Course Chem 343 Lecturer Gellman

Day Fri. Date 11/16/12

Notes Taken By Brian Total # of Pages 5

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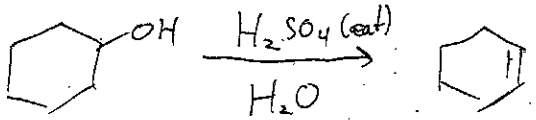
DO NOT STAPLE

• Recall:

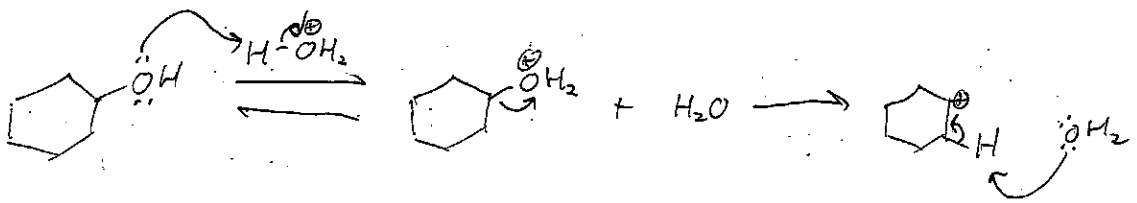


• David Mortensen teaching

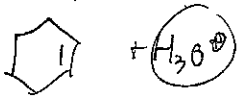
mech

$H_2O + H_2SO_4 \rightleftharpoons H_3O^{\oplus} + HSO_4^{\ominus}$

• H_2SO_4 is more acidic than $H_3O^{\oplus}$
∴ eq. favors right side

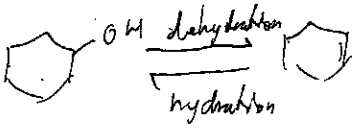


• H_2O is a good leaving group!



regenerated

- This is **E1**; if 2° or 3° alcohol
- Acid catalyzes rxn by converting it into good LG (+ $\overset{\oplus}{O}H_2$)
- Reverse of alkene **hydration**



↳ How can we favor dehydration?

- Use low $[H_2O]$
- boil off alkene as it's formed ( has lower bp than 

)

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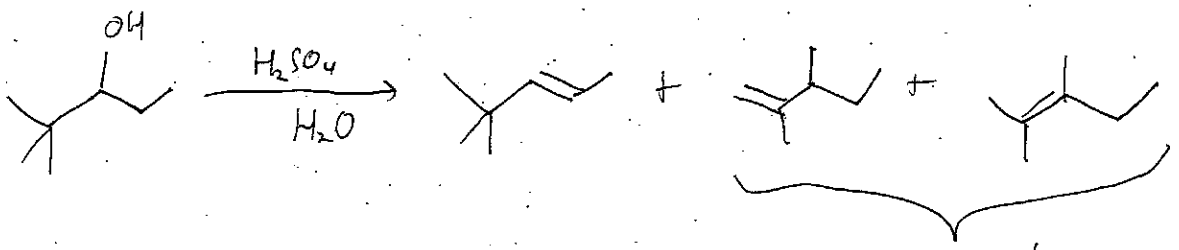
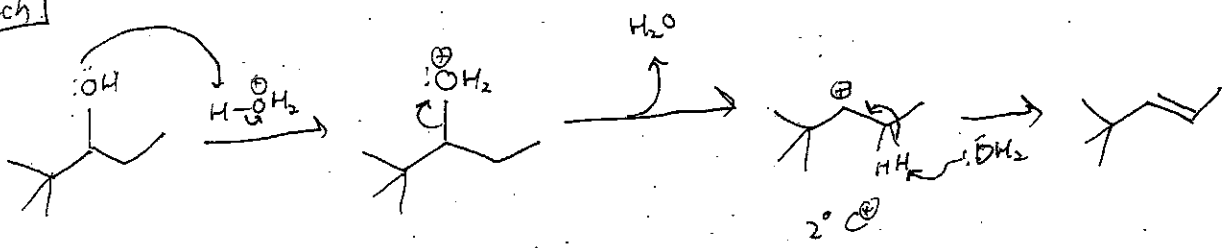
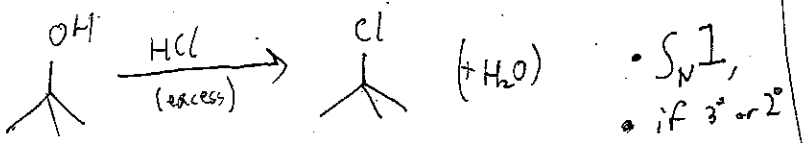
- Rearrangement is possible when $C^{\oplus}$ is formed



mech!



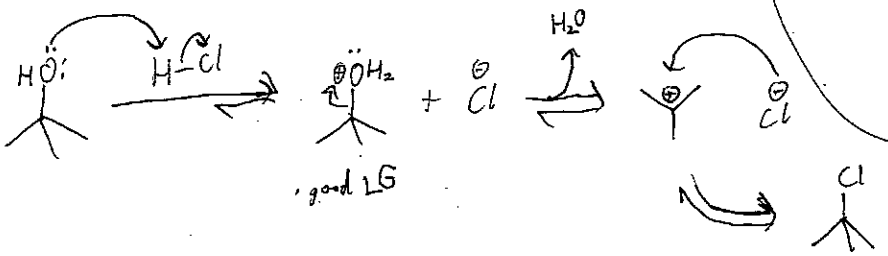
- If we use HI, HBr, HCl:



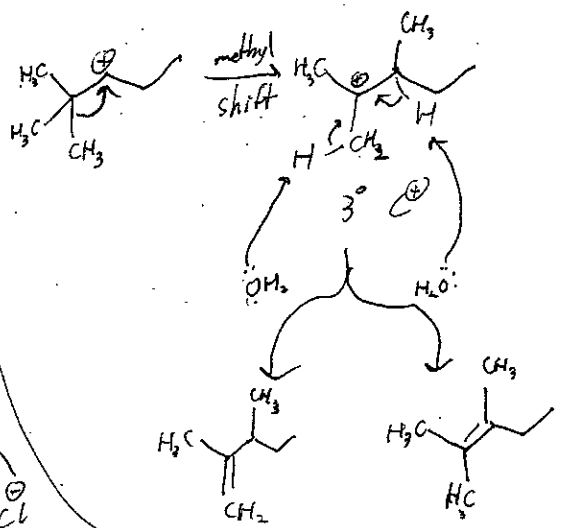
- S_N1,
- if 3° or 2°

- We get substitution!

mech:



or



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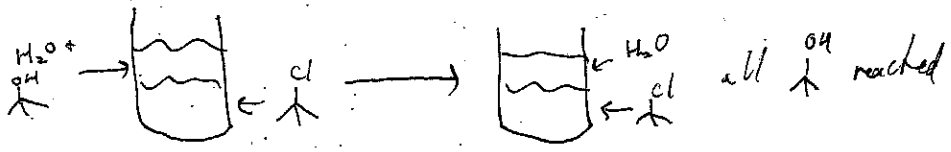
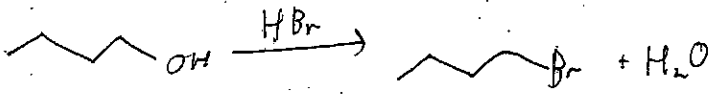
- How does this reaction go forward if each step is reversible?
  -  is insoluble in H_2O, so it phase separates



- S_N1 w/ 2°, 3° alcohols
- S_N2 w/ 1° alcohols

ex.



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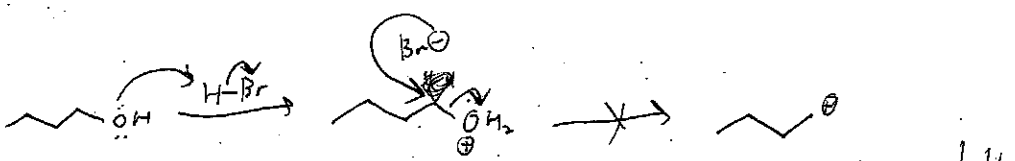

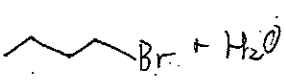

- These reactions require strong acid, which often is too harsh to use on more sensitive molecules

↳ ∴ It's useful to have milder methods to do these rxns.

Solution! Activate –OH as LG in mild way by forming sulfonate ester

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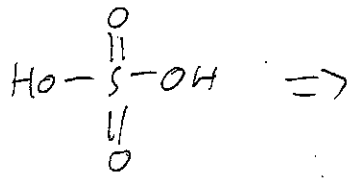
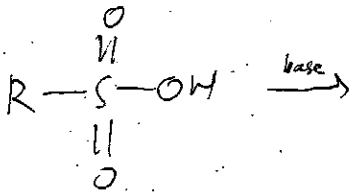


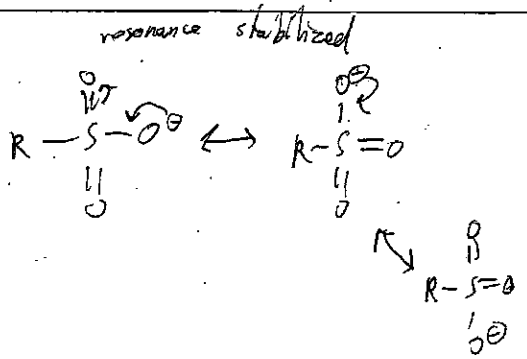
$pK_a = -3$



strong acid.

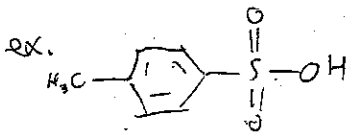
R = CH_3, CF_3, , etc

sulfonic acid



resonance stabilized

ex.

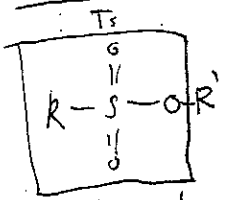


p-toluenesulfonic acid

(tosyl)

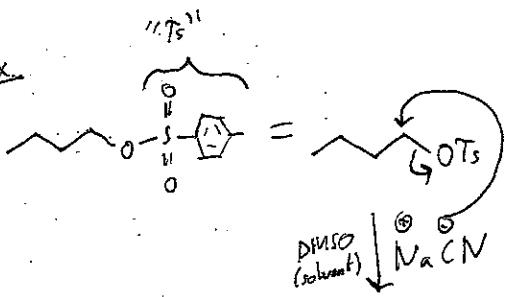
($TsOH$)

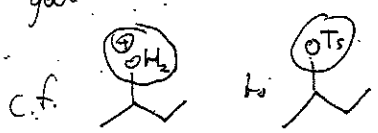
sulfonic acid



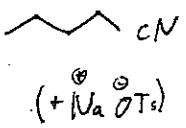
good LG!

ex.



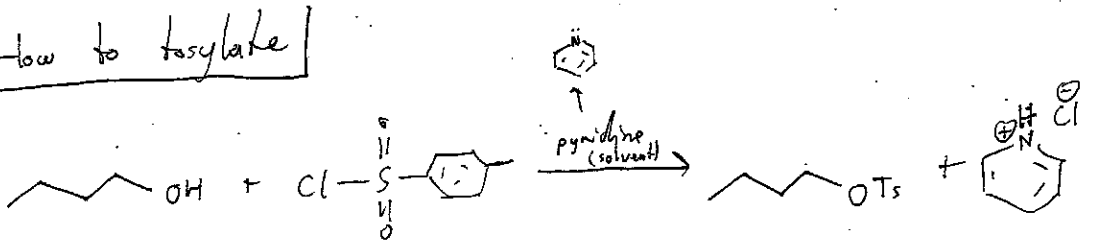


c.f. to both good LG's!



• S_N2 mech

• How to tosylate



"$TsCl$"

• Cl is a good LG!

• pyridine neutralizes HCl formed

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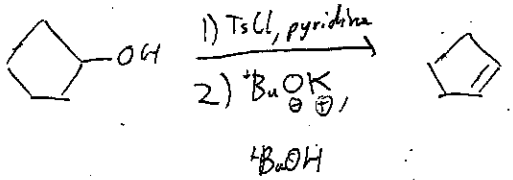

- We can do elimination on a tosylated -OH just like we can w/ an alkyl halide!
  - ↓ for this reason, -OTs is considered a "pseudo-halide" — it behaves a lot like -Br, -I, etc.