

Today

Other Reactions
16.11-16.13, 16.15

Next Class

Reactions at the α -Carbon
17.1-17.3, 17.6

Test 3 on Chap 16 Postponed until 4/22

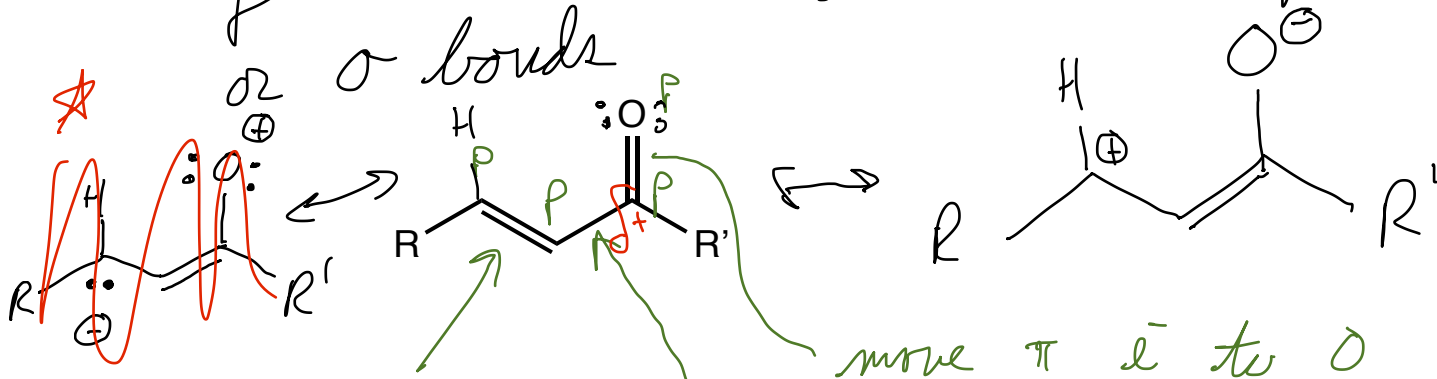
Additional Zoom Office Hours:

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

Tomorrow 9:30 – 10:30

α, β -unsaturated carbonyls: introduction resonance contributors Section 16.15, 16.16

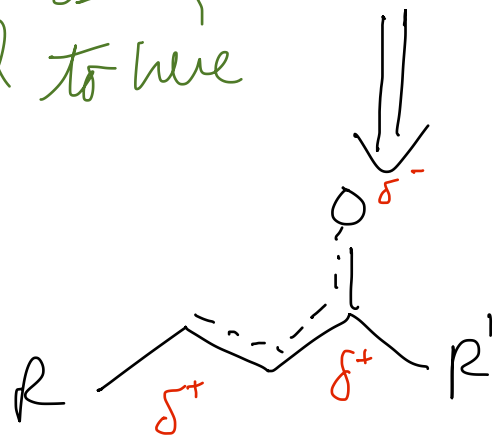
just move π bonds and lp e^- 's not atoms
 or σ bonds



move this π bond to here

move π e^- to O

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



* too much going wrong with this drawing

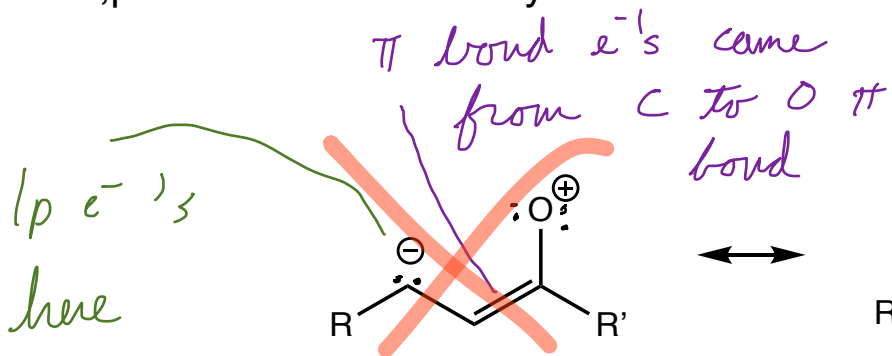
"wrong" charges
 O atom with an incomplete octet

The β -C of an α, β -unsaturated carbonyl is electrophilic

α,β -unsaturated carbonyls

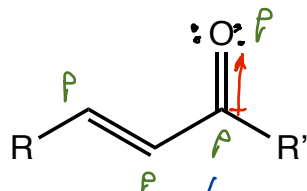
4 p orbitals in a row

Resonance



unreasonable & unimportant resonance contributor

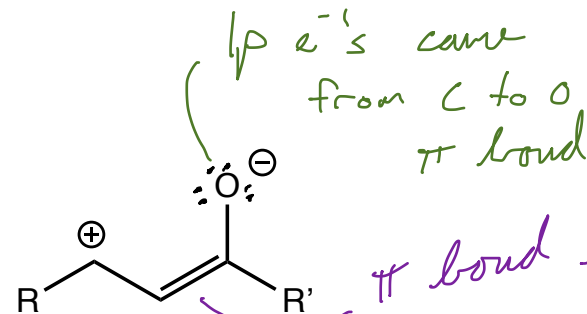
breaks **three** Lewis structure rules:
 O has an incomplete octet
 unnecessary charge separation exists
 more electronegative atom is (+)
 while the less electronegative atom is (-)



good & important resonance contributor

follows all Lewis structure rules

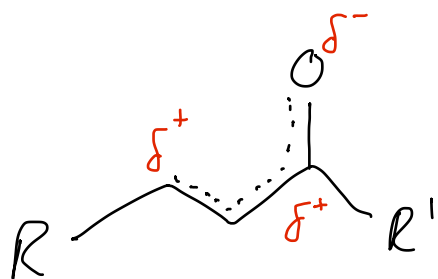
one electrophilic C?



reasonable & important resonance contributor

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

π bond e^- 's came from the original C to C π bond



no, two electrophilic C's because of the extended π system

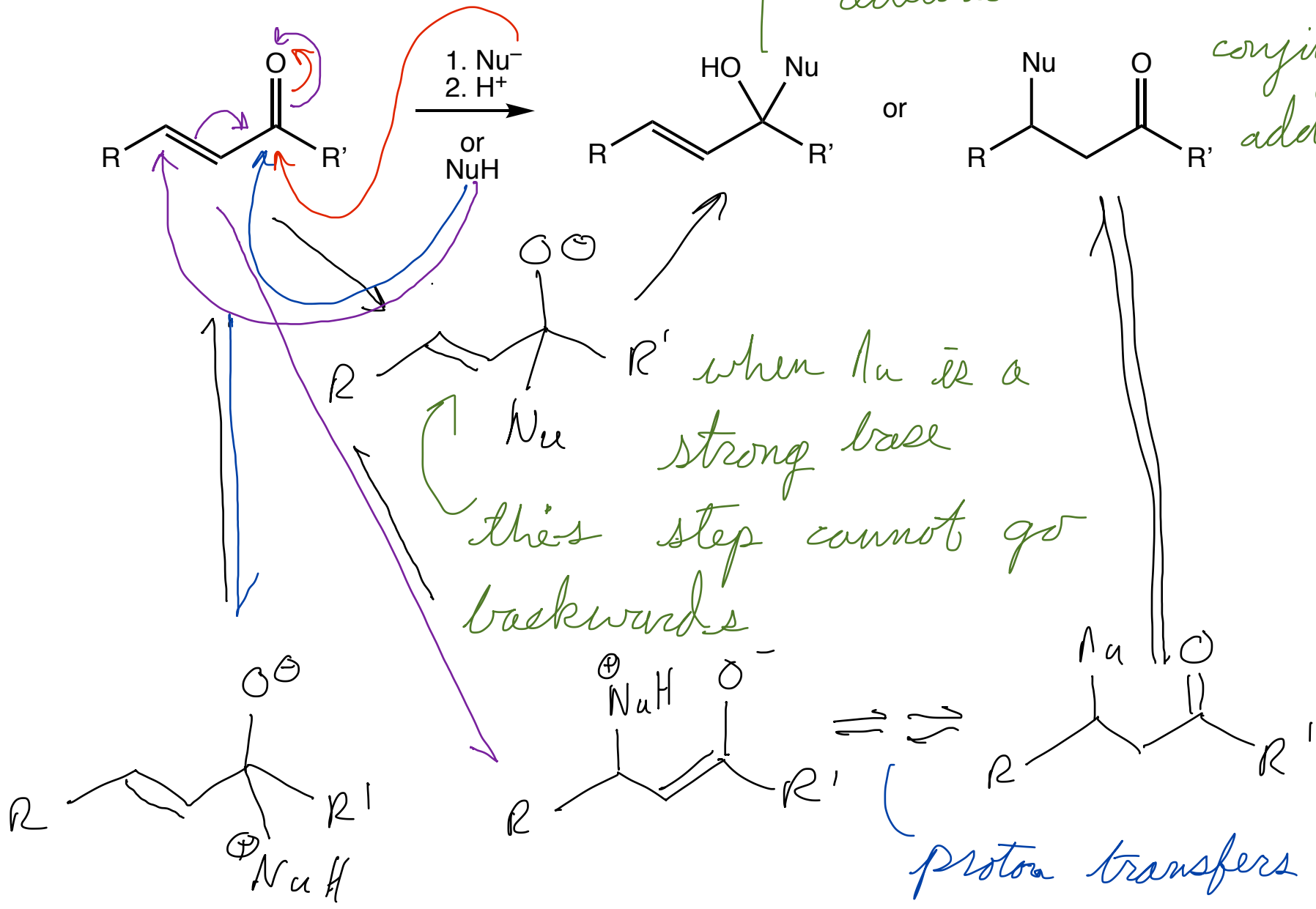
MO theory is a lot of work so sometimes we use the kludge called resonance

α,β -unsaturated carbonyls: kinetic vs thermodynamic control

Section 16.15, 16.16

nucleophilic addition

conjugate addition



when Nu is a strong base this step cannot go backwards

proton transfers

weak bases can be released from the C=O's C.

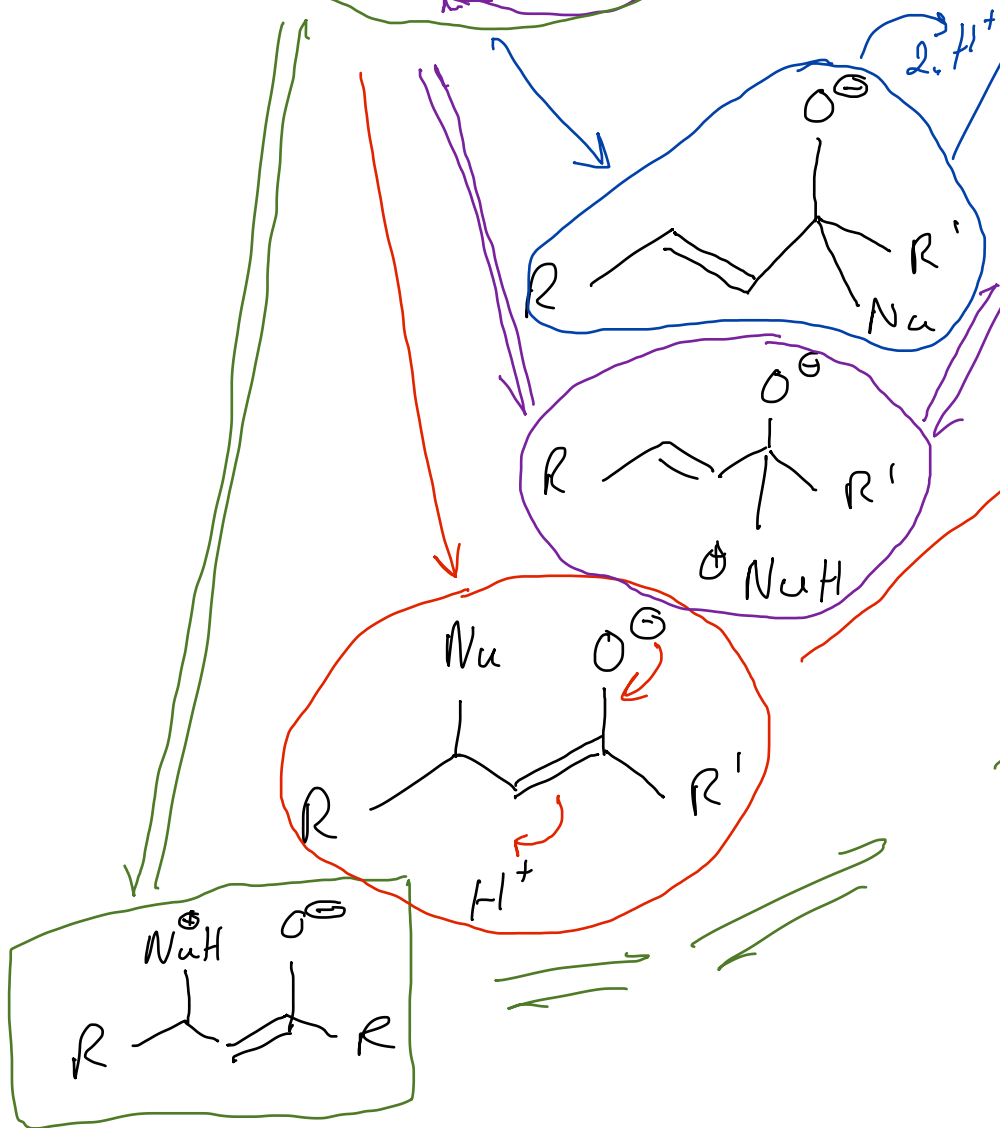
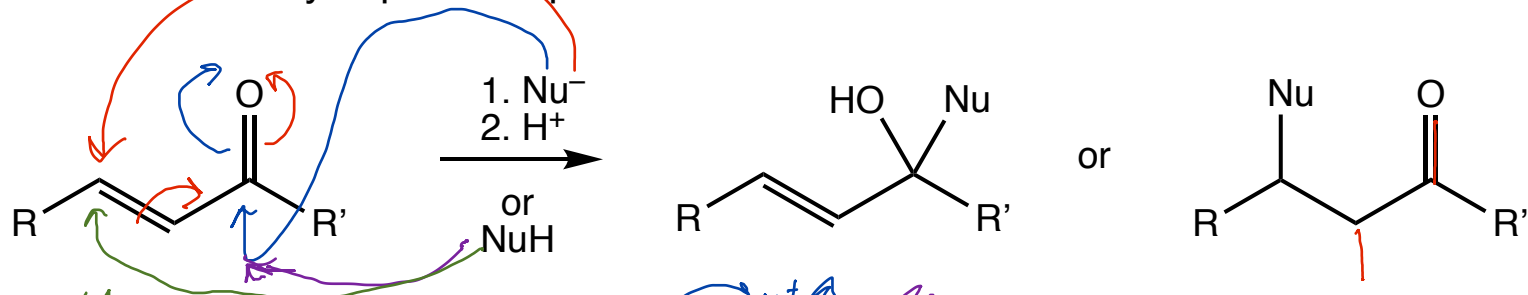
reactions with single direction arrows are under **kinetic control**. What ever happens fastest gives the most product.

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

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

α, β -unsaturated carbonyls: paths to products

Section 16.15, 16.16

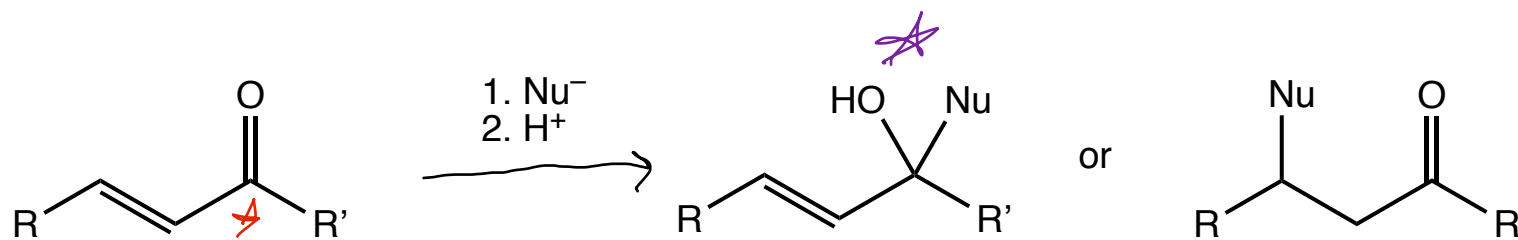


H^+ transfers

H^+ transfers

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

Both the Nu^\ominus and the NuH can react with either C atom



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

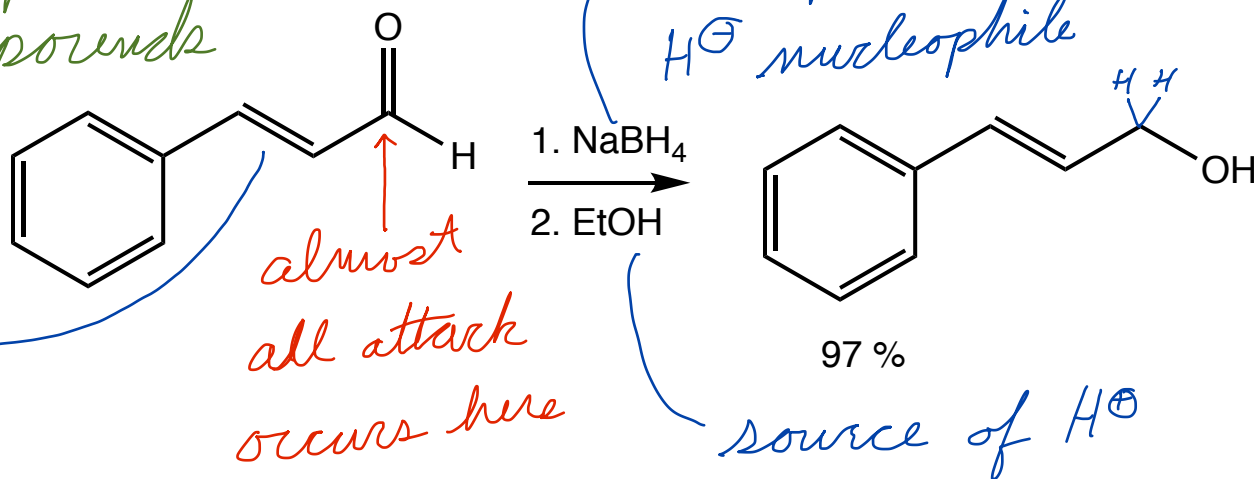
* This C is most positive since it is closest to the O. This C should be the best target & lead to the major prod.

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

Still it is difficult to predict the outcome.

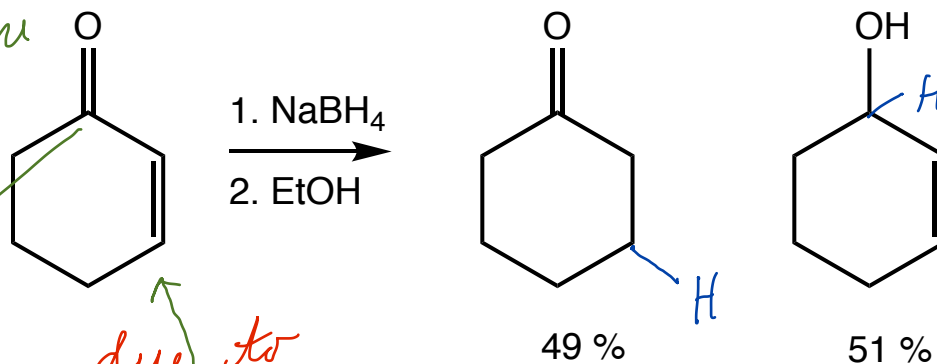
Aldehydes are very reactive $C=O$ compounds

no crowding
no destabilization of π bond



less reactive ketone

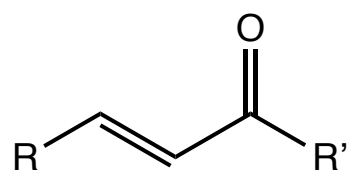
the ring is interfering -- crowding



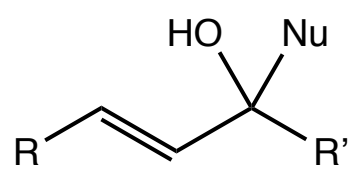
as reactivity of $C=O$ C is lower more reaction occurs farther away

α,β -unsaturated carbonyls: thermodynamic control

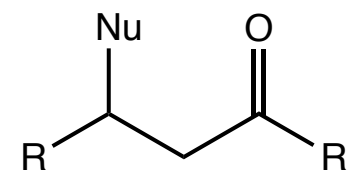
Section 16.15, 16.16



NuH



or



α,β -unsaturated carbonyls: carboxylic acid derivatives

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