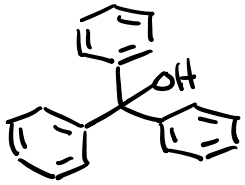
Grignard Formal

Due Next Monday on 27th

Introduction for Grignard



Nothing Special about triphenyl methanol

The product is not important.

If product is not important, then what is?

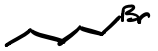
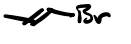
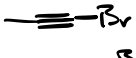
Grignard Rxn that we are interested in.

⟹ 1st Rxn we have shown to make C-C bonds

⟹ 1st Carbon nucleophile

⟹ Reaction extremely general

Reversal of polarity = Umpolung (Sp?)

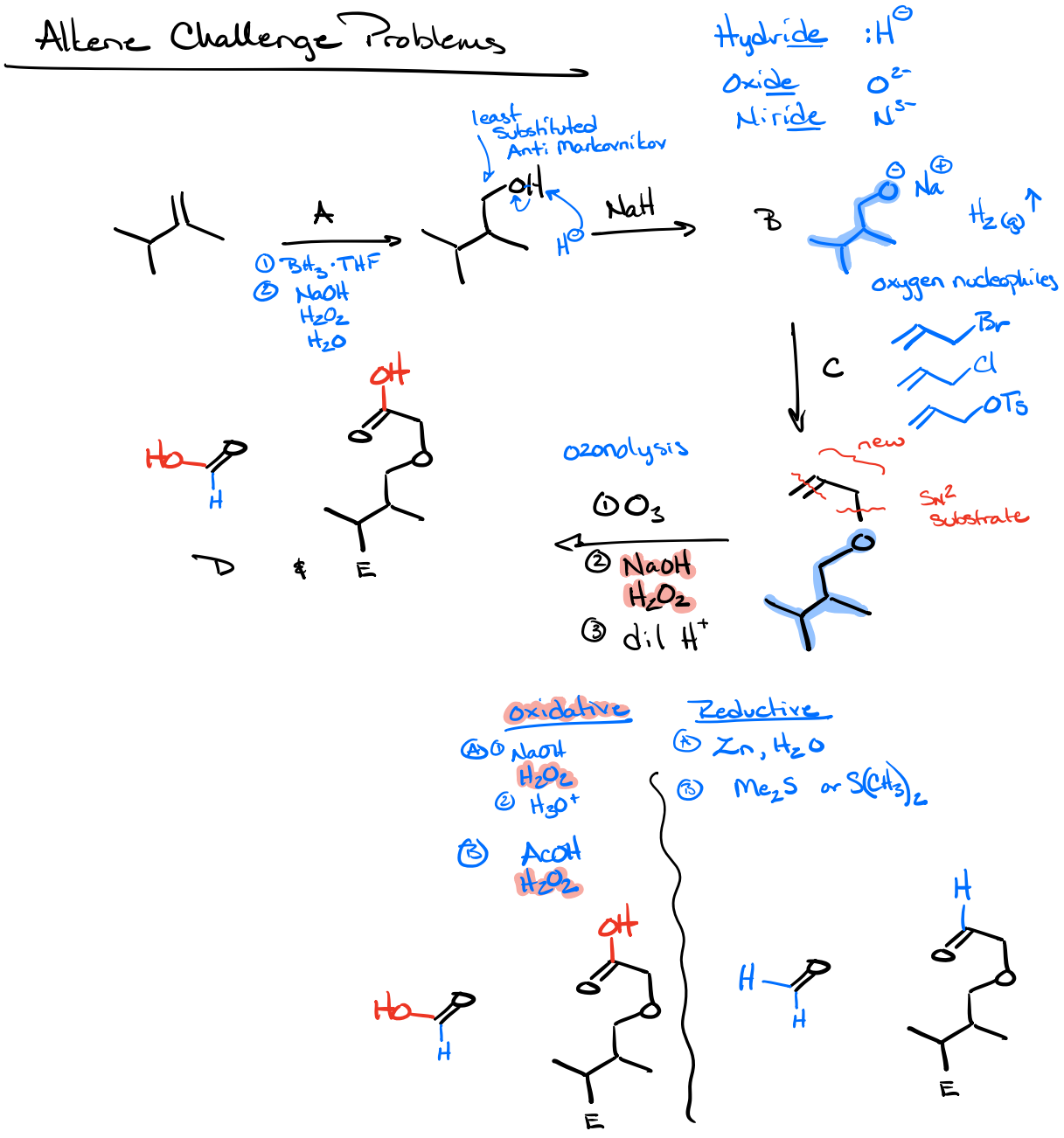
R	
Alkyl	
Alkenyl	
Alkynyl	
Aryl	

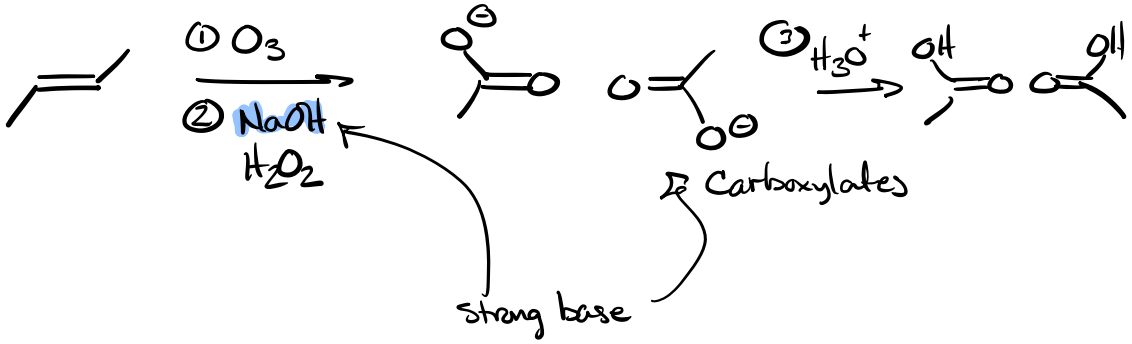
* Allows for Synthesis of new Carbon-Carbon bonds.

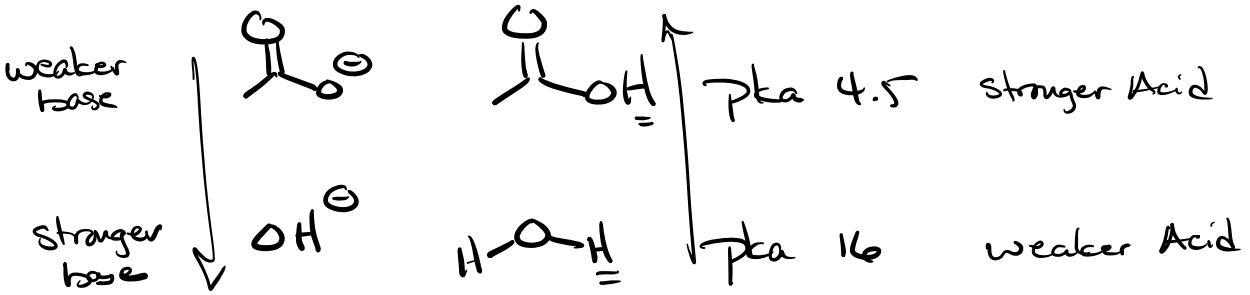
Intro

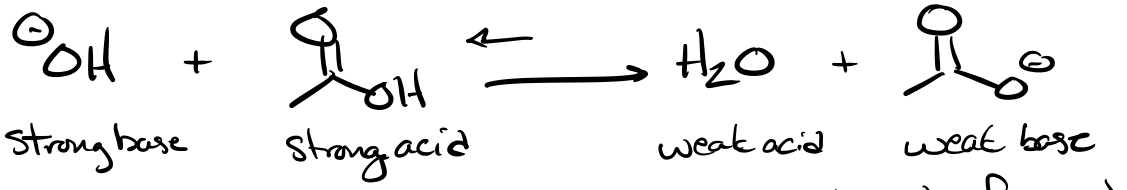
- Grignard as Chemist & Nobel prize
- Synthesis and the need to make new Carbon-Carbon bonds

Alkene Challenge Problems



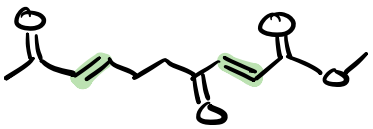






weak side favored

Find Compounds A & B



H_2, Pd/C → **A** $(C_{11}H_{18}O_4)$ — 3 units unsat

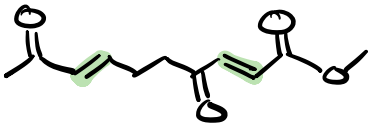
① O_3 ② Me_2S (Reductive Ozonalysis) ← **B** $(C_{11}H_{18}O_2)$ — 3 units unsaturation

units of unsaturation

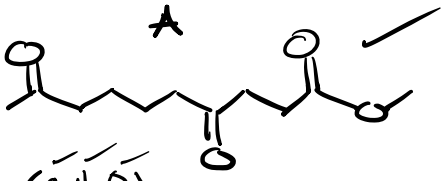
$$C_n H_{(2n+2+N-X)} \Leftarrow \text{for Saturation}$$

$$\text{units of unsat} = \frac{(\#H \text{ for Saturation} - \#H \text{ in molecule})}{2}$$

$C_{11}H_{(2\cdot11+2)} = C_{11}H_{24}$ $\qquad \frac{24-18}{2} = 3$ units

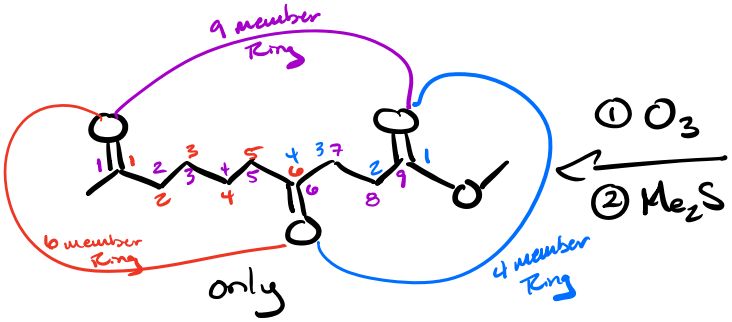


H_2, Pd/C → **A**



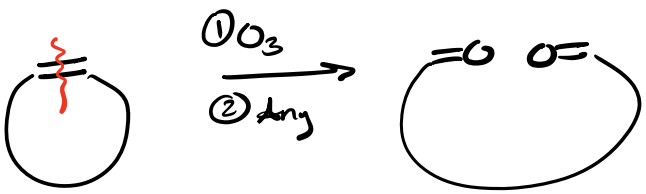
$(C_{11}H_{18}O_4)$

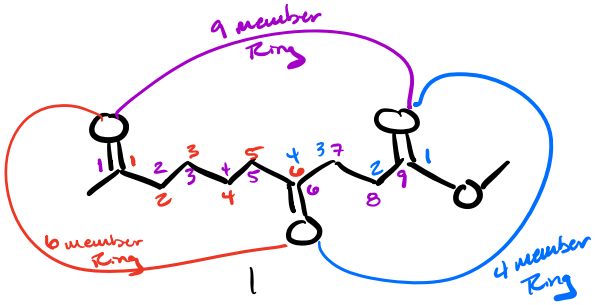
3 units unsat ✓



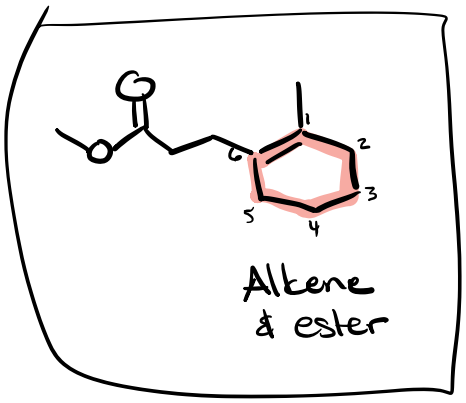
① O_3 ② Me_2S ← **B**

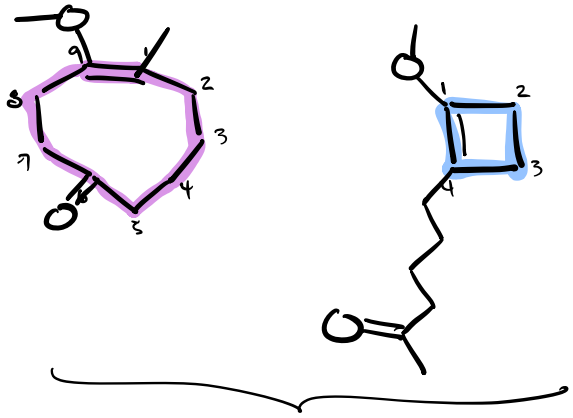
3 ways to go back to a cyclic molecule


① O_3
② Zn


9 member Ring
6 member Ring
4 member Ring

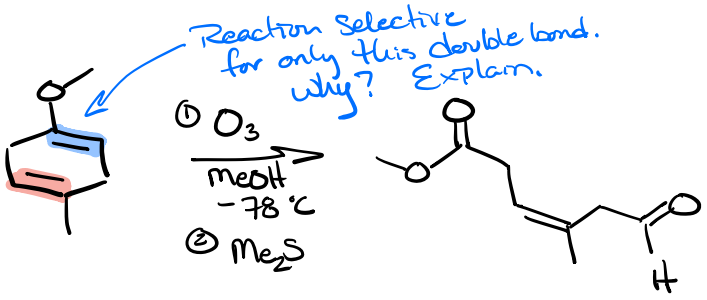
1


Alkene & ester

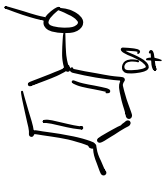


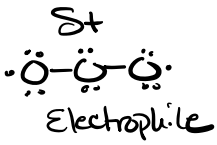
enol ether

−78°C
Dry Ice / Acetone

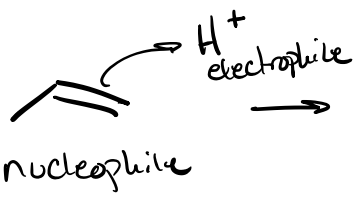


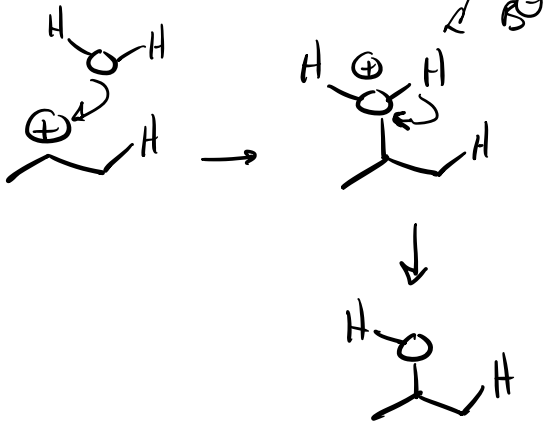
Question Could it be that oxygen is EWG & makes alkene stronger δ+ ?



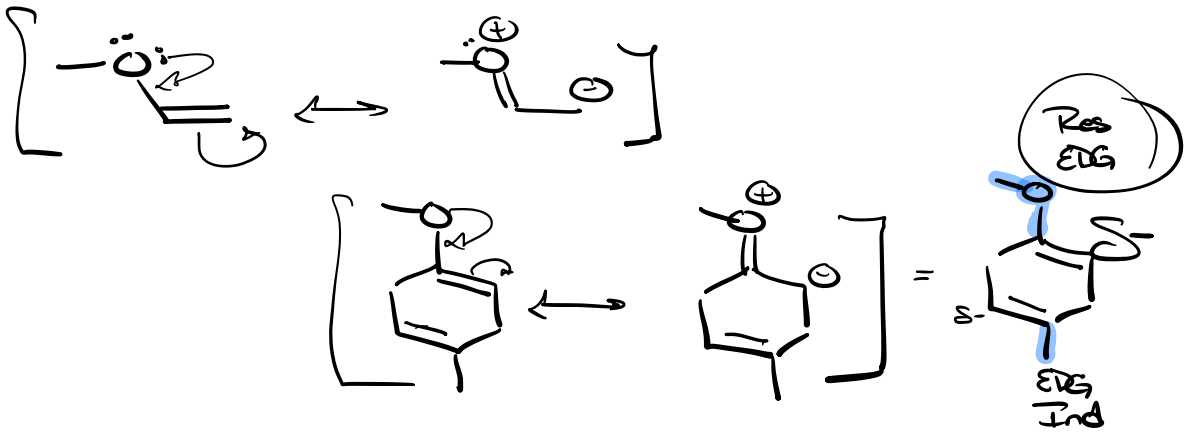


Electrophilic addition to alkenes

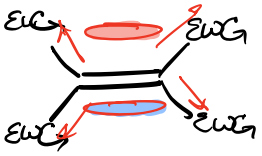




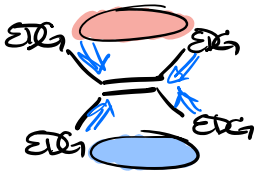
Question — Oxygen as EDG by Resonance



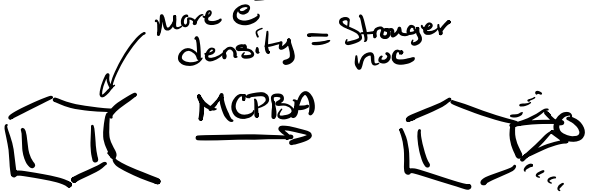
would that be consistent w/ electrophilic addition where alkene is nucleophile?

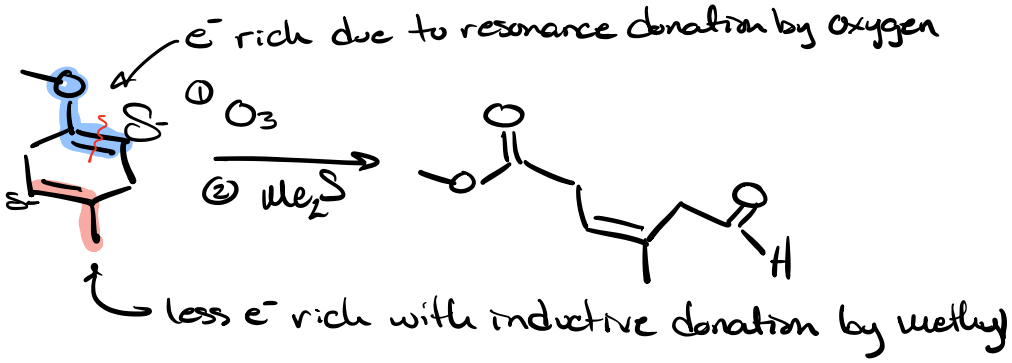


weak nucleophile

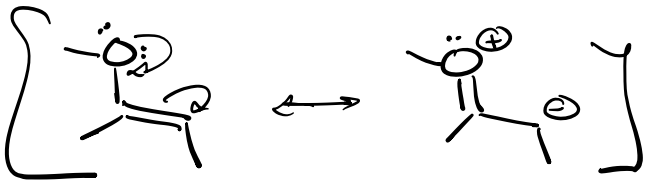


Stronger nucleophile

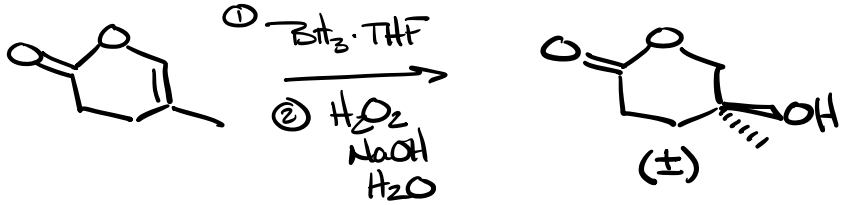




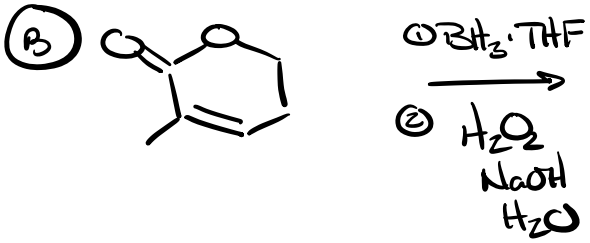
Electrophilic addition can be selective for more e⁻ rich alkene as stronger nucleophile



Give the products of both.

(A) 

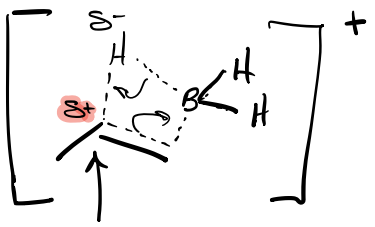
Lactone Challenge

(B) 

① no alkyl or hydride Shift

② Syn add

③ Electronics Govern ⇒ not Sterics

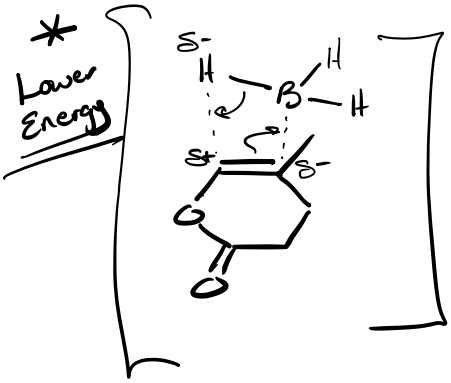


want δ+ on most Stable

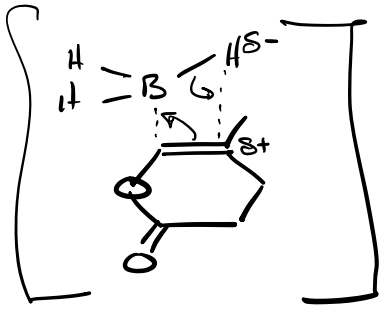
& Boron goes opposite the Most Stable δ+

(A) Two possibilities

* Lower Energy



or



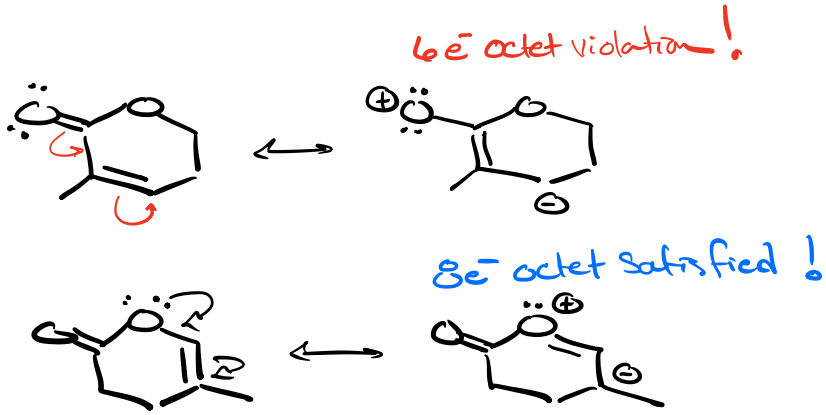
which is better ⇒ lower energy?

Induction

Stronger

Resonance

(B)


6e⁻ octet violation!
8e⁻ octet satisfied!
EWG
Bad
Breaks oxygen octet
EDG
Good & Outstanding