

LEC 22

CHEM 30 A

Mar 7th

①

- ① SOLVENT
- ② REARRANGEMENT
- ③ NEIGHBORING GROUP PARTICIPATION
- ④ PHASE TRANSFER CATALYSIS Sect 8-7)
- ⑤ INTRO to β ELIMINATION
- ⑥ MECHANISMS ⑦ STEREOCHEMISTRY ⑧ SUMMARY

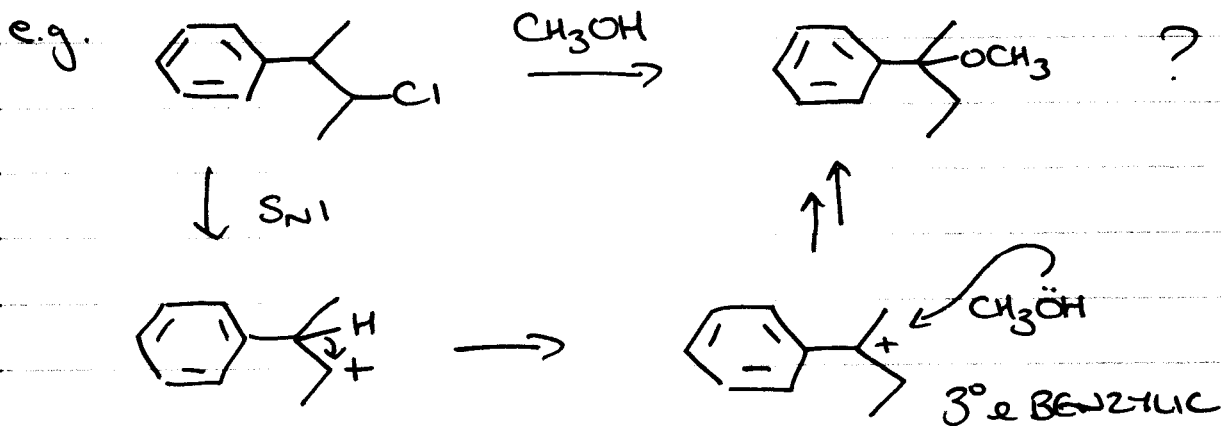
READ 8.8-8.11 PROBLEMS 8.4-8.8, 8.36-8.45

① SOLVENT

S_N2 DISFAVORED IN PROTIC SOLVENTS
(ground state energy lowered by solvation)

S_N1 FAVORED IN PROTIC SOLVENTS
(transition state energy lowered by solvation)

② REARRANGEMENT ($S_N1 - C^+$)

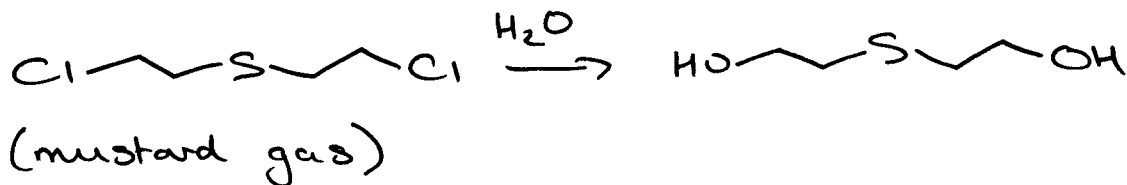


Summary

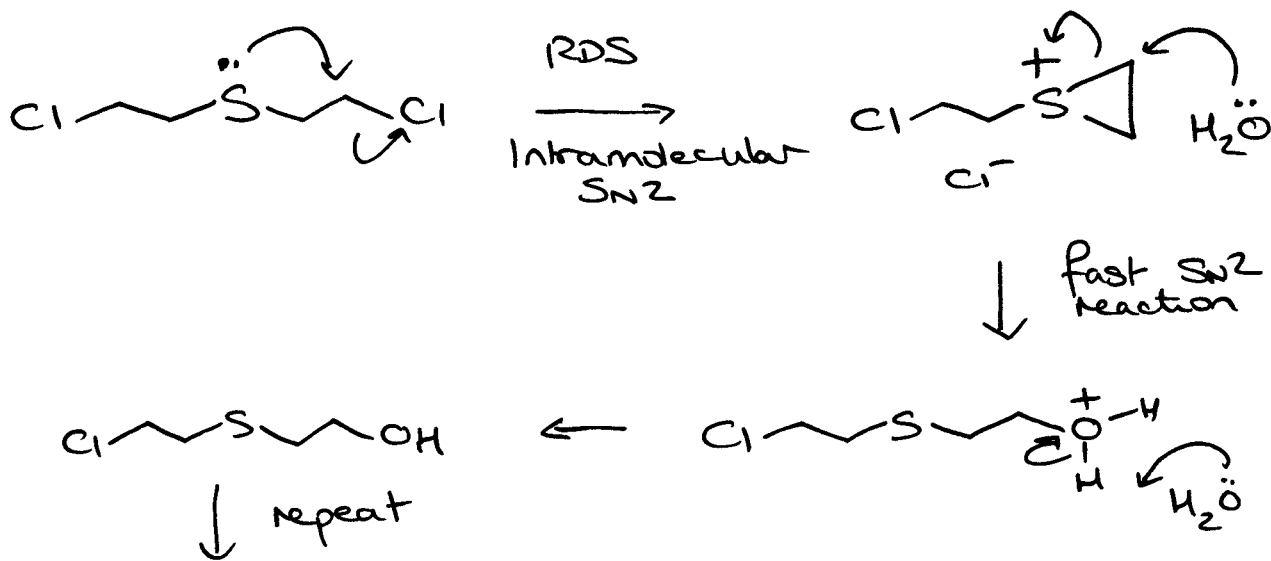
ELECTROPHILE	SN2	SN1
Me/1°	✓	X
2°	GOOD NUC POLAR APROTIC	POOR NUC POLAR PROTIC (GOOD LG)
3°	X	✓

- gets complicated => ELIMINATION

③ NEIGHBORING GROUP PARTICIPATION



v. rapid reaction, even though H₂O poor nucleophile



3

Overall rate = $k[\text{Cl}-\text{C}-\text{S}-\text{C}-\text{Cl}]$

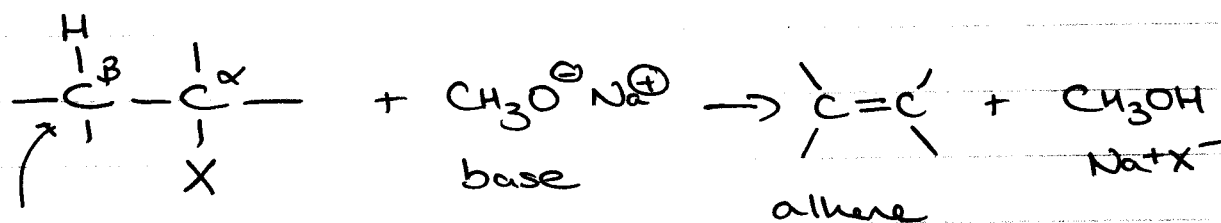
INDEPENDENT of $[\text{Nuc}]$

- Two consecutive $\text{S}_{\text{N}}2$ reactions with kinetics of an $\text{S}_{\text{N}}1$ reaction

④ PHASE TRANSFER CATALYSIS (Read Sect 8.7)

⑤ INTRO to β -ELIMINATION

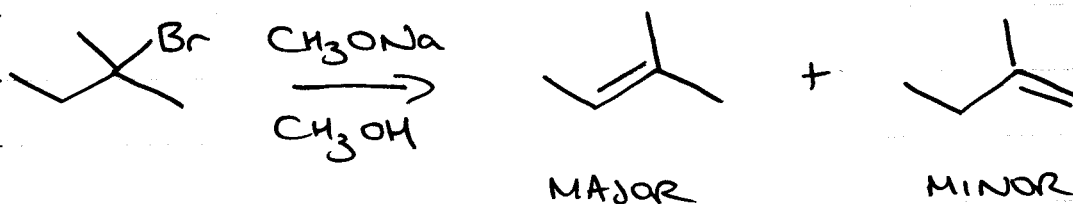
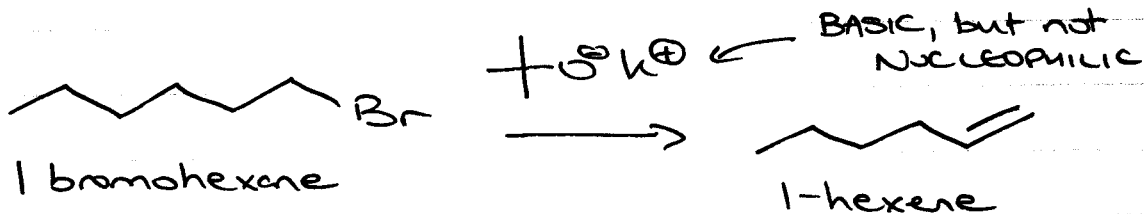
- DEHYDROHALOGENATION (one example)

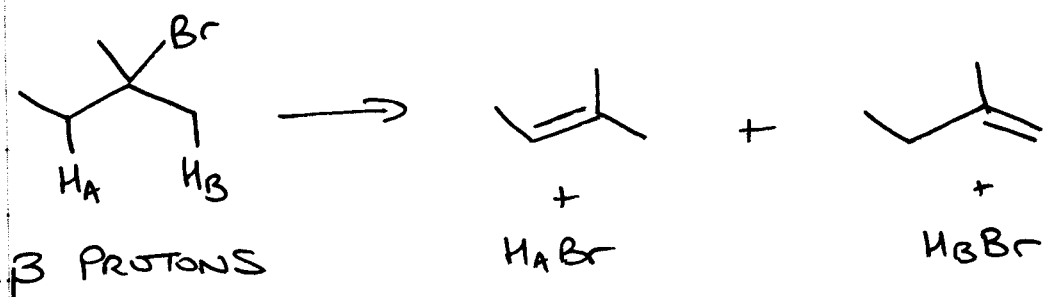


β elimination

ELIMINATION competes w/ SUBSTITUTION

- examples of ELIMINATION reactions





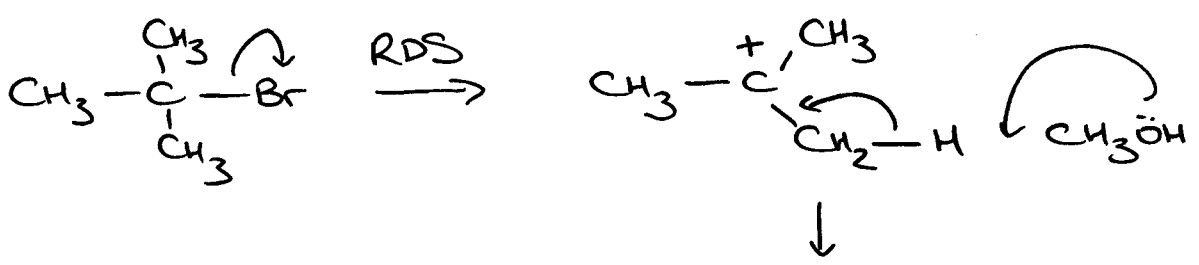
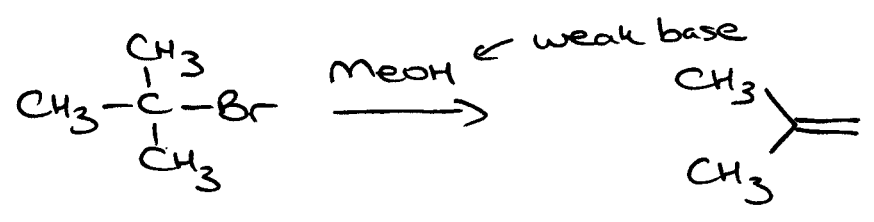
ZAITSEV'S RULE \rightarrow major product is the MOST SUBSTITUTED ALKENE (more STABLE)

... and there are EXCEPTIONS to this rule...

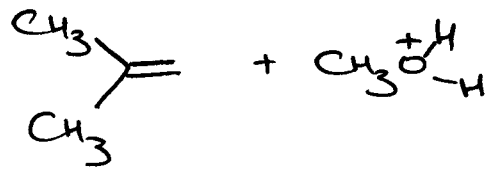
⑥ MECHANISMS

(like S_N reactions, two limiting ones)

E1 (elimination unimolecular)

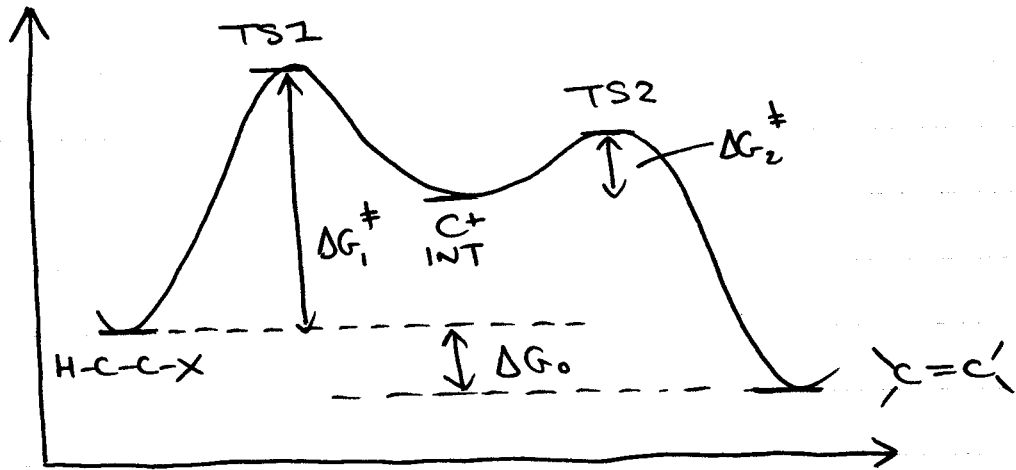


COMPETES WITH S_N1 REACTION

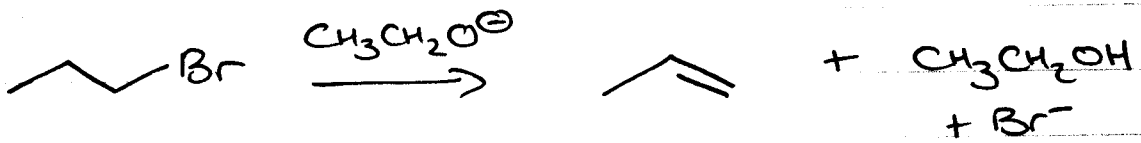


$\text{rate} = k_1 [(\text{CH}_3)_3\text{C}-\text{Br}]$

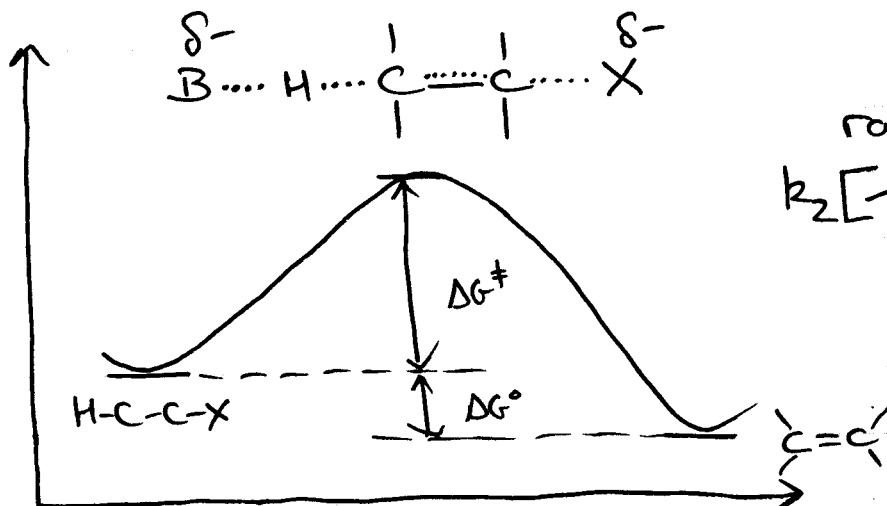
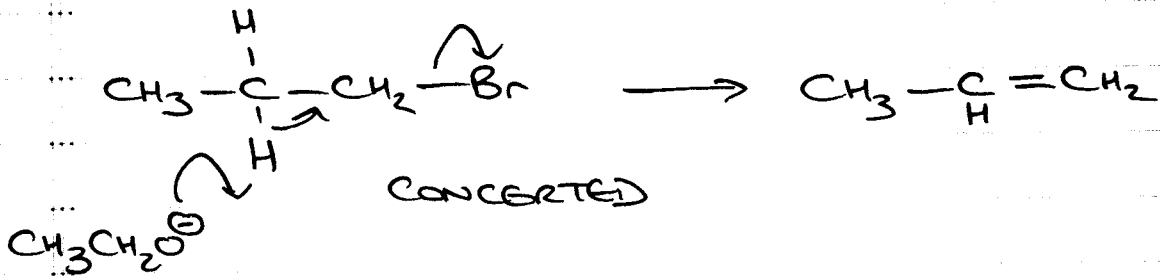
- energy profile



E2 (elimination bimolecular)

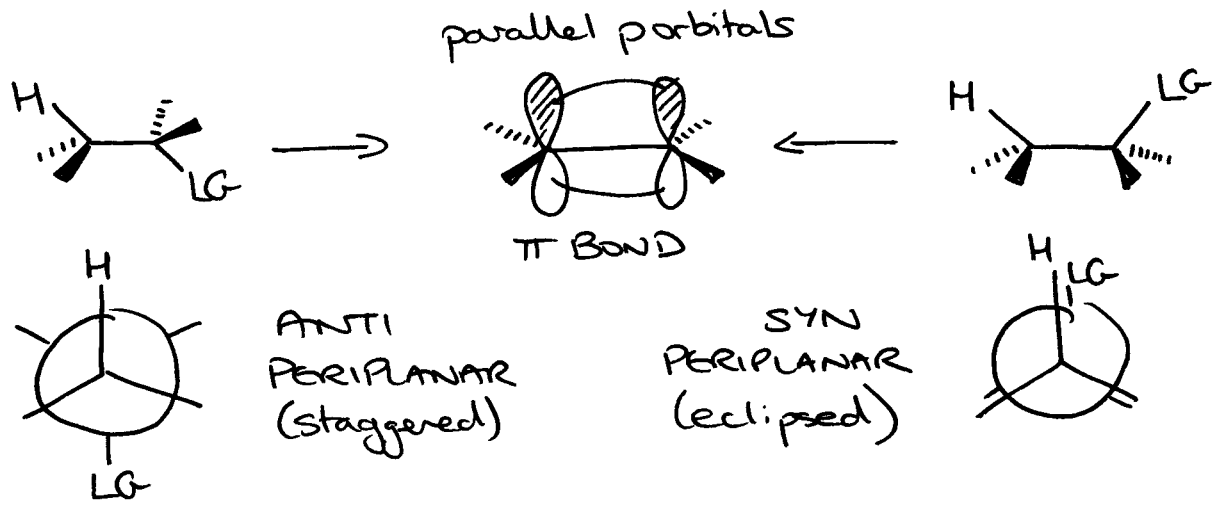


(competes w/ SN2)

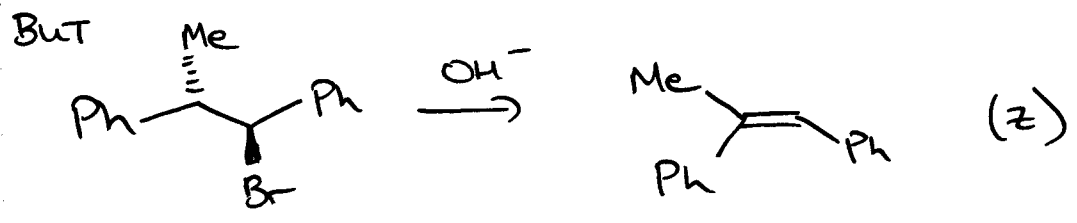
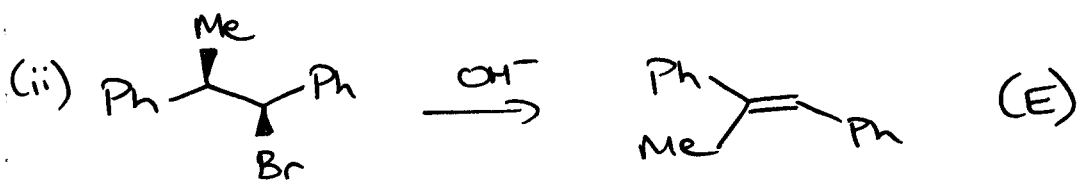
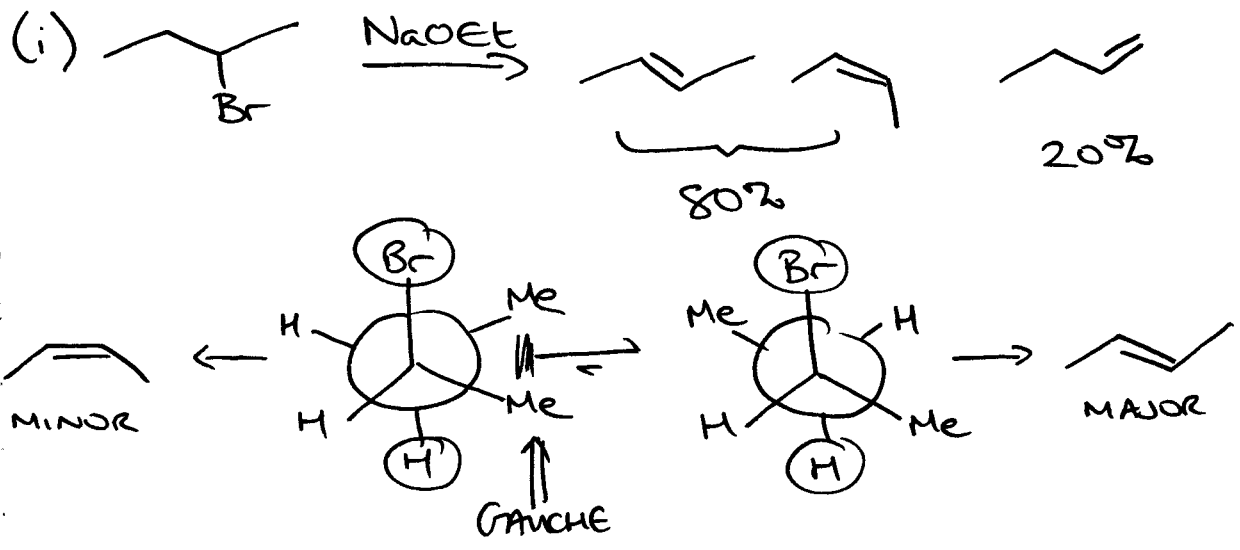


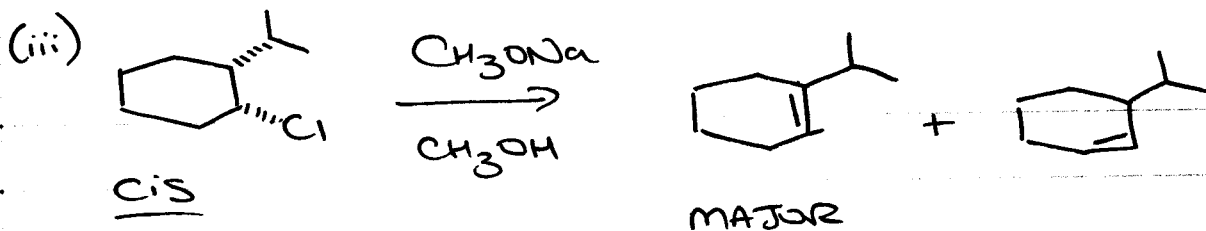
$$\text{rate} = k_2 [\text{~Br}] [\text{Base}]$$

⑦ STEREOCHEMISTRY

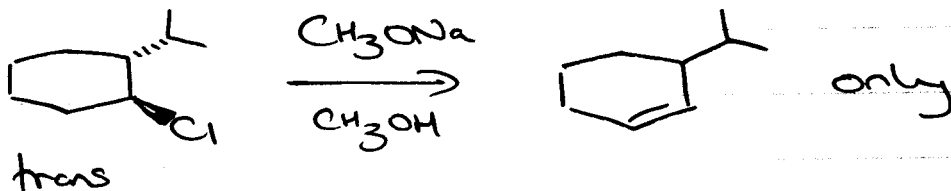


Generally, antiperiplanar geometry is preferred in an E2 reaction (exceptions)

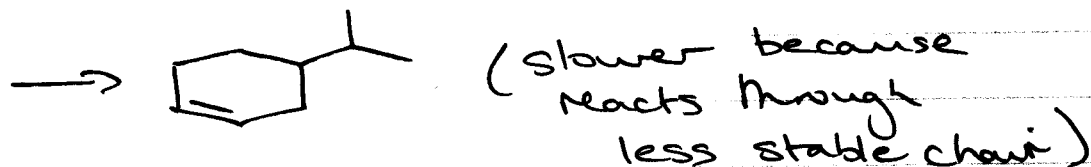
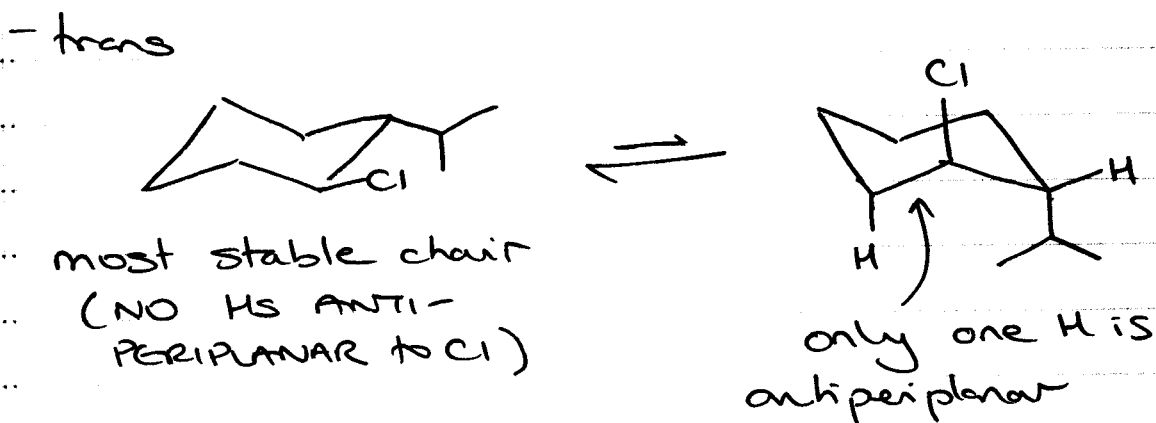
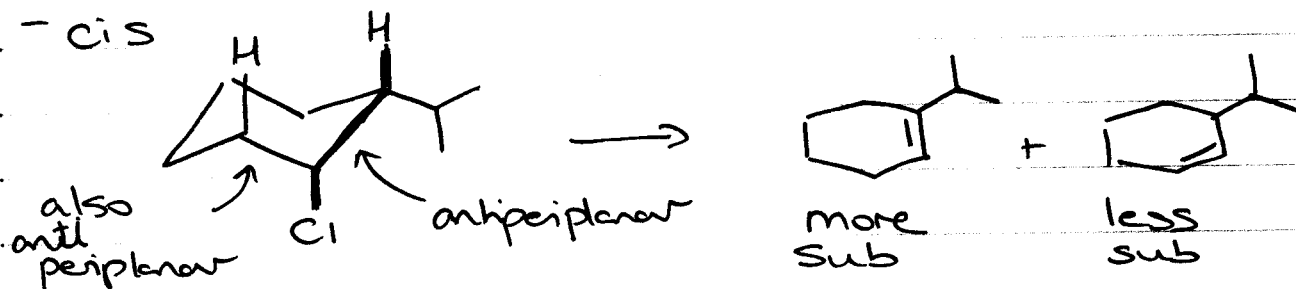




BUT



also: cis reacts faster than trans \Rightarrow why?



⑧ SUMMARY E1/E2

Alkyl halide

E1

E2

METHYL

— Elimination Impossible —

1° (RCH₂X)

Does NOT happen

Favored elimination mode

2° (R₂CHX)

(H₂O / ROH)
weak bases
allylic, benzylic
substrates

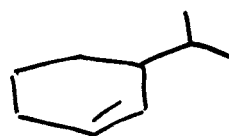
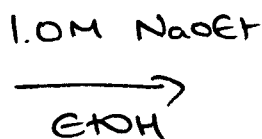
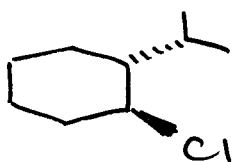
Strong bases (RO⁻)
(HO⁻)

3° (R₃C-X)

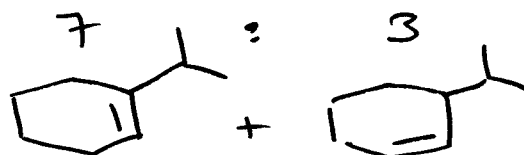
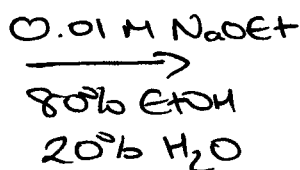
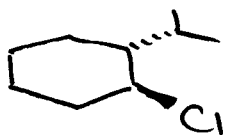
Weak bases

Strong bases

— Reaction conditions

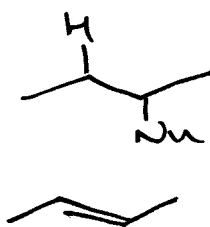
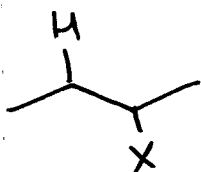


E2 conditions



E1 conditions

UP NEXT — SUBSTITUTION vs ELIMINATION



SUBSTITUTION

ELIMINATION