

## ELIMINATION

READ: 8.8-8.11

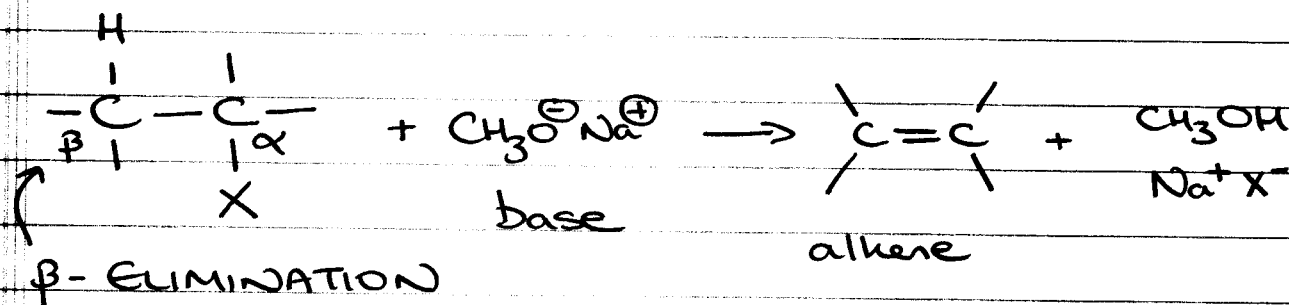
- ① INTRODUCTION
- ② MECHANISMS
- ③ STEREOCHEMISTRY
- ④ E1/E2 Summary
- ⑤ SUBSTITUTION VS ELIMINATION

PROBLEMS:

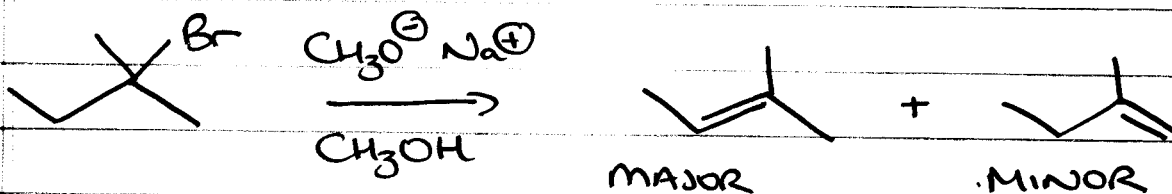
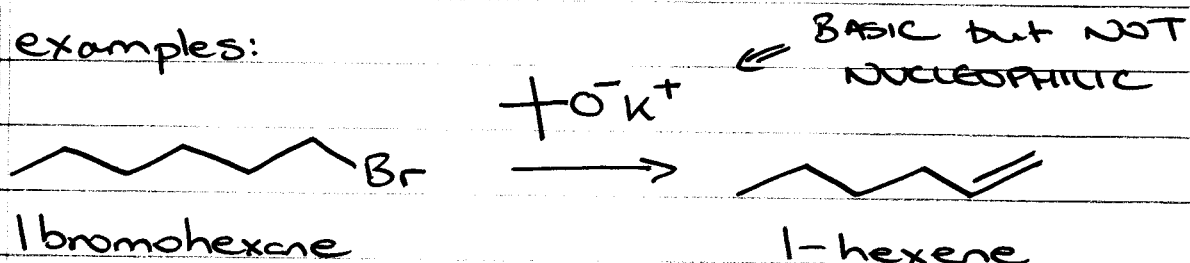
8.6-8.8, 8.36-8.45

## ① INTRODUCTION

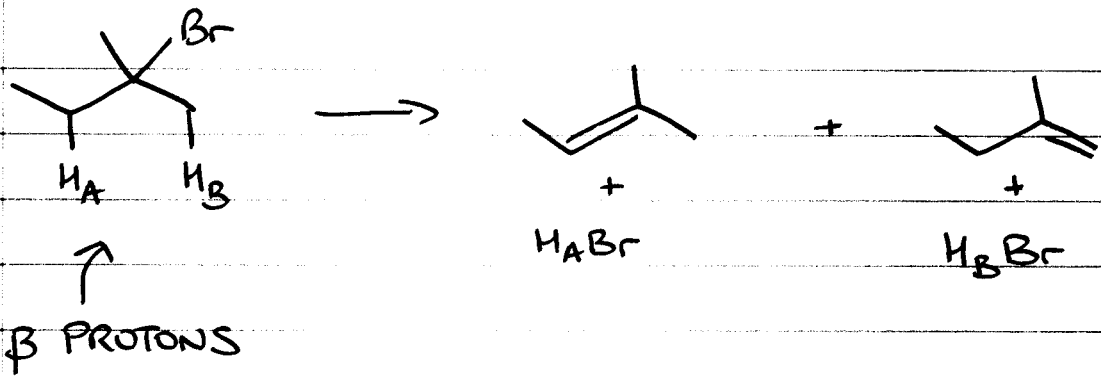
- one example is DEHYDROHALOGENATION

SUBSTITUTION/ELIMINATION  $\Rightarrow$  competing reactions

examples:



2

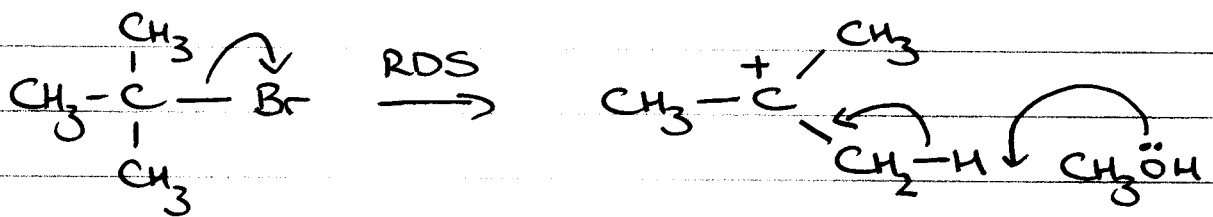
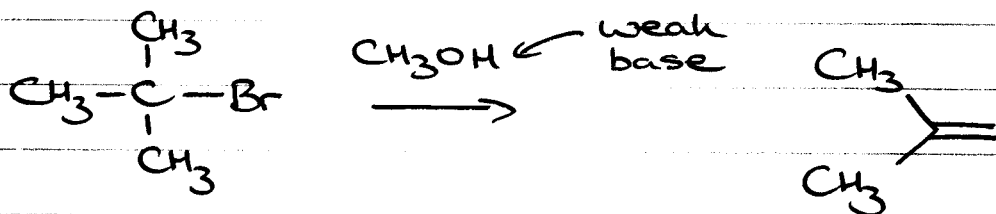


ZAITSEV'S RULE  $\longrightarrow$  major product is the MOST SUBSTITUTED ALKENE  
 (There are EXCEPTIONS TO THIS RULE)

2) MECHANISMS

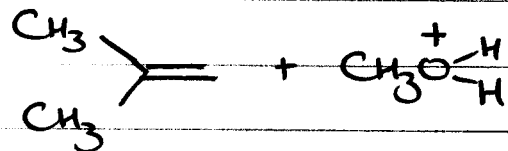
(Just like substitution reactions  $\Rightarrow$  TWO LIMITING MECHANISMS)

E1 (elimination unimolecular)

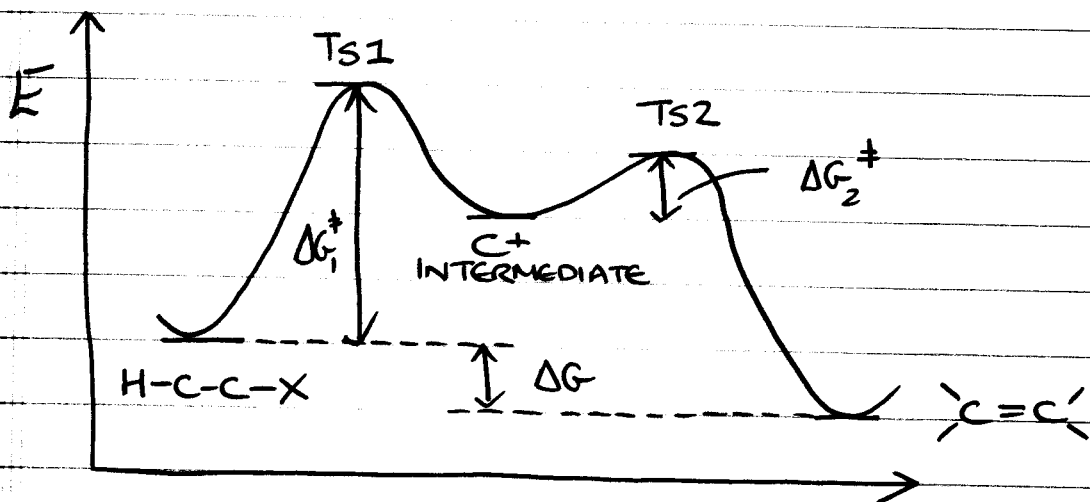


COMPETES WITH S<sub>N</sub>1 REACTION

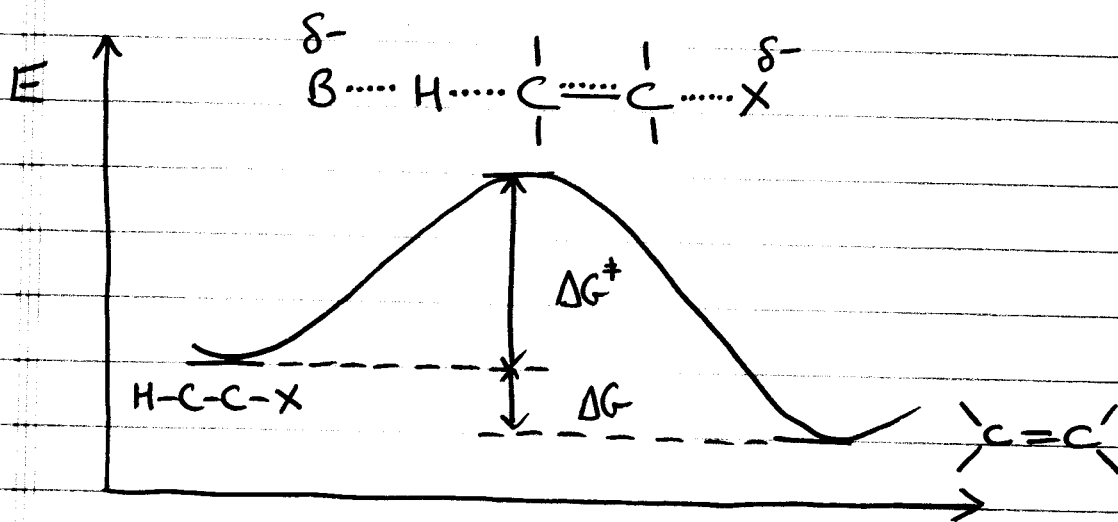
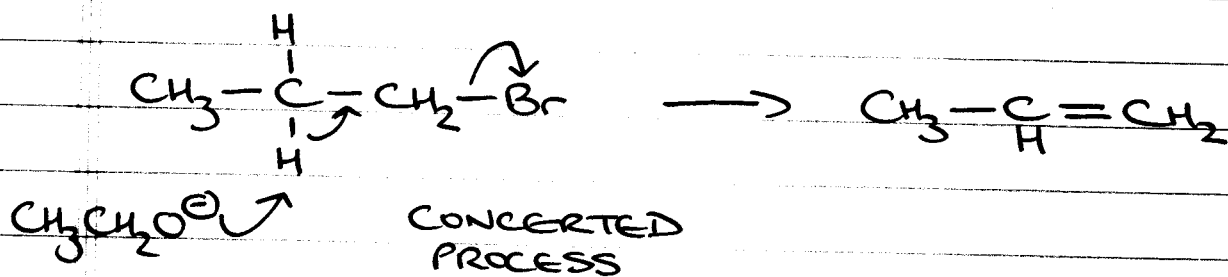
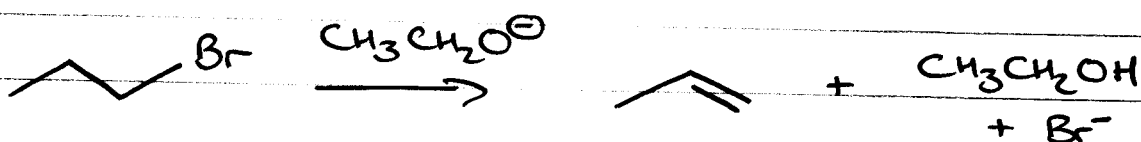
rate =  $k_1 [(\text{CH}_3)_3\text{C}-\text{Br}]$



(3)

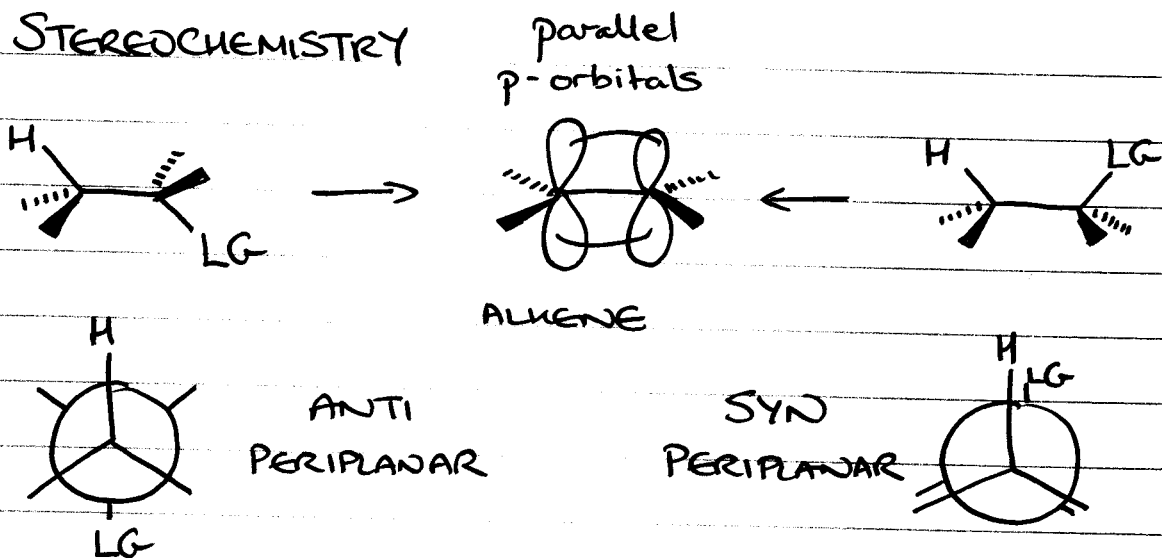


- E2 (elimination bimolecular)



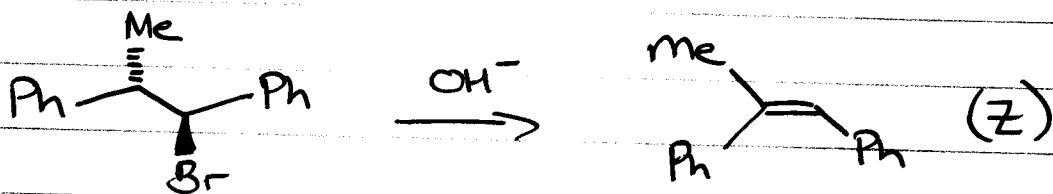
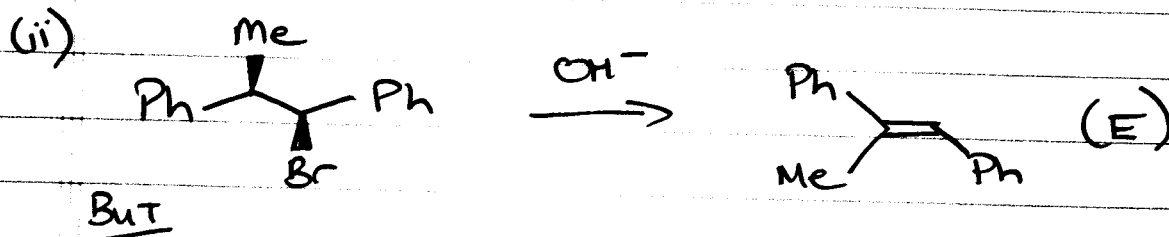
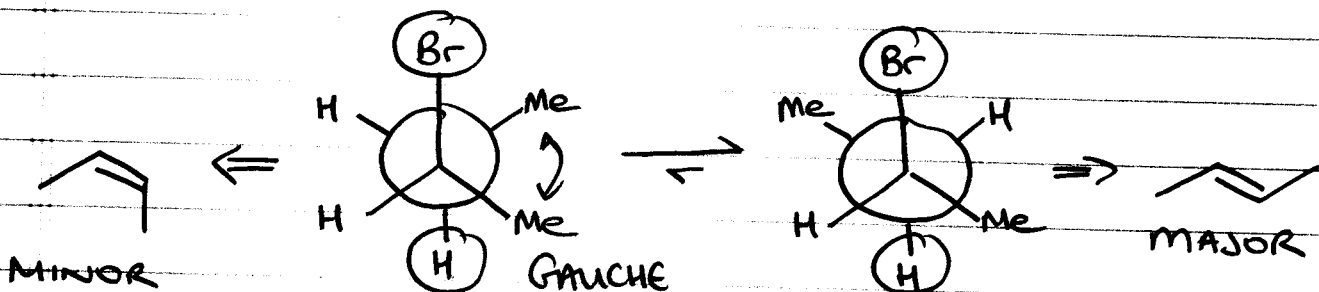
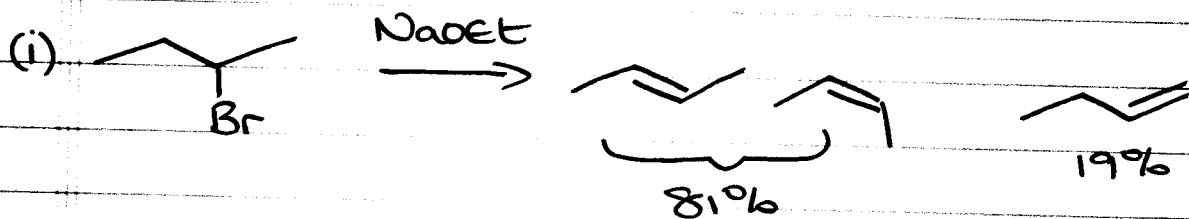
$$\text{rate} = k_2 [\text{C}_2\text{H}_5\text{CH}_2\text{CH}_2\text{Br}] [\text{Base}]$$

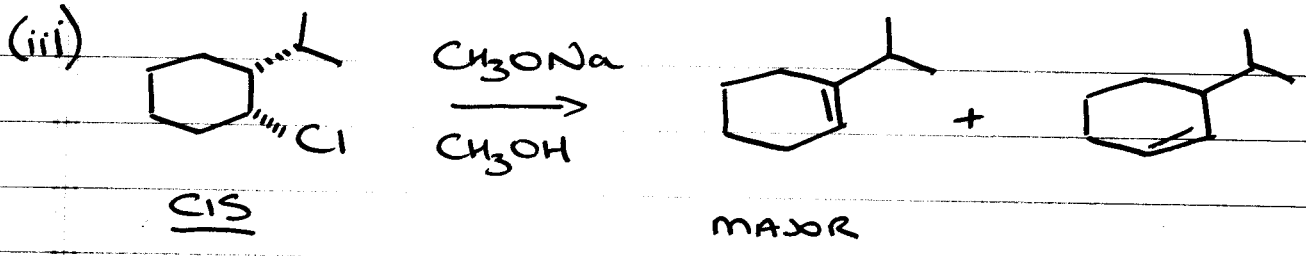
③ STEREOCHEMISTRY



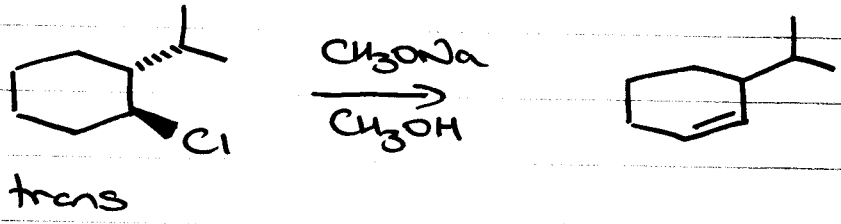
WITH A FEW EXCEPTIONS, AN ANTI PERIPLANAR GEOMETRY IS PREFERRED IN AN E2 REACTION

examples



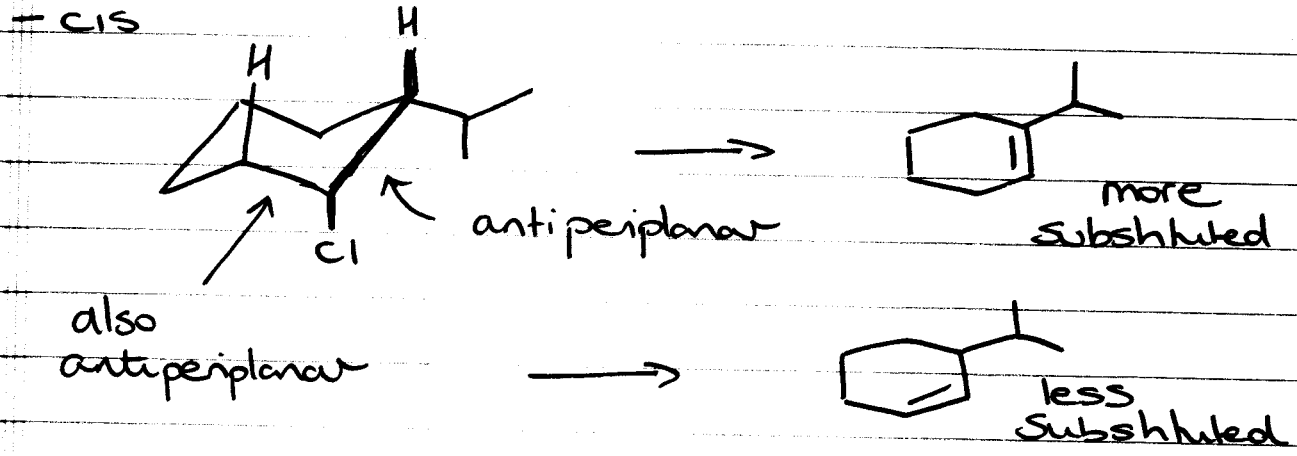


BUT

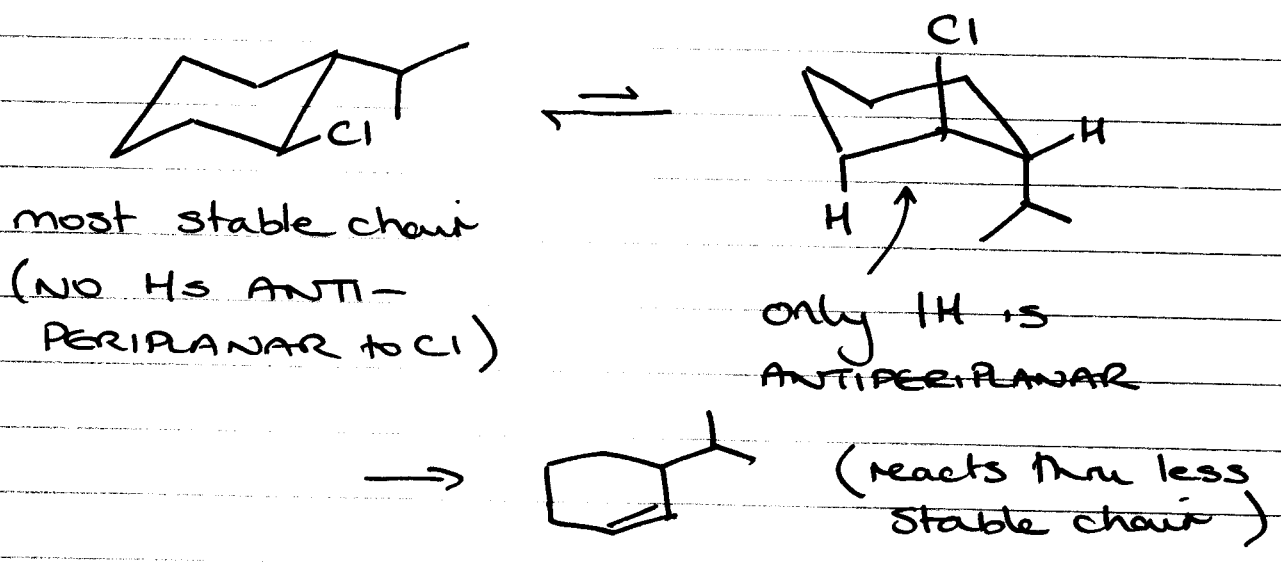


ALSO: CIS reaction FASTER THAN TRANS.

WHY?



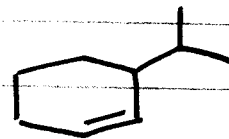
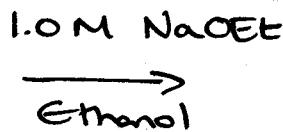
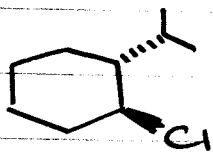
- trans



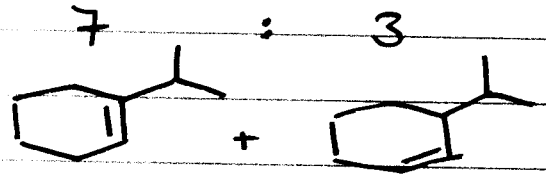
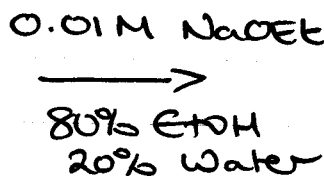
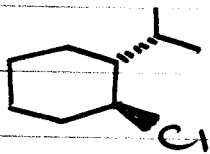
# ④ E1/E2 Summary

ALKYL HALIDE	E1	E2
METHYL	ELIMINATION IMPOSSIBLE	
1° (RCH <sub>2</sub> X)	DOES NOT HAPPEN (1° C <sup>+</sup> )	FAVORED ELIMINATION MODE
2° (R <sub>2</sub> CHX)	(H <sub>2</sub> O / ROH) WEAK BASES (ALLYLIC, BENZYLIC SUBSTRATES)	STRONG (RO <sup>-</sup> ) BASES (HO <sup>-</sup> )
3° (R <sub>3</sub> C-X)	WEAK BASES	STRONG BASES

## Reaction conditions

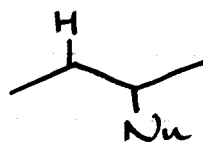
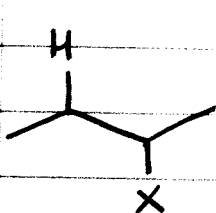


E2 conditions



E1 conditions

## ⑤ SUBSTITUTION VS ELIMINATION



SUBSTITUTION



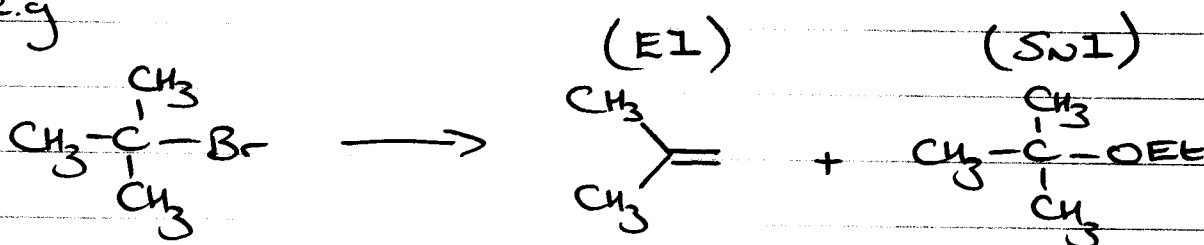
ELIMINATION

(i)  $S_N1$  vs  $E1$ 

- basicity of nucleophile

STRONG-BASE  $\Rightarrow$   $E1$  WEAK-BASE  $\Rightarrow$   $S_N1$

e.g



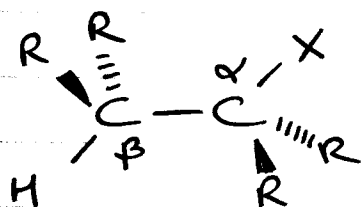
EtOH	20%	80%
EtONa/EtOH	90%*	10%

\* actually E2!

Affinity for proton vs affinity for carbon

(ii)  $S_N2$  vs  $E2$ 

- structure of substrate



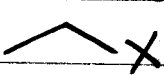
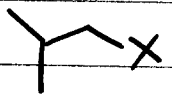
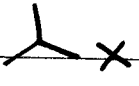
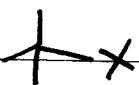
BRANCHING AT  $\alpha$  AND/OR  $\beta$  SLOWS DOWN  $S_N2$  REACTION, HAS LITTLE EFFECT ON  $E2$  REACTION  $\Rightarrow$  ALSO INCREASES STABILITY OF ALKENE FORMED IN  $E2$  REACTION.

- attacking species

nucleophilicity ↑  
basicity ↑

greater S<sub>N</sub>2 : E2  
greater E2 : S<sub>N</sub>2

- SUMMARY

	Poor Nuc (H <sub>2</sub> O, R-OH)	Weakly Basic Nuc (I <sup>-</sup> , RS <sup>-</sup> , RCOO <sup>-</sup> )	(UNHINDERED) Strongly Basic Nuc (RO <sup>-</sup> )	(HINDERED) Strongly Basic Nuc (tO <sup>-</sup> )
CH <sub>3</sub> X	NO reaction	S <sub>N</sub> 2	S <sub>N</sub> 2	S <sub>N</sub> 2
 X	NO reaction	S <sub>N</sub> 2	S <sub>N</sub> 2	E2
 X	NO reaction	S <sub>N</sub> 2	E2	E2
 X	S <sub>N</sub> 1/E1 (slow)	S <sub>N</sub> 2	E2	E2
 X	S <sub>N</sub> 1/E1	S <sub>N</sub> 1/E1	E2	E2

Again, 2° substrates BORDERLINE

attacking Nu → pKa conjugate acid ≥ 11 (elimination)  
 ↘ pKa conjugate acid < 11 (substitution)

Higher temperatures favor ELIMINATION reactions over SUBSTITUTION  
 (ΔG = ΔH - TΔS)