

①

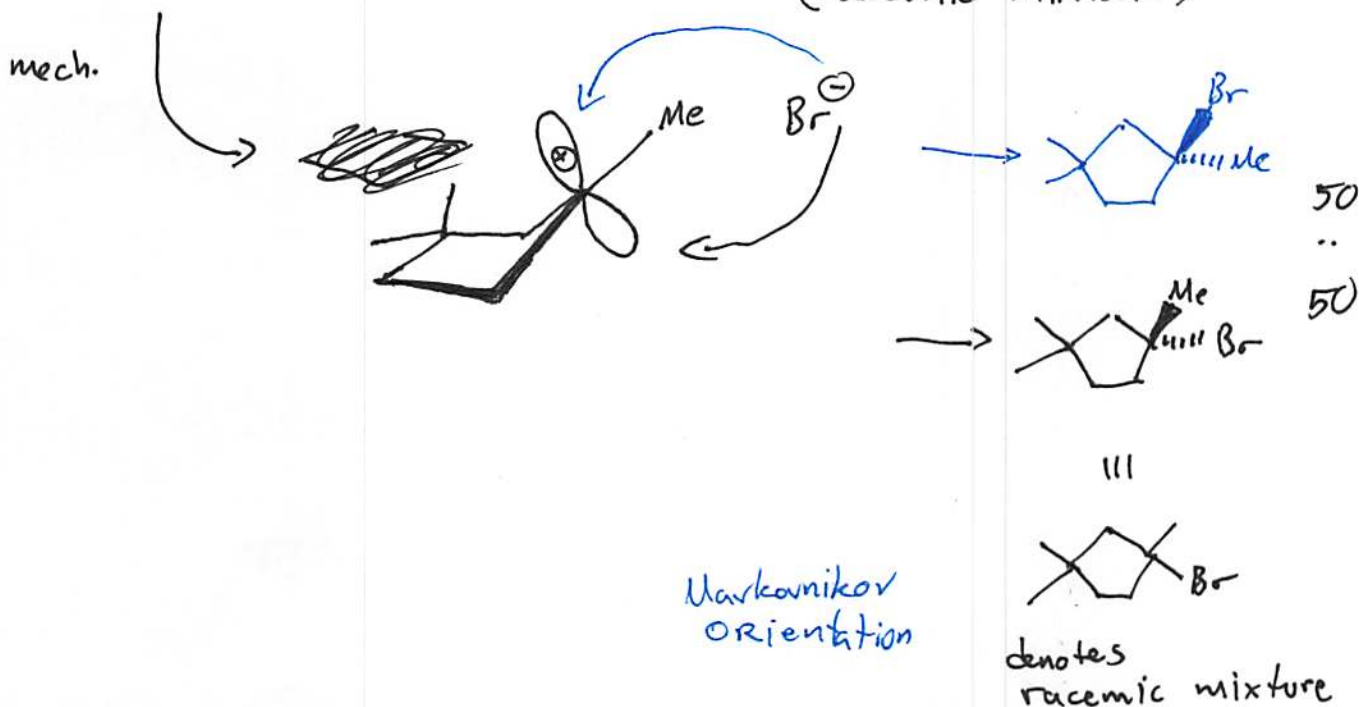
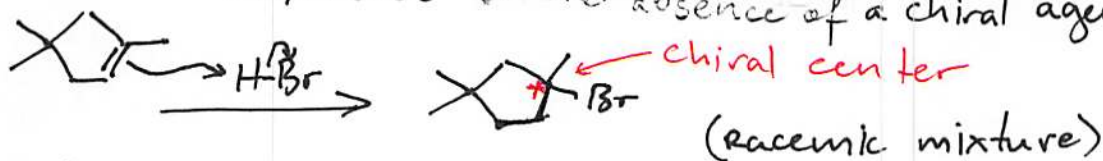
Reactions of Alkenes II

① Addition of HX ($X = Cl, Br, I$) (via carbocation)



- Keep in mind, carbocations can rearrange ~~to more~~ stable cations and/or to release ring strain.

- When chiral centers are formed, add'n of HX yields racemic mixtures in the absence of a chiral agent.



Let's talk about Alkene REACTIONS!

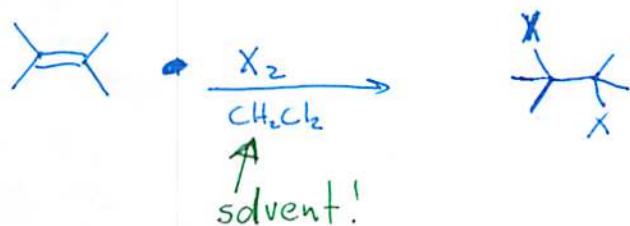
① Addition of Hydrogen Halides (HX)

~~② Addition of Hydrogen Halides (HX)~~

② Addition of Halogens (X_2)

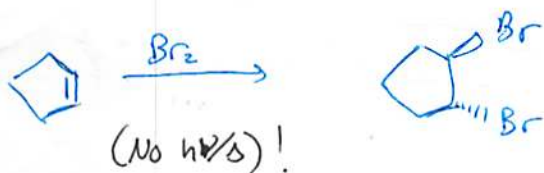
- $X = Br$ or Cl (F_2 is too reactive, I_2 does not react w/ most alkenes)
- Test for unsaturation.
- also ICl or $BrCl$

ex.



Halogens add to the double bond.

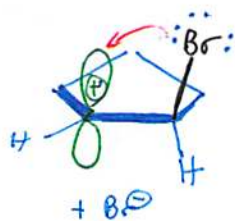
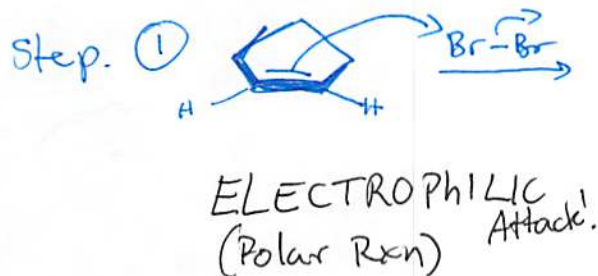
But... Check this out:



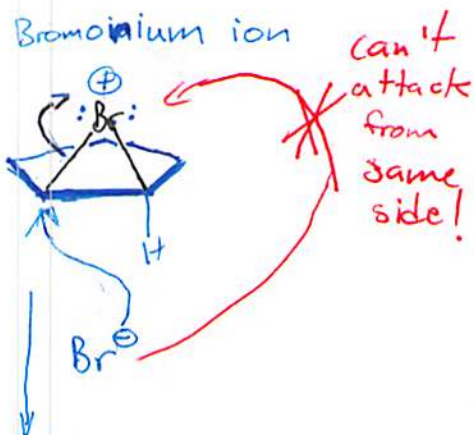
Bromine atoms are trans!

NO cis!

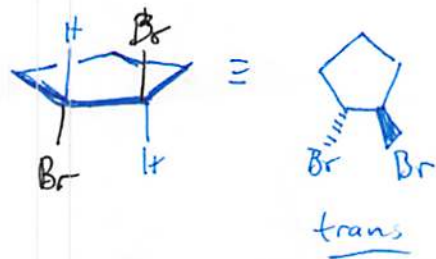
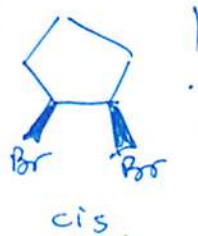
What happened? ⇒ MECHANISM



Step 2 ⇒



Not formed



Key Points:

(Halonium)

① The Bromonium ion is a reasonable intermediate

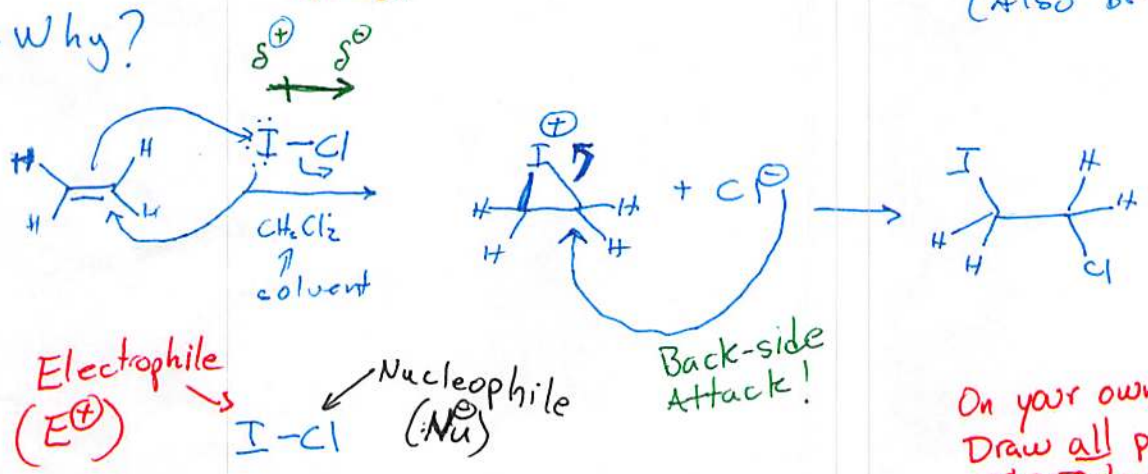
- keep in mind that there are some cases where the chemistry is dominated by a carbocation, not bromonium.

* - HOWEVER, for the purpose of this class, we'll just say that it's mainly bromonium.

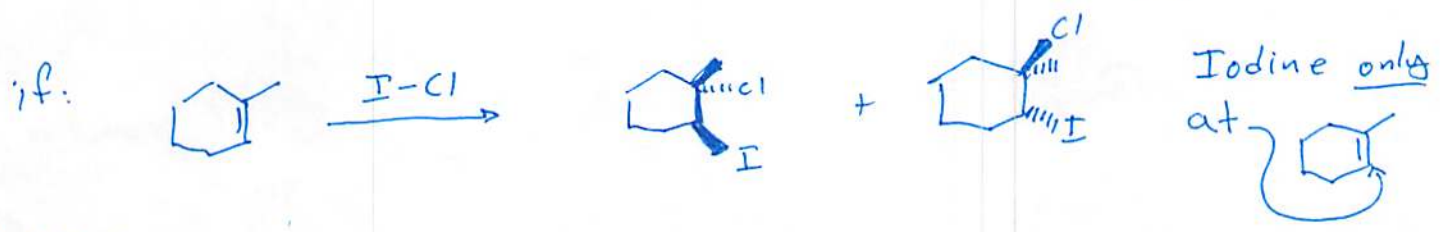
* ② Generally, the halogens are Cl_2 & Br_2 , not I_2 and F_2 is too reactive.

- BUT: I-Cl allows you to introduce 2 different halogens. (Also Br-Cl)

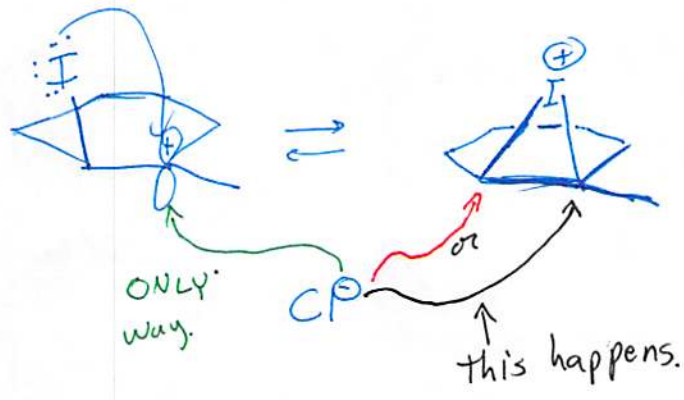
- Why?



On your own: Draw all possible products.



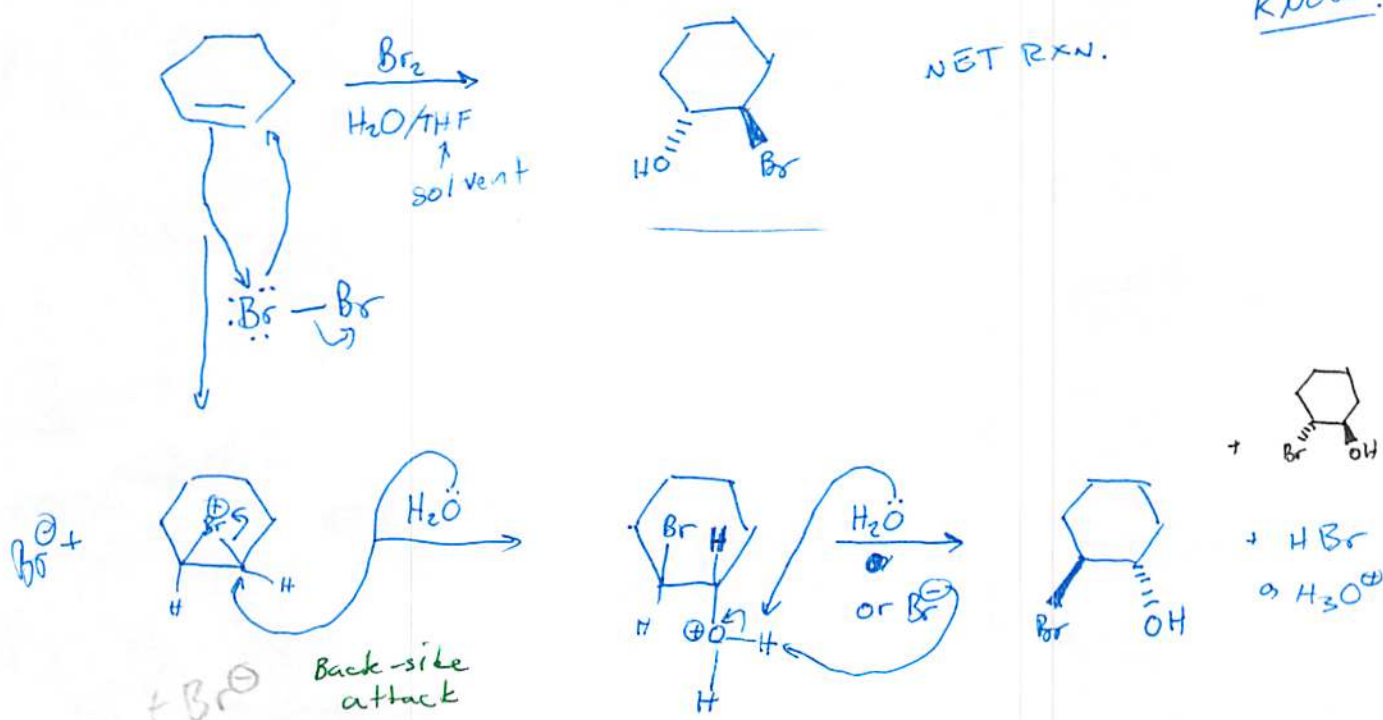
what that means:



In this iodium ion, the Cl^- attacks the carbon that is derived from the more stable carbocation.

④ Addition of halogens in water (Halohydrin Formation)

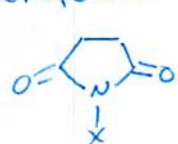
KNOW!!



Issues: - Many alkenes are not very soluble in H_2O or in H_2O /organic mixtures
- Br^\ominus lingers and can also do another attack

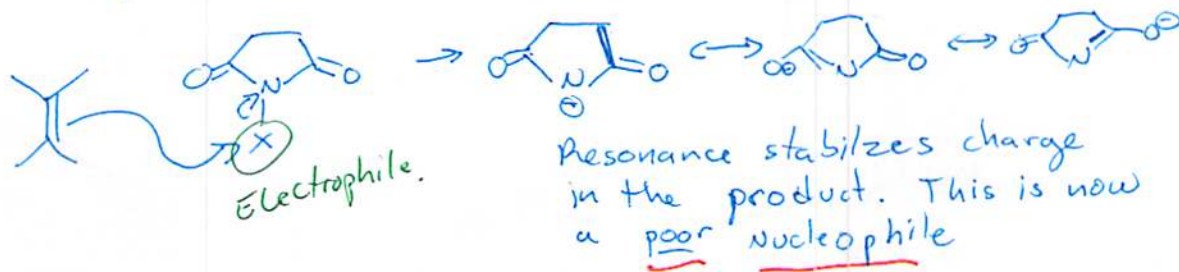
How to avoid these issues?

- Use a different source of halogen! (another electrophile)



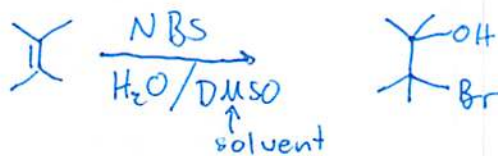
$\text{X} = \text{Cl}$, N-Chlorosuccinimide (NCS)
 Br , N-Bromosuccinimide (NBS)
 I , N-Iodosuccinimide (NIS)

Good electrophile because:



On your own,

Try the mechanism:



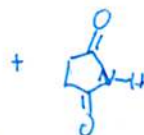
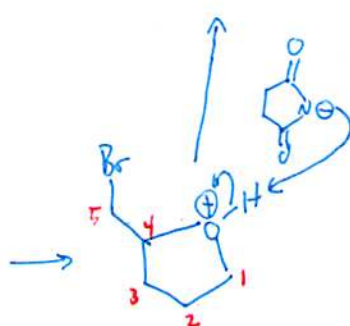
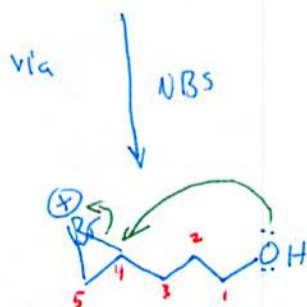
① C

Let's look at some reactions:



← An Ether!

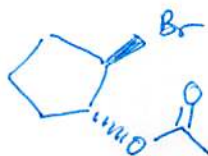
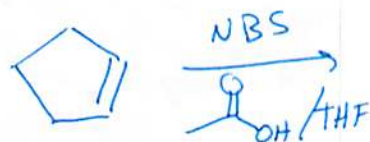
(instead of using water, use an alcohol).



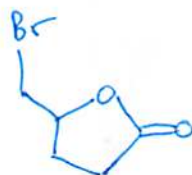
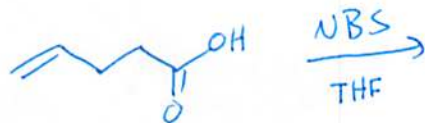
Intramolecular Rxn.

5 & 6 member rings is favorable.

Forming 5-member rings is faster than 6 member rings.



← An Ester!



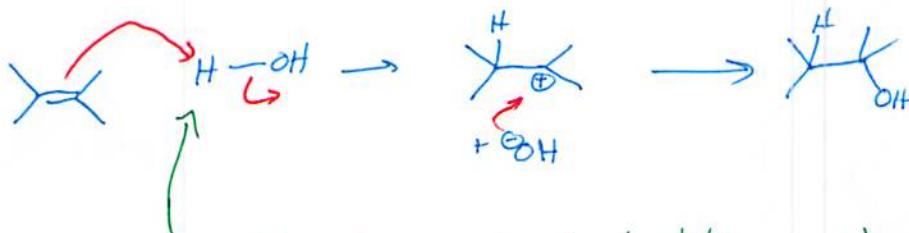
← cyclic ester!
(also known as Lactones)

you should try the mechanisms for these reactions!!

⑤ Addition of H_2O .

- In principle, it's reasonable to think of $H-OH$ adding to a ~~carb~~ double bond.

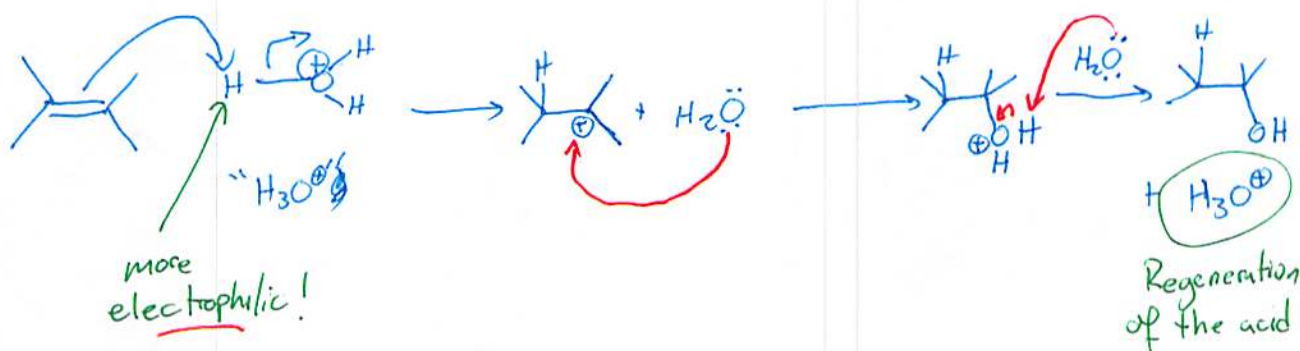
Like this:



(Not acidic enough)

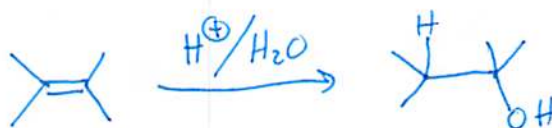
- However, this H is not electrophilic enough.

- We need a little bit of acid (H^+) to ~~add~~ make the reaction proceed.



- MARKOVNIKOV ADDITION.

A way to write the above Rxn:

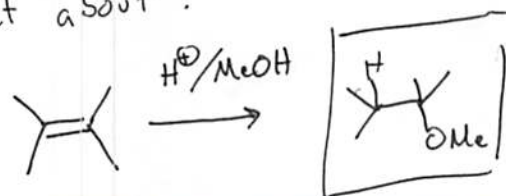


or H_3O^+

or HCl/H_2O
cat

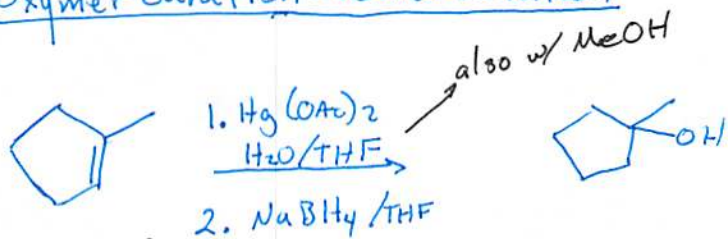
What about H^+/H_2S ?

What about?



~~Don't forget to check the regiochemistry of the addition.~~

⑥ Oxymercuration-mercuration



- Markovnikov orientation

- ~100% yields

- No rearrangements!

!!

- Also works with ROH instead of H₂O

This notation means two rxns were carried out. (ethers)

THF was ~~used~~ used as a solvent

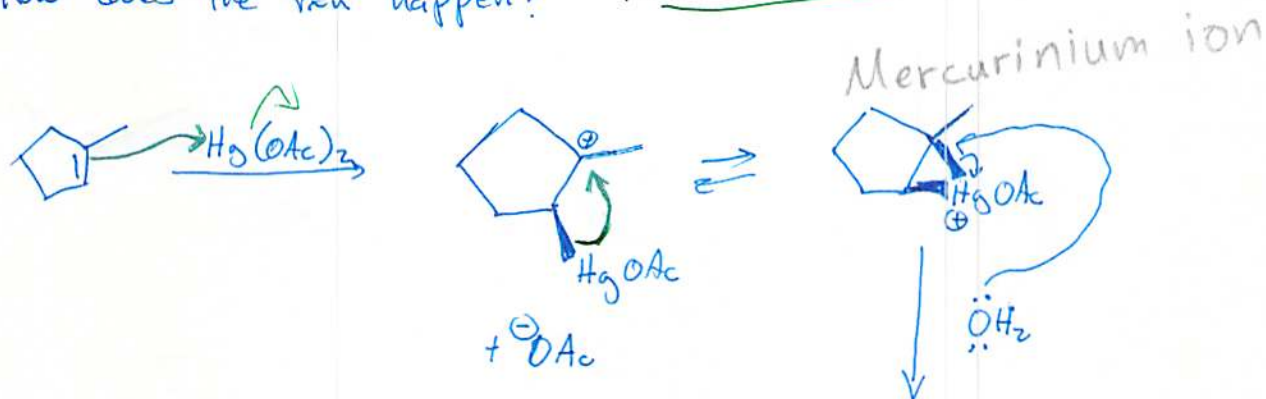
- THF = tetrahydrofuran (an ether)

Hg(OAc)₂ is electrophilic

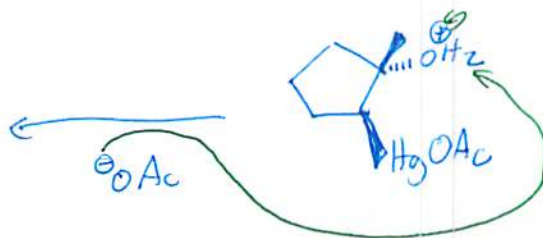
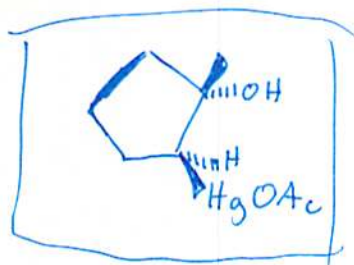
OAc = acetate = (from acetic acid)

∴ Hg²⁺ ()₂

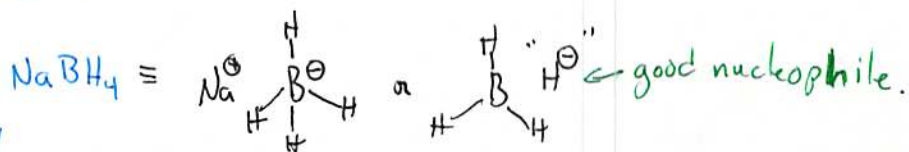
How does the rxn happen? Know mechanism for exam!



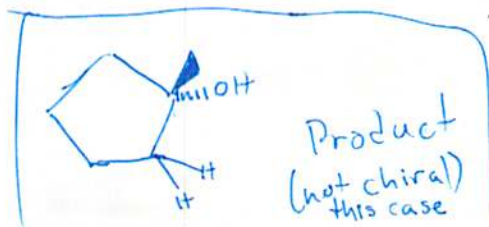
Can be isolated



Part 2.



← good nucleophile.



Product
(not chiral)
this case