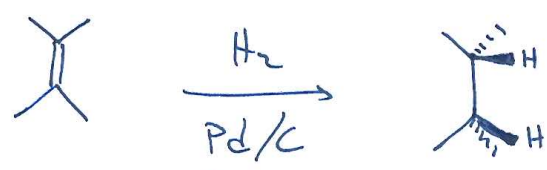


# ⑬ Hydrogenation (Reduction)



Need this catalyst!

(also works w/  $PtO_2$ )

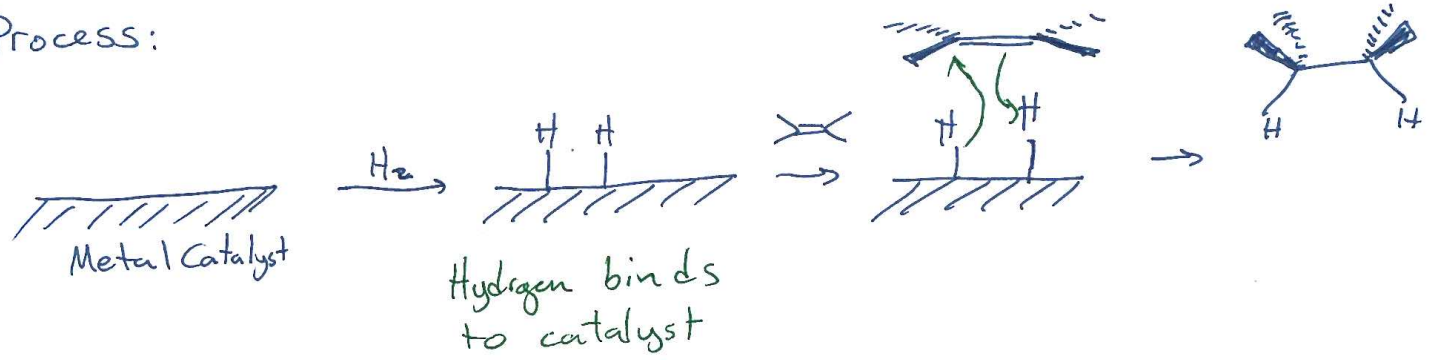
Syn ~~cis~~-addition of hydrogen across the double bond!

Does not work for benzene:

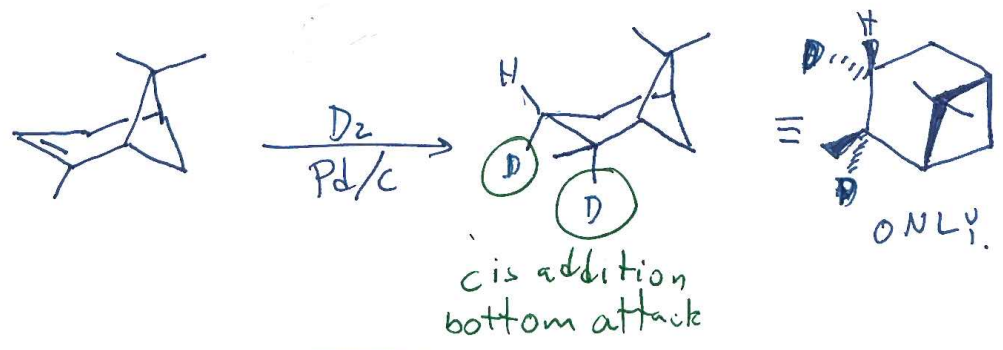


~~cis~~ cis addition!

Process:



$\alpha$  pinene?



Heat of hydrogenation of several alkenes:

$\Delta H$ (Kcal/mol)	-26.3	-26.8	-27.2	-28.2	-29.9	-32.5

less exothermic,  
MORE stable  
(less reactive)

easier to form than  $\rightarrow$

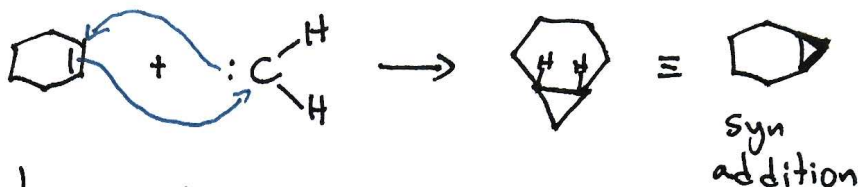
More exothermic  
Less stable.  
(more reactive)

(2)

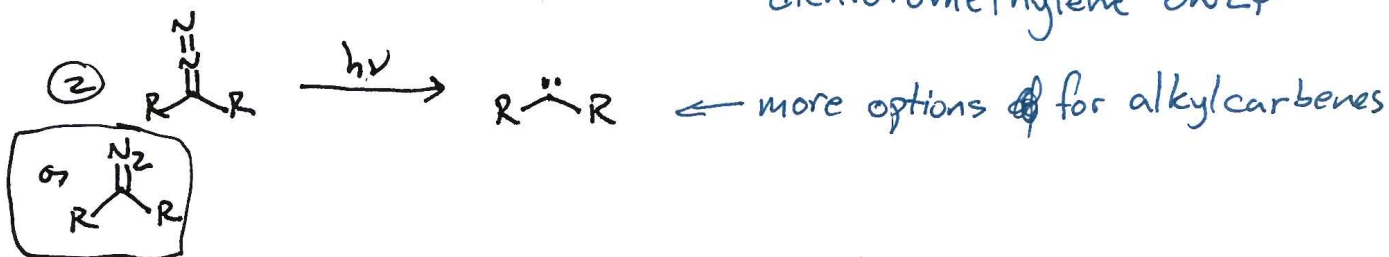
## Addition of Carbenes - Cyclopropanation

Carbene:  $R-\ddot{C}-R' \rightarrow$  highly reactive  
- unfilled octet

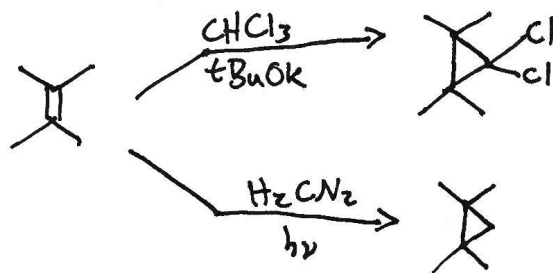
In general,  
Reaction:  
Mechanism



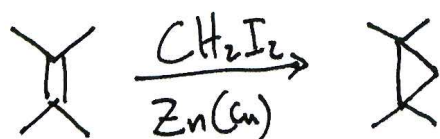
2 ways to generate carbenes:  
Base & Chloroform



Net Reactions:



Another useful Cyclopropanation: Simmons-Smith Reaction



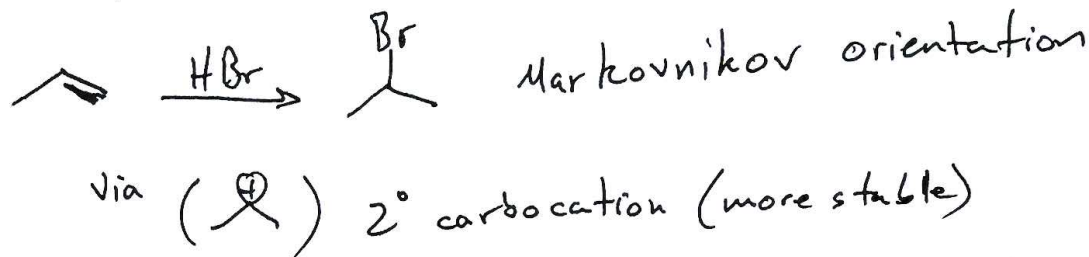
No carbene intermediate → clean reaction

# Alkenes & Radicals

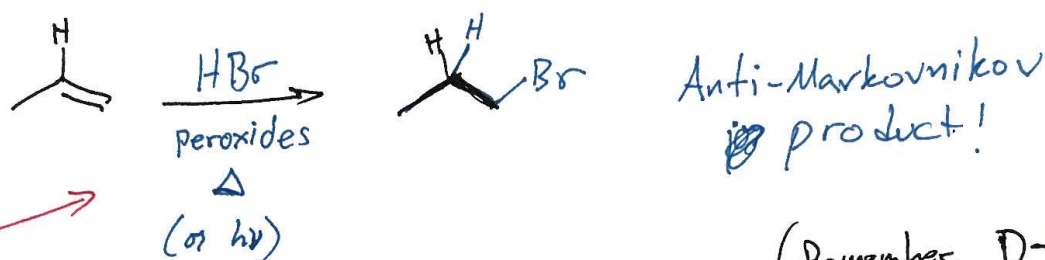
Radical stability:  
 $3^\circ > 2^\circ > 1^\circ > \cdot\text{CH}_3$

3

Blas + from the past:



However, if the reaction conditions are changed:



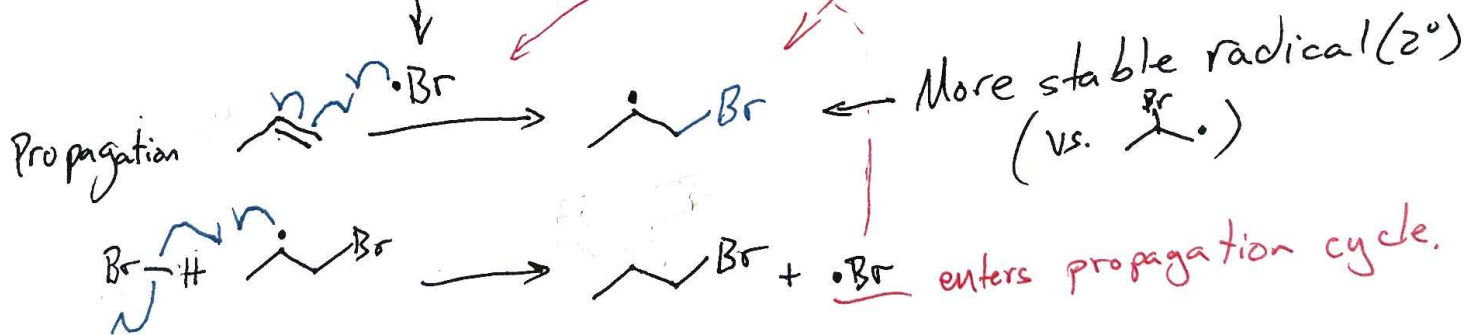
Radical Mechanism

(NO CARBOCATIONS!)

HOW?

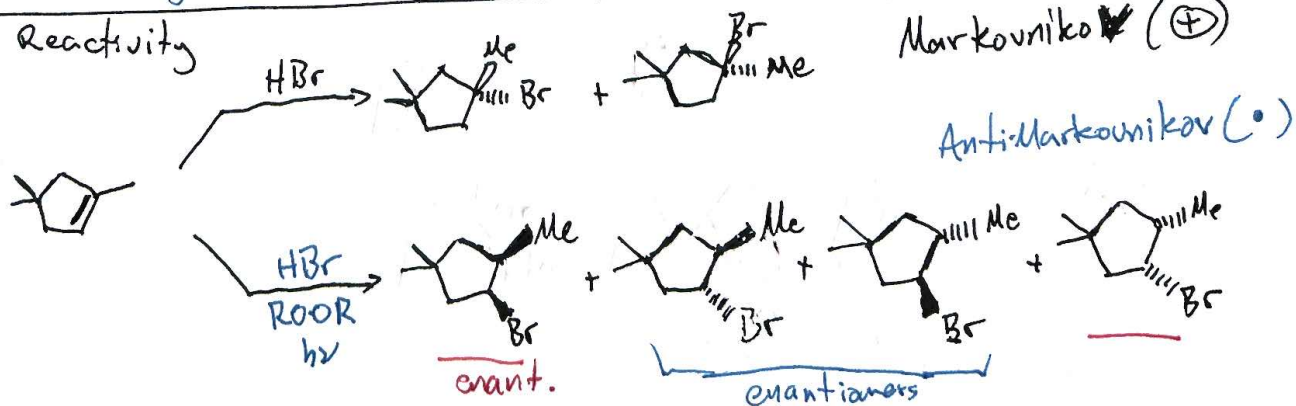
(Remember, D-Br can also be used)

No: HI/Peroxides,  $\Delta$   
 HCl/Peroxides,  $\Delta$



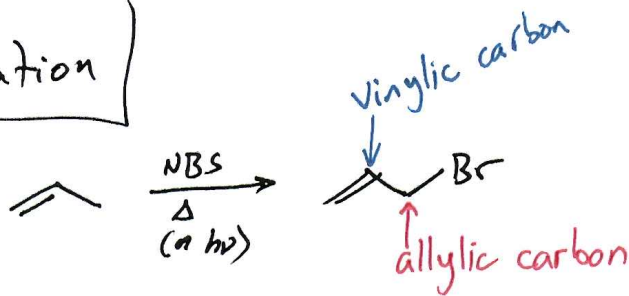
Termination  $\Rightarrow$  Any 2 radicals recombining.

Compare Reactivity

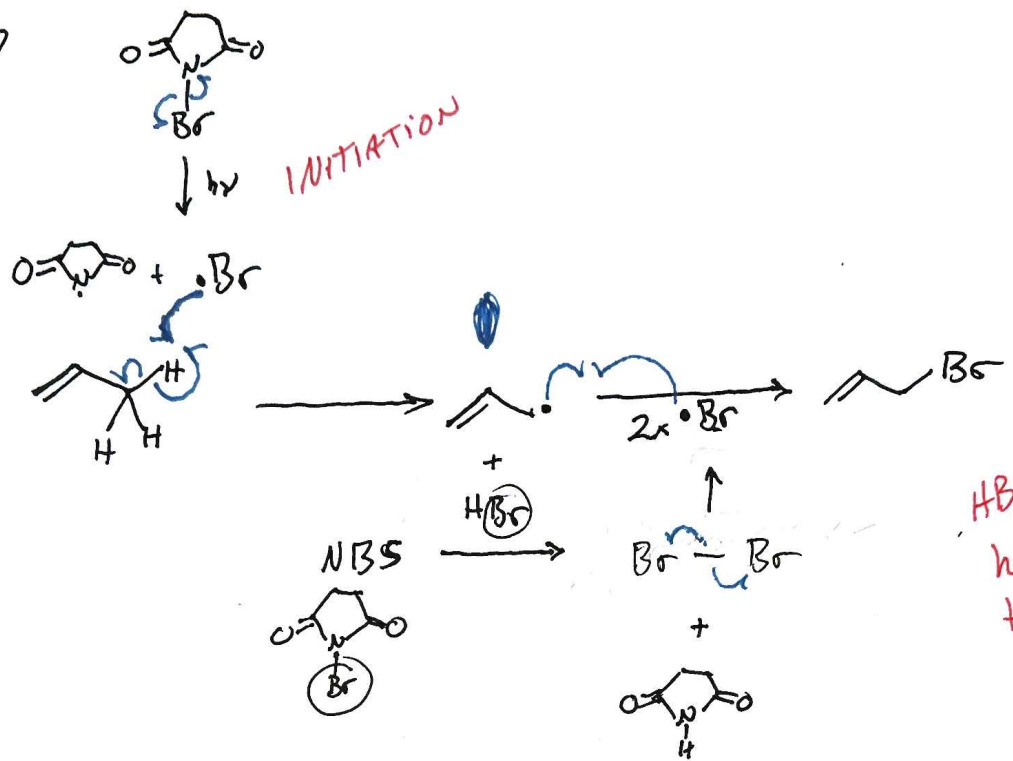


# Allylic Bromination

Net rxn:



How?

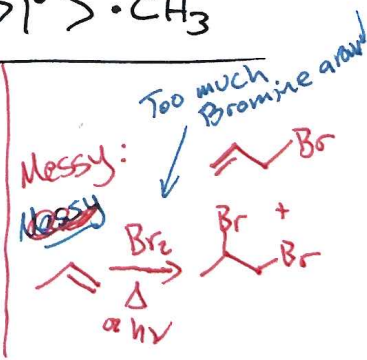
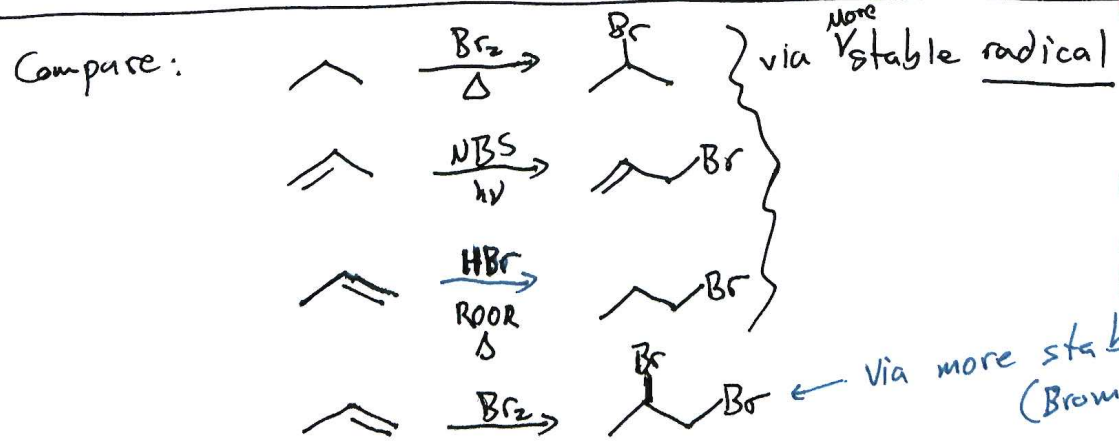


HBr is consumed here. therefore, this rxn is not like HBr/ROOR, \Delta

Why not?



Radical stability  $3^\circ \text{Allyl} > 2^\circ \text{Allyl} > 1^\circ \text{Allyl} > 3^\circ > 2^\circ > 1^\circ > \cdot CH_3$

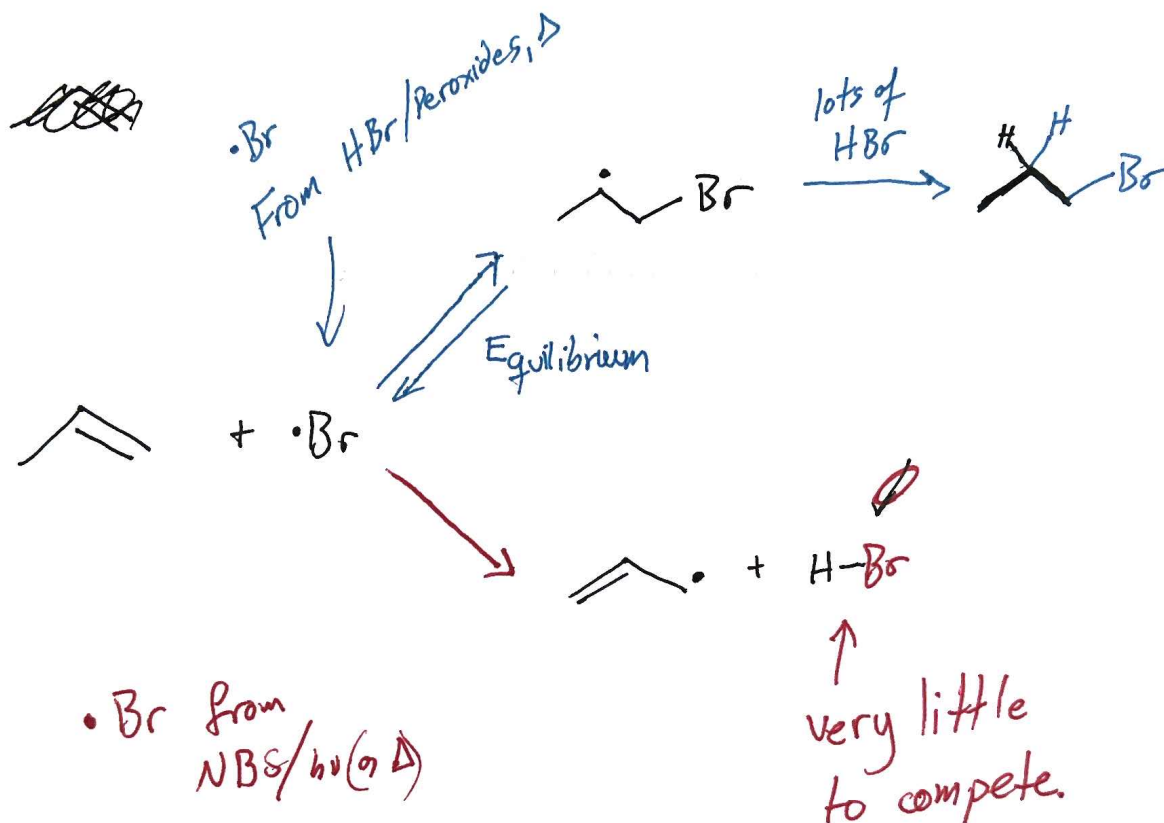


via more stable carbocation (Bromonium ion)

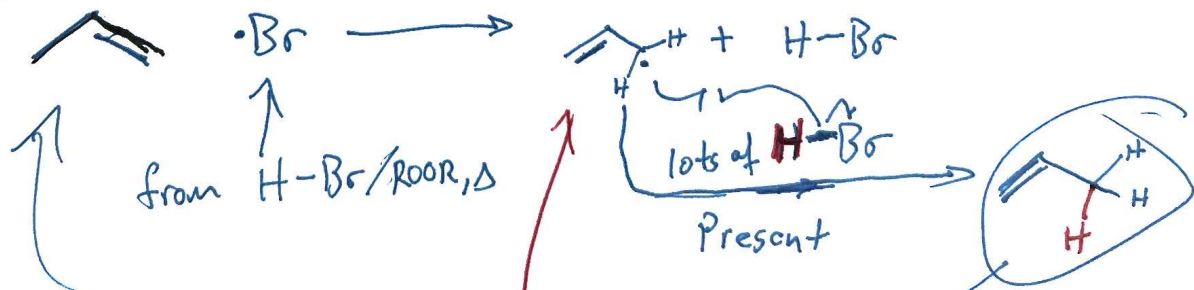


Why is it different path using HBr/peroxides,  $\Delta$  (or hv) and NBS/hv ( $\Delta$ )?

The  $\cdot\text{Br}$  can do both! However...



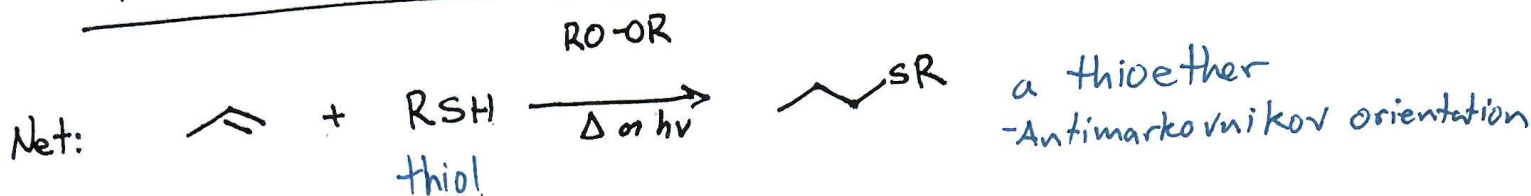
Consider: if  $\cdot\text{Br}$  ~~abstracts~~ abstracts  $\cdot\text{H}$  from HBr/ROOR,  $\Delta$



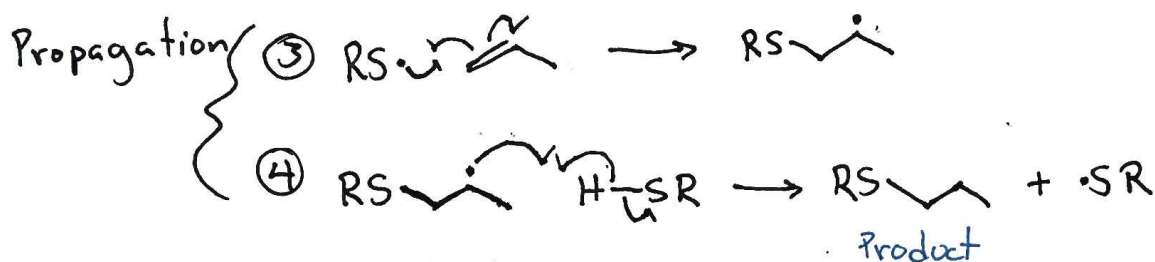
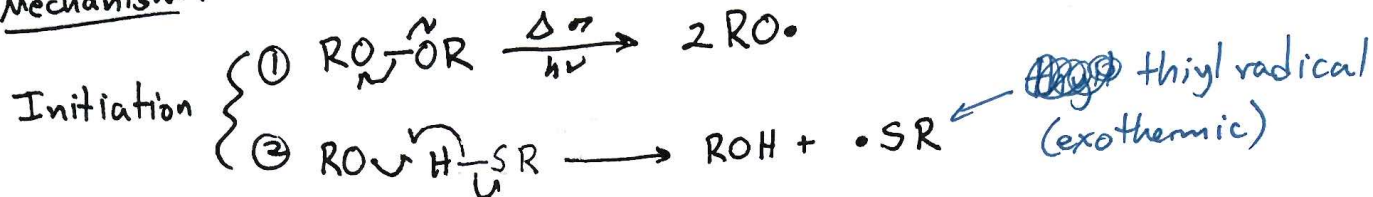
We go back to starting material

Small chances that this Allylic radical will see another  $\cdot\text{Br}$  before encountering H-Br again

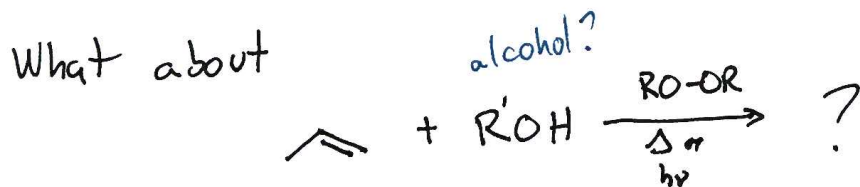
# Thiol-ene Reaction



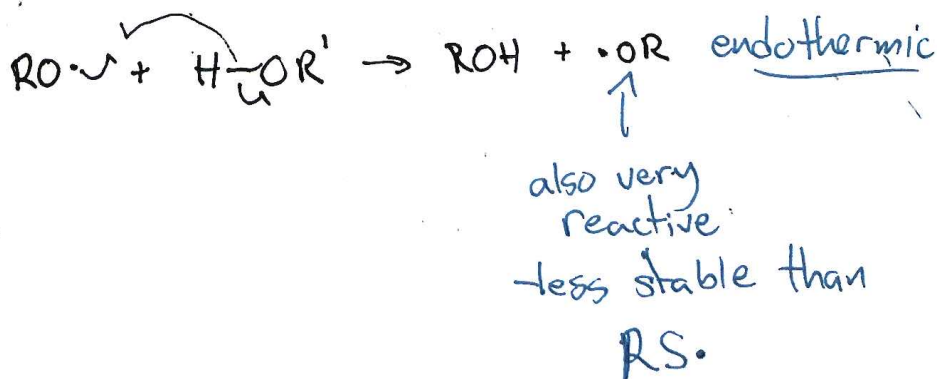
## Mechanism:



Termination ⑤ etc. 2 radicals coming together.

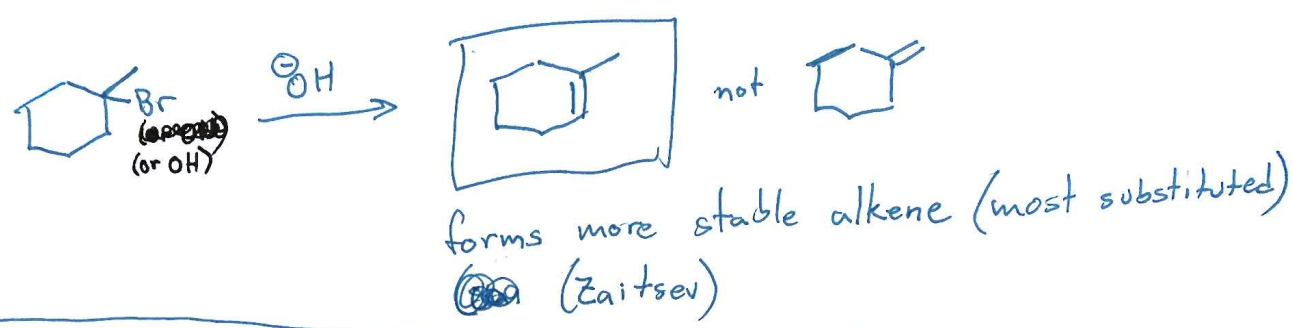


won't work  
because of  
initiation  
(take too much  
energy)

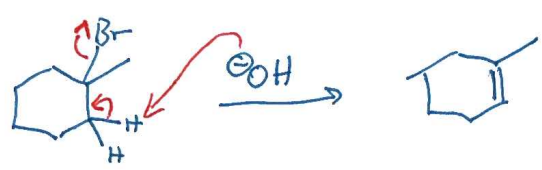


# Synthesis of Alkenes

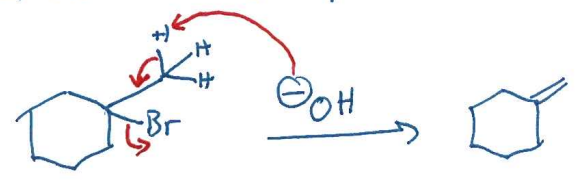
- ① Cracking (Pyrolysis of Alkanes)
- ② Elimination of halides and alcohols



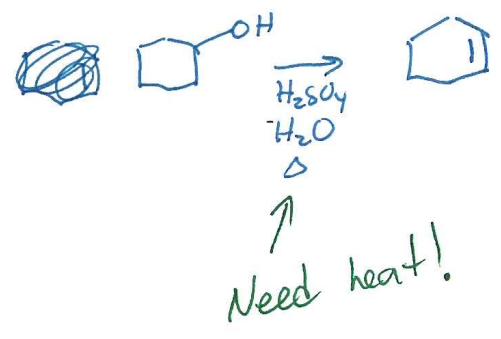
Path 1 = Preferred



Path 2: "No bueno" (not preferred)



Also w/  $H_2SO_4$



Now you know how to make an alkene and convert it to: alcohols, carbonyls, diols, aldehydes, esters, ethers, polymers, etc!