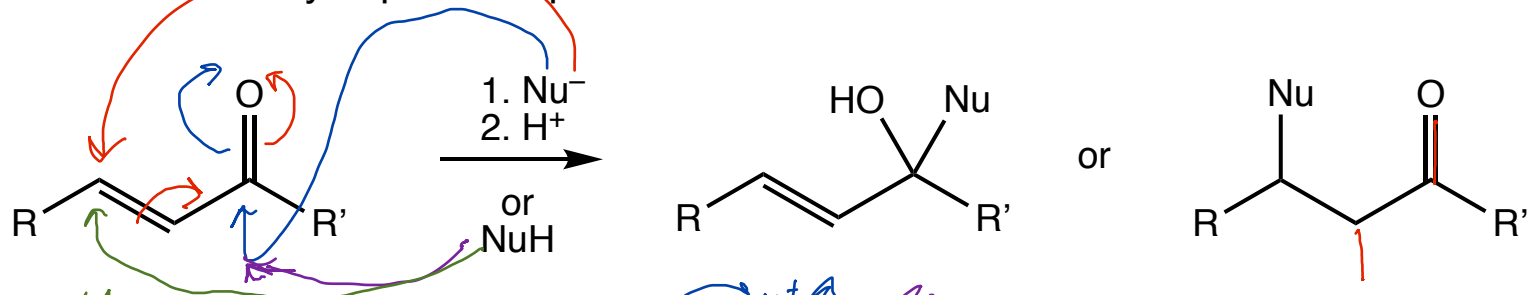
reactions with single direction arrows are under **kinetic control**. What ever happens fastest gives the most product.

reactions that have equilibrium arrows are under **thermodynamic control**.  
The most stable product is the major product.

strong base  $\text{Nu}^- = \text{R}_3\text{C}^\ominus, \text{H}^\ominus, \text{RC}\equiv\text{C}^\ominus$

$\alpha, \beta$ -unsaturated carbonyls: paths to products

Section 16.15, 16.16



$\text{H}^+$  transfers

$2. \text{H}^+$

$\text{H}^+$  transfers

more than 1 step but I didn't count them so not necessarily 3.

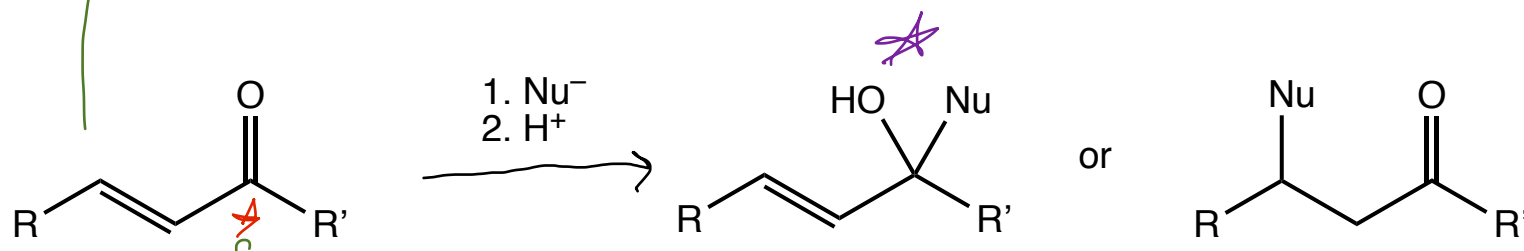
Both the  $\text{Nu}^\ominus$  and the  $\text{NuH}$  can react with either C atom

$\alpha, \beta$ -unsaturated carbonyls: kinetic control

conjugate addition

1,4 addition

Section 16.15, 16.16



When the nucleophile is a strong base the reaction is under kinetic control and the product that forms fastest is major

$*$  This  $C$  is most positive since it is closest to the  $O$ . This  $C$  should be the best target & lead to the major prod.

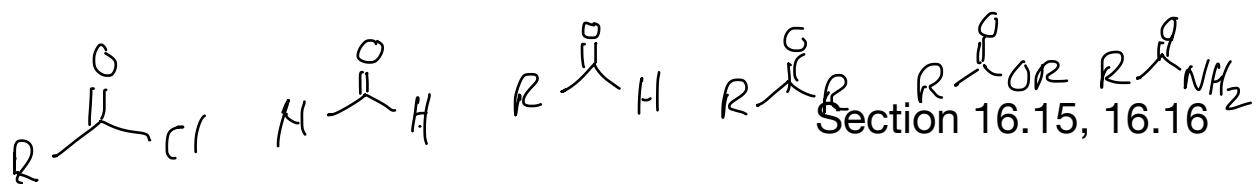
Crowding at  $*$  carbon will lower the yield of  $*$   
If  $C$  to  $C$   $\pi$  bond is destabilized the yield of  $*$  will be lowered

Kinetic control ... reversible or irreversible reactions?

Thermodynamic ~~&~~ control requires reversible reactions. Rxns go back and forth so more stable compound can form an increase its conc



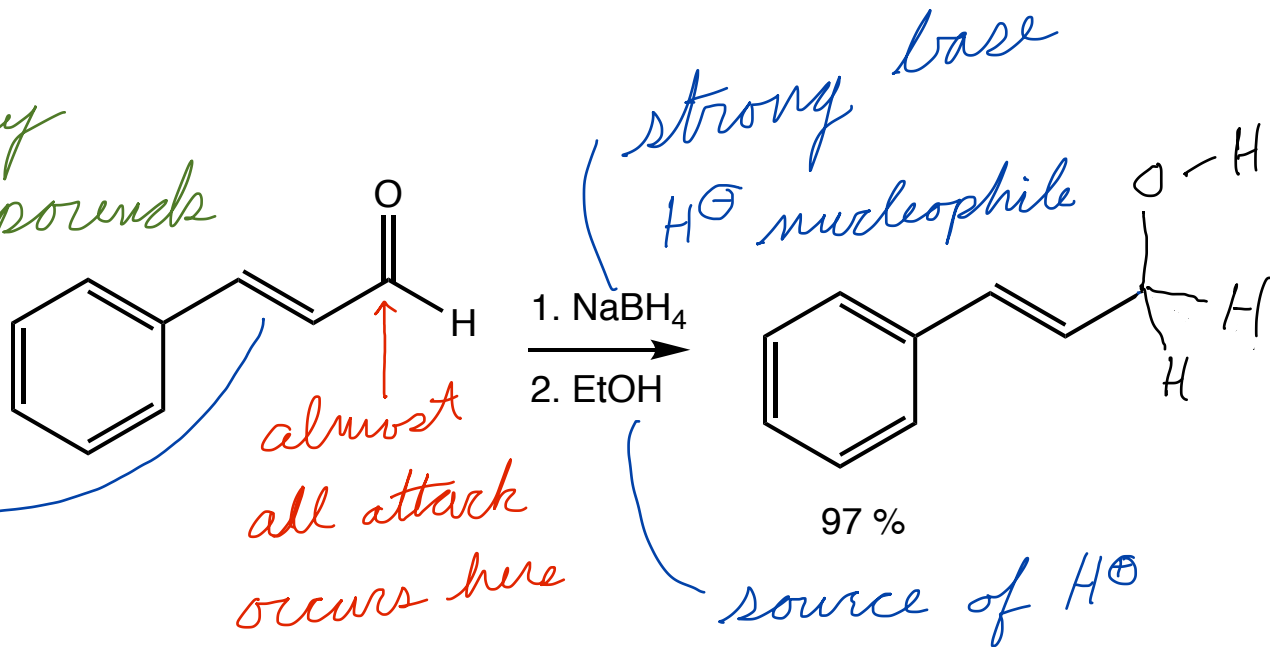
$\alpha,\beta$ -unsaturated carbonyls



Still it is difficult to predict the outcome.

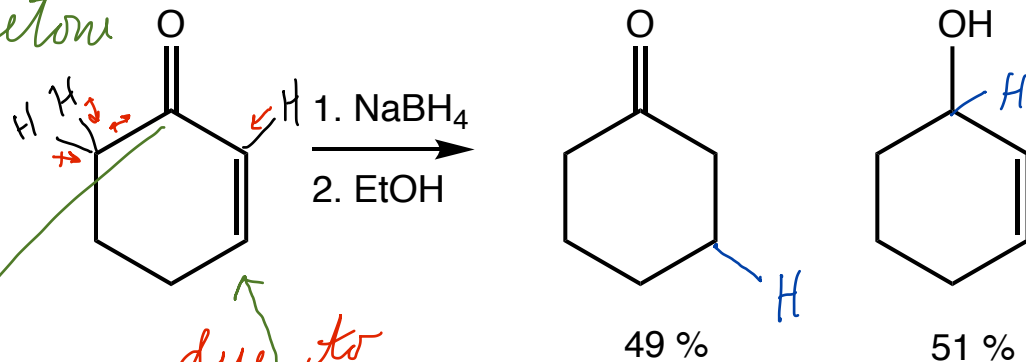
Aldehydes are very reactive  $C=O$  compounds

no crowding  
no destabilization of  $\pi$  bond

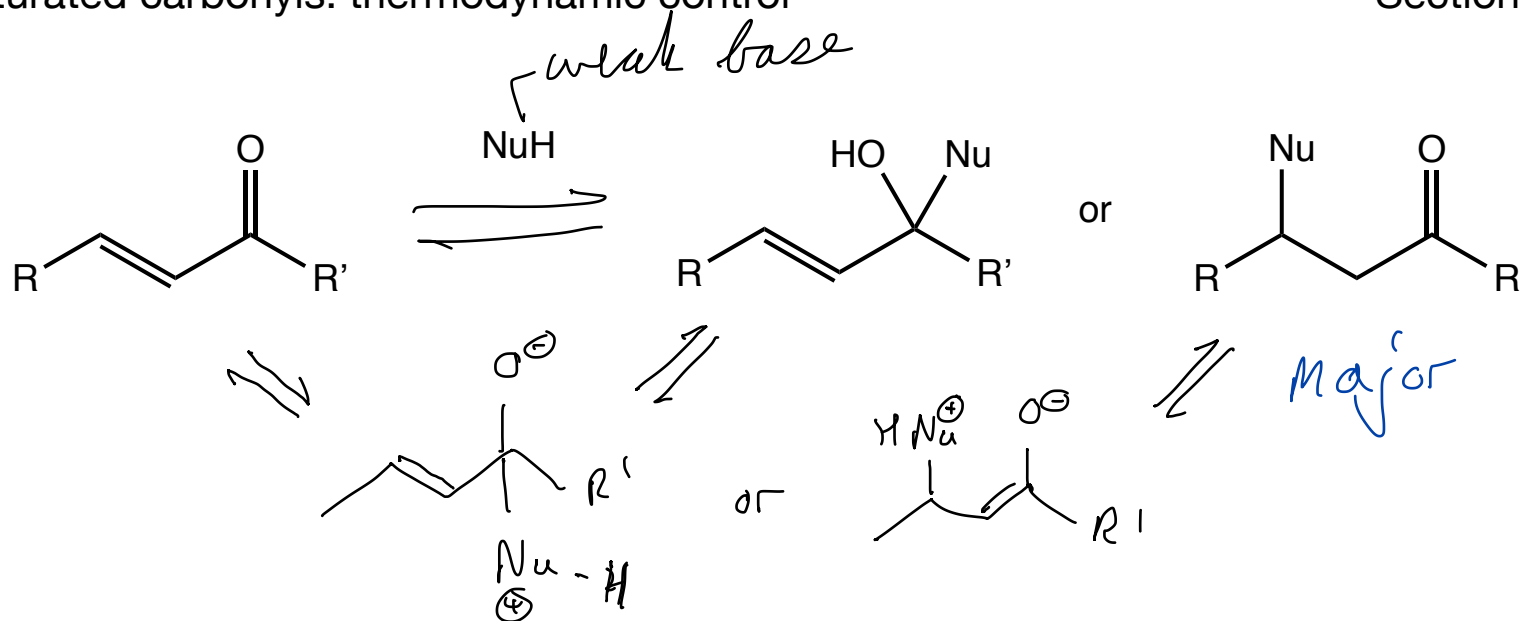


less reactive ketone

the ring is interfering - crowding



still a decent target so  $\text{H}^+$  can attack  $C=O$



more of the more stable product

the one with the  $C=O$

