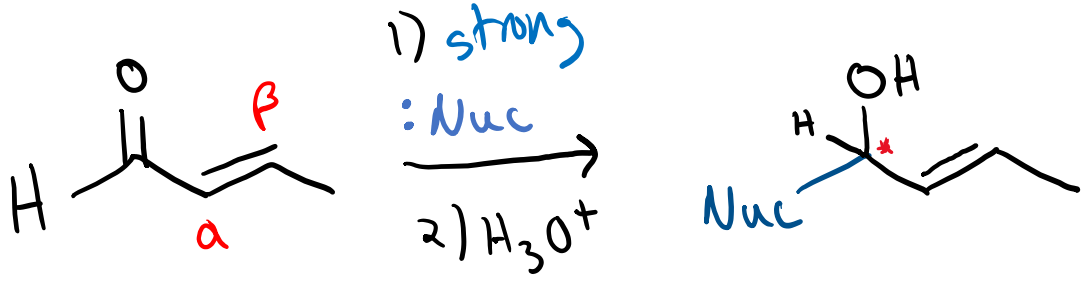
No recitation or quiz on Friday

Conjugate Addition & Michael Addition

Diels Alder intro

4/3/2023

1,2- vs 1,4-addition: Strength of Nucleophiles and Regioselectivity



strong nuc → 1,2 -addition favored

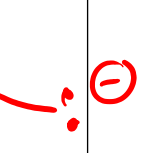
☆

$LiAlH_4$ "$H:^{\ominus}$" $pK_{aH} \approx 38$

$RMgBr$ "$R:^{\ominus}$" $pK_{aH} = 50$

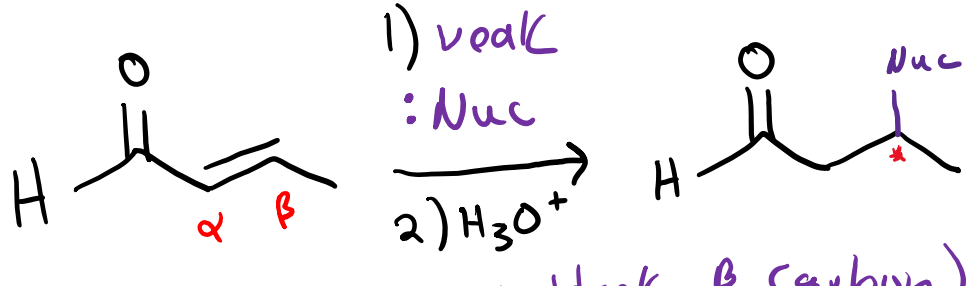
moderate (bad)

$pK_{aH} = 20$



enolate

(mix of 1,2- vs 1,4)

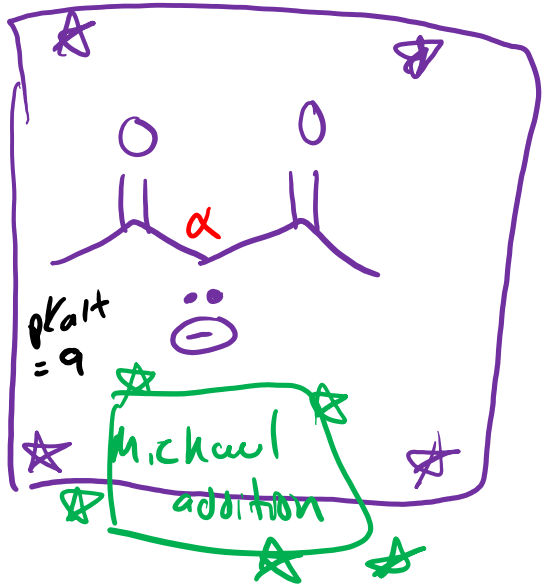


(attack β carbon)

☆ weak nuc → 1,4 addition

$pK_{aH} \approx 16$

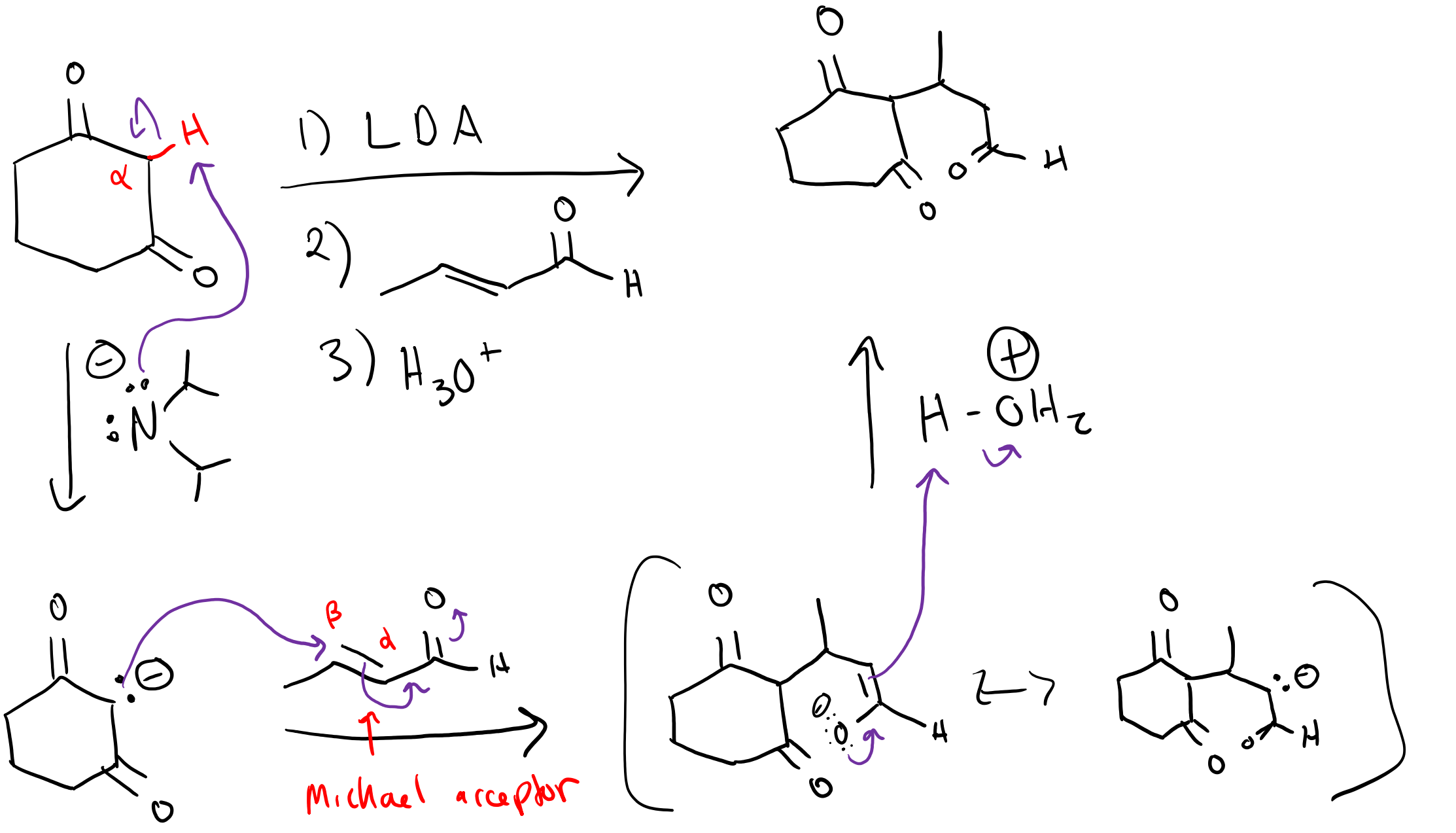
HNR_2 $pK_{aH} = 10$



R_2CuLi N/A

↳ weaker $C:^{\ominus}$ nuc. than Grignard

Michael Addition

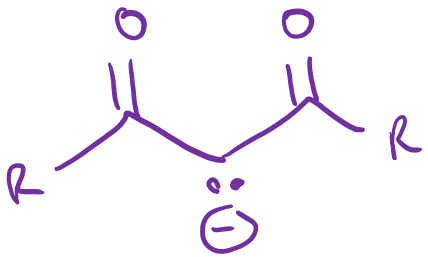


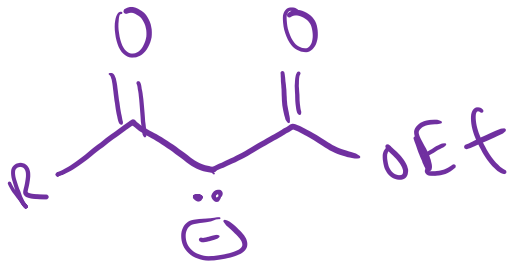
Michael Donors and Acceptors

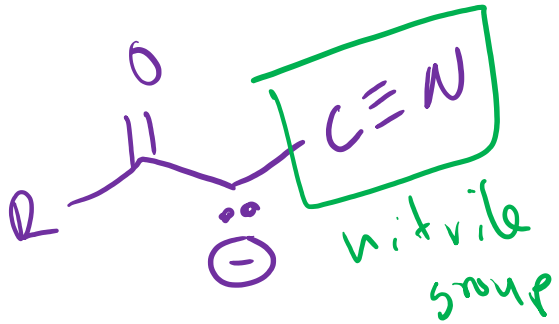
★ C≡N act a lot like C=O ★
(nitriles) (carbonyls)

Michael Donors

anything w/ doubly stabilized enolate







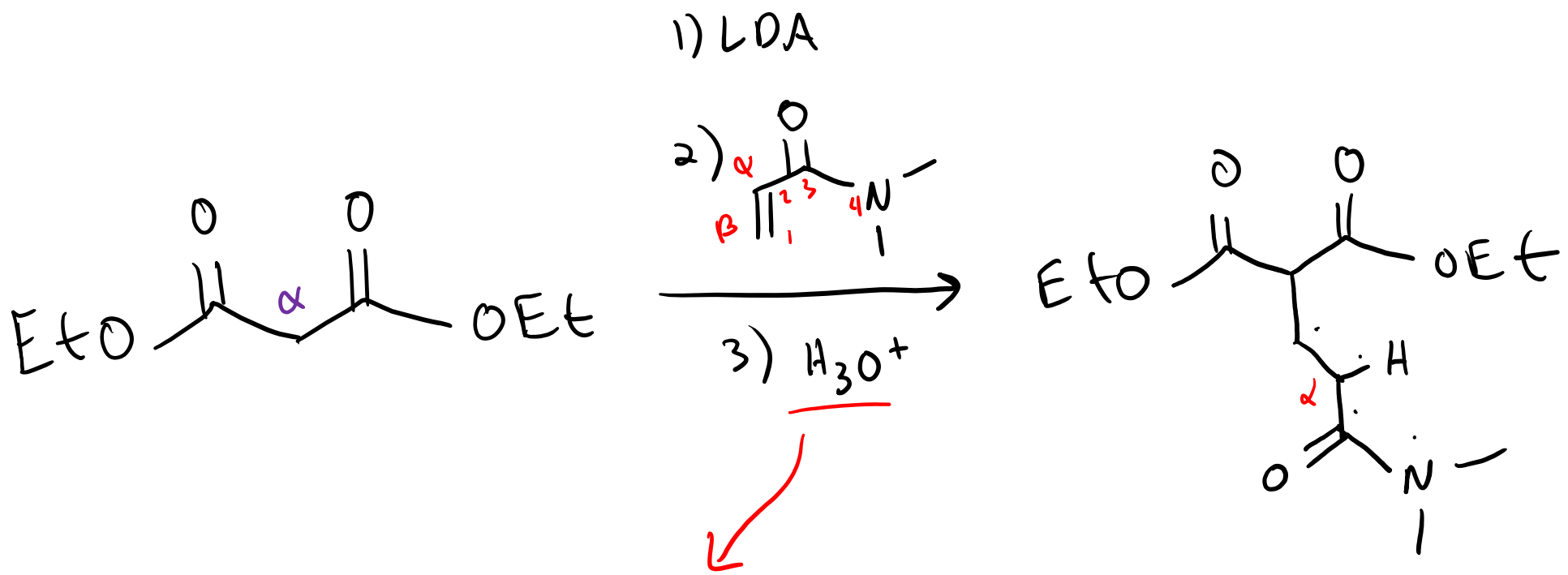
-OEt & -CN can react more too....

Michael Acceptors

α,β- unsat. carbonyls
(no carboxylic acids)


(R = alkyl or H)

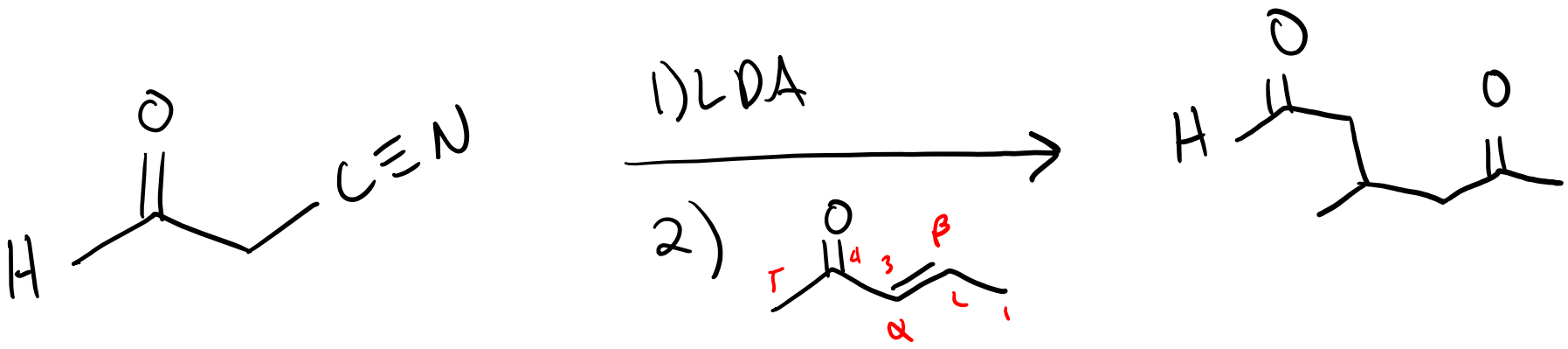
Michael Addition: Examples

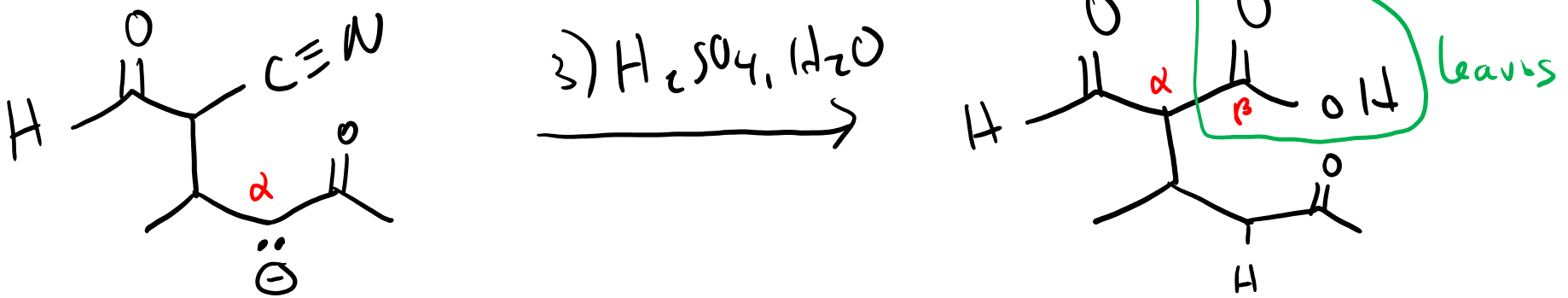


excess would hydrolyze esters into carb. acids

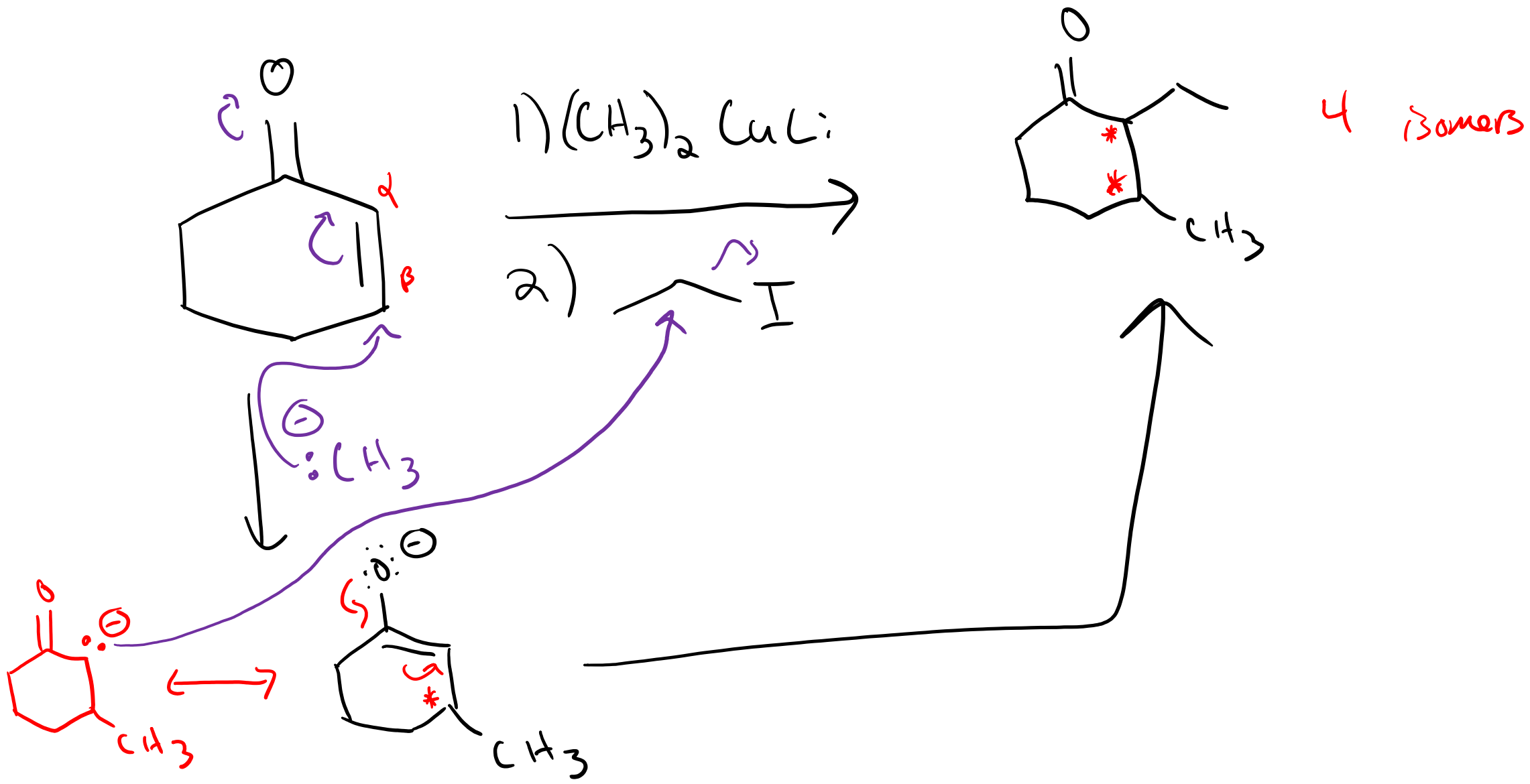
could also decarboxylate w/ Δ at that point

Michael Addition: Examples



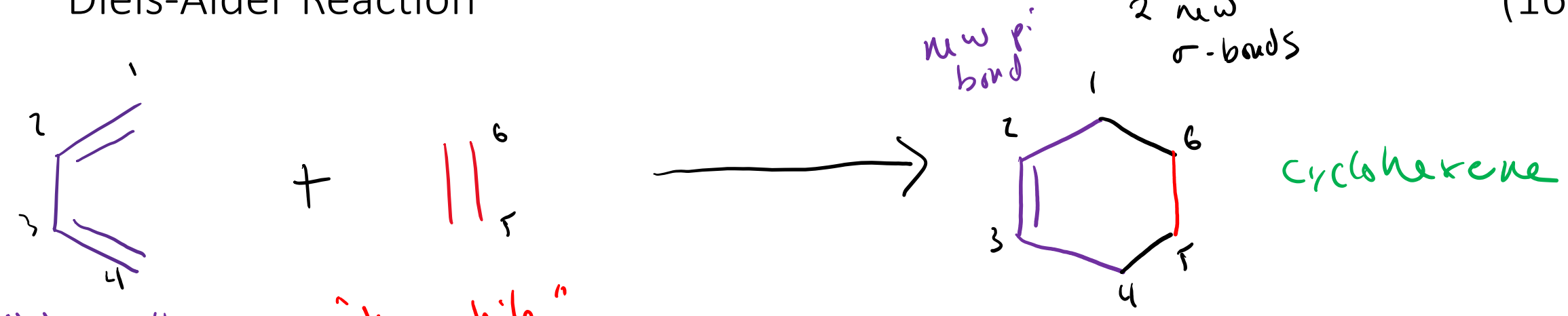


~~Michael~~ Conjugate Addition: Examples



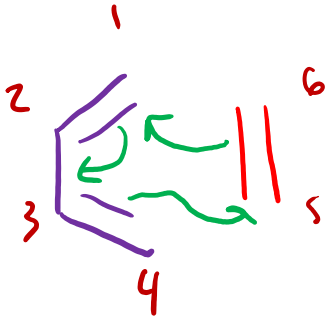
Diels-Alder Reaction

(16.7)



mechanism: concerted 4+2 cycloaddition

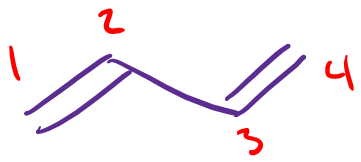
- concerted → 1 step
- 4+2 → 4 π e⁻ (diene), 2 π e⁻ (dienophile)
- cycloaddition → ring forming
- π-bonds become σ-bonds



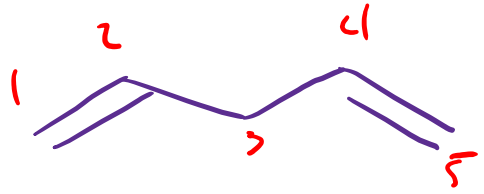
Requirements of the Diene

① The diene must be conjugated (1,3-diene)

✗ not conjugated
no Diels-Alder!



✓ conjugated

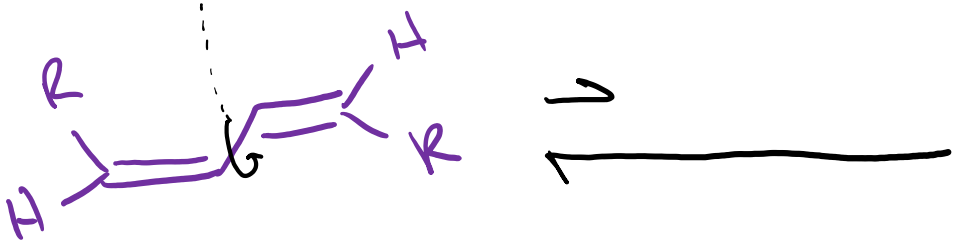


✗ not conj.

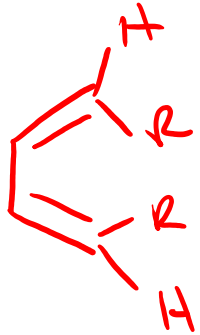
---

② The diene must be in the "s-cis" conformation to react

think rotation here



"s-trans"

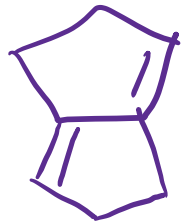


"s-cis"
reactive!

R = H	95%	5%
R = CH_3	99.5%	0.5%

Special Cases: rotation is impossible

100% s-cis
always! very reactive in D.A. rxn



100% s-trans
no D.A. rxn!