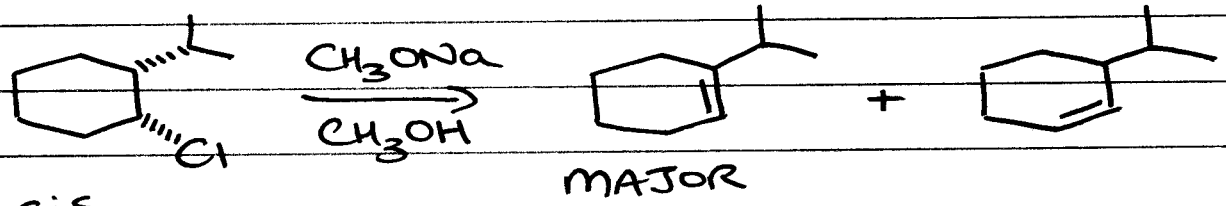
LEC (23) CHEM 30A Jun 3rd

1. STEREOCHEMISTRY
2. REGIOSELECTIVITY
3. SYN ELIMINATION
4. E1 vs E2
5. S_N vs E
6. SYNTHESIS

3rd Ed
Review Ch 8
Q 8.42 – 8.50
(except 8.46g,h)

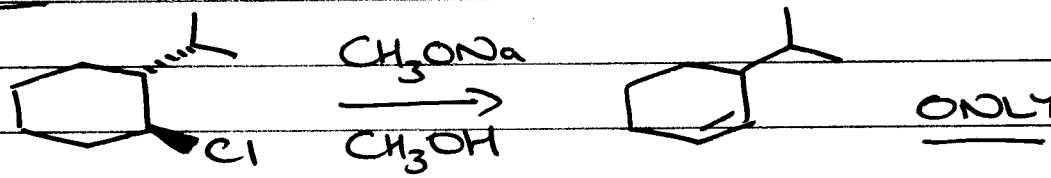
4th Ed
Review Ch 9
Q 9.43 – 9.53
(except 9.47g,h)

(1) STEREOCHEMISTRY cont



cis

BUT

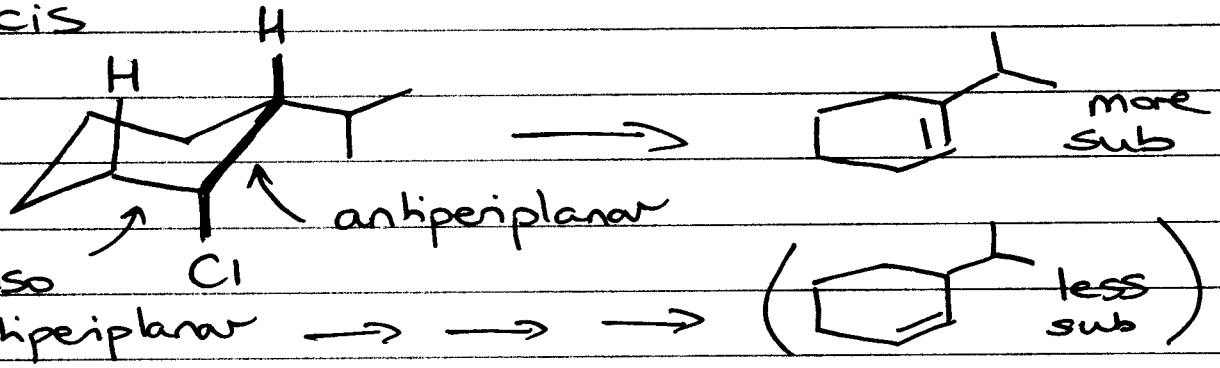


ONLY

trans

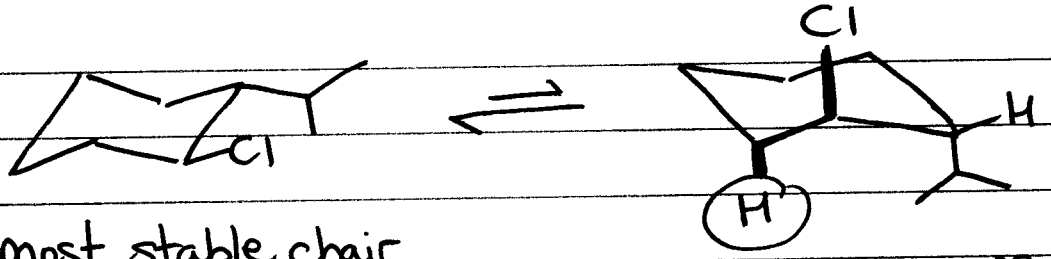
also: cis reaction FASTER than trans – WHY?

– cis



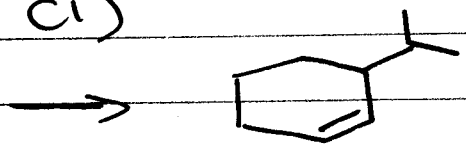
also antiperiplanar → → → ( )

- trans



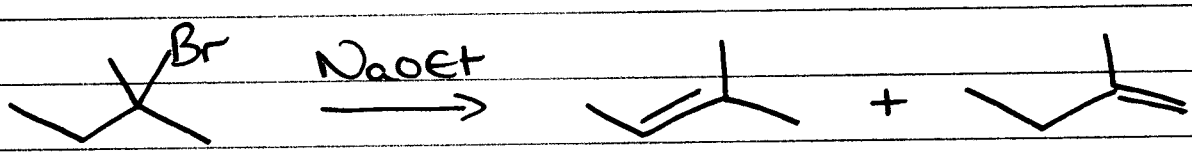
most stable chair
(no Hs ANTIPERIPLANAR to Cl)

ONLY ONE H IS ANTIPERIPLANAR



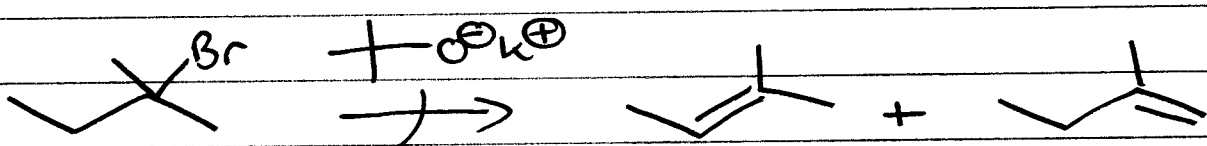
slower because reacts through less stable chair

(2) REGIOSELECTIVITY



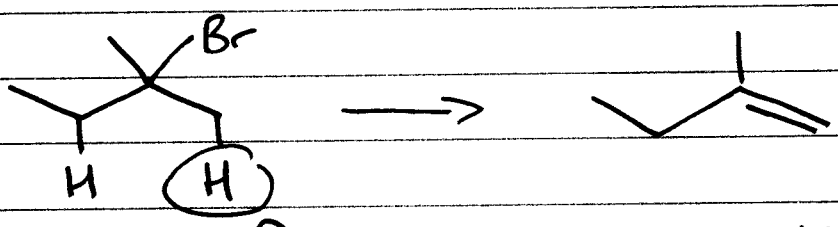
MAJOR (70%) MINOR (30%)

ZAITSEV SELECTIVITY → more sub, more stable alkene



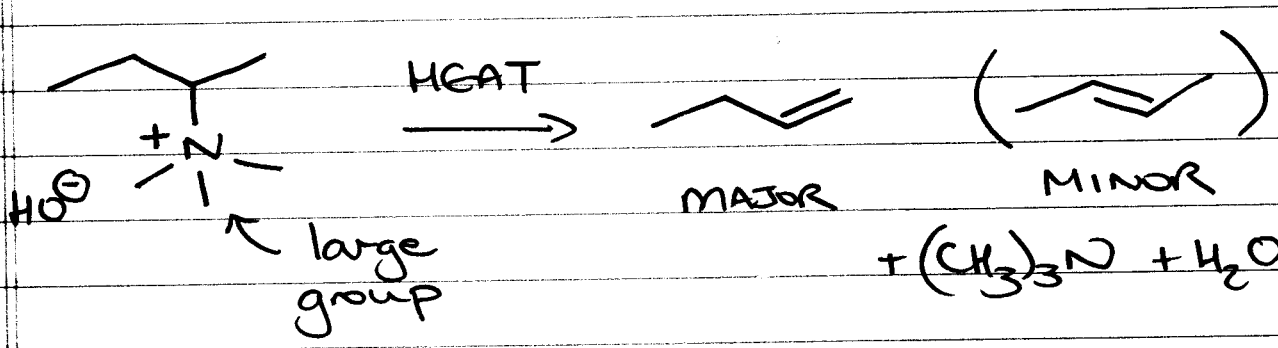
bulky base MINOR (30%) MAJOR (70%)

HOFMANN SELECTIVITY → least sub alkene preferred

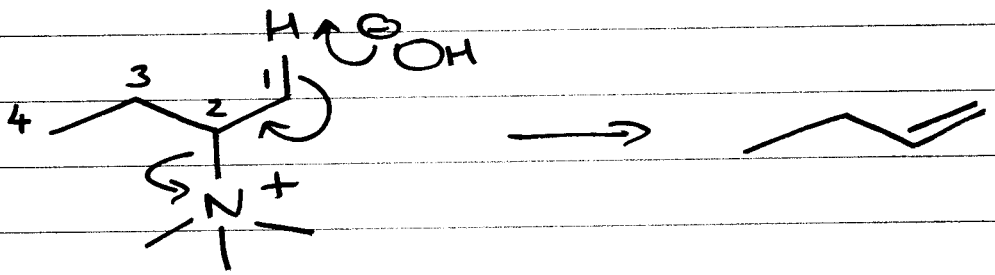


↑ more accesible β-H

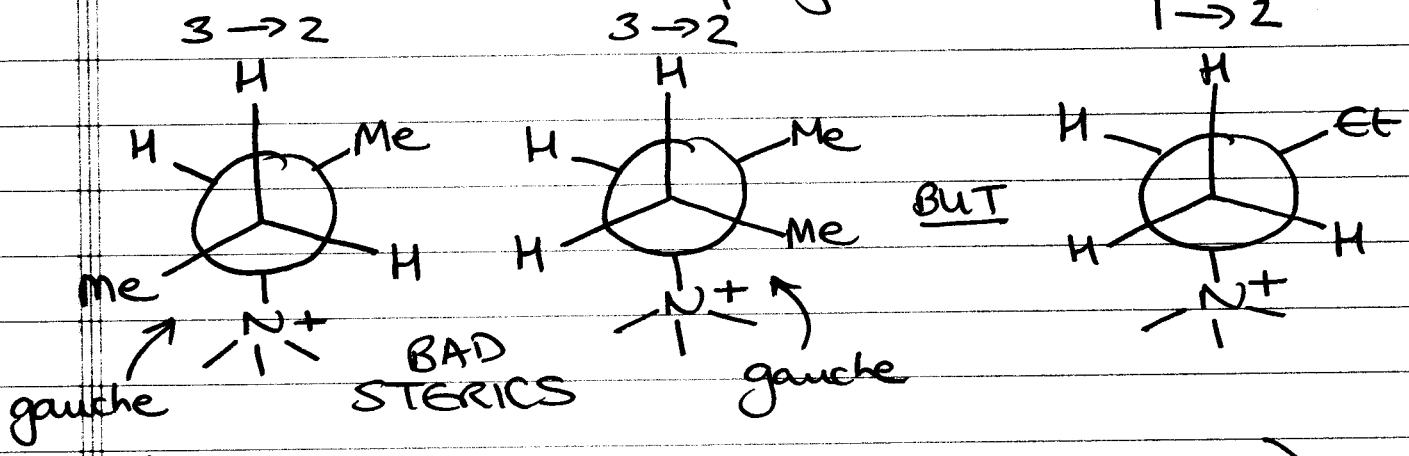
Common reaction w/
QUATERNARY AMMONIUM SALTS



PROCEEDS w/ ANTISTEREOSPECIFICITY

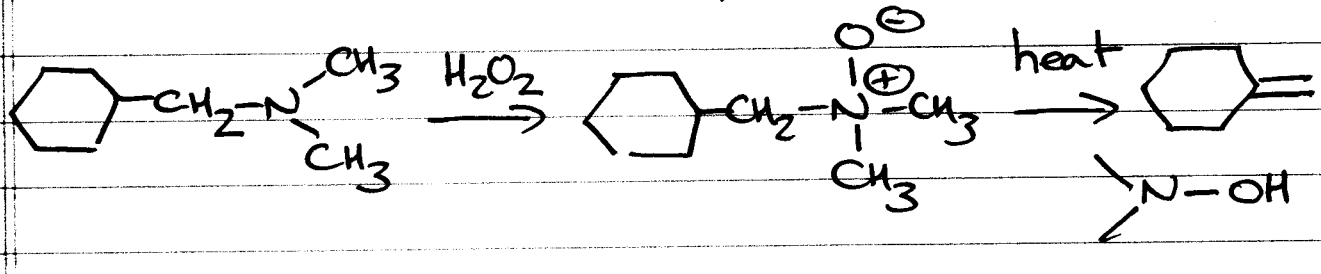


consider NEWMAN projections

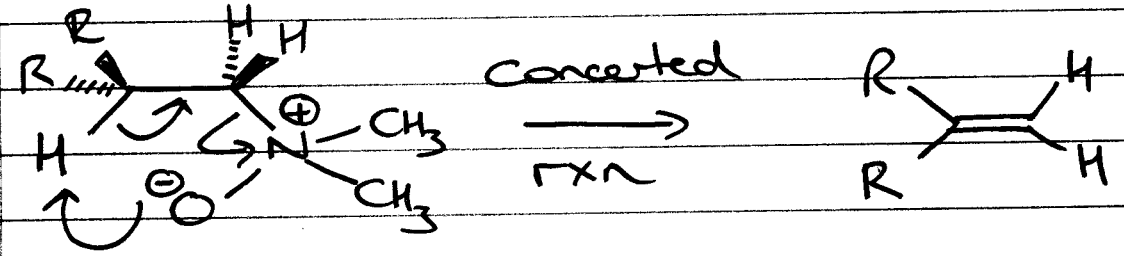


(also electronic effects.... don't worry)

(3) SYN ELIMINATION (cope elimination)

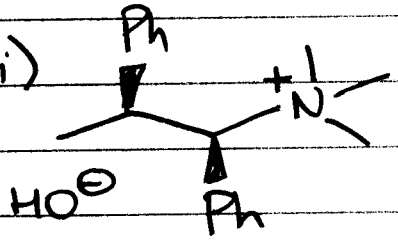


mechanism

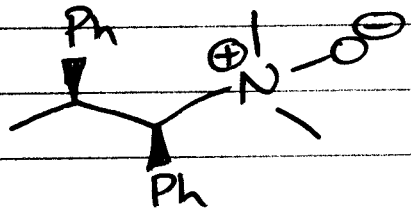


SYN

- figure out the products of these reactions

(i) 

heat → ?

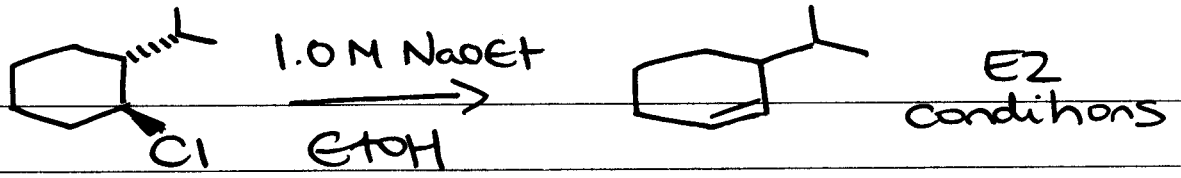
(ii) 

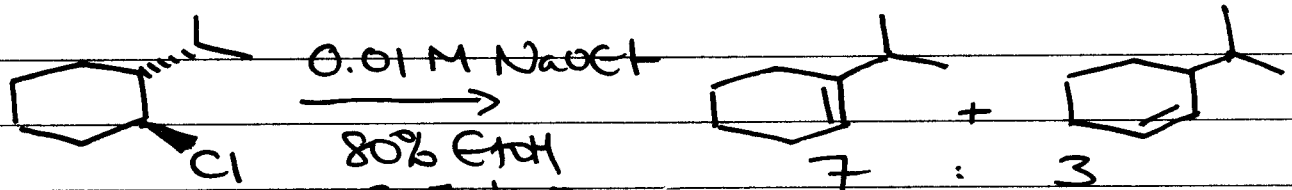
heat → ?

(4) E1 vs E2

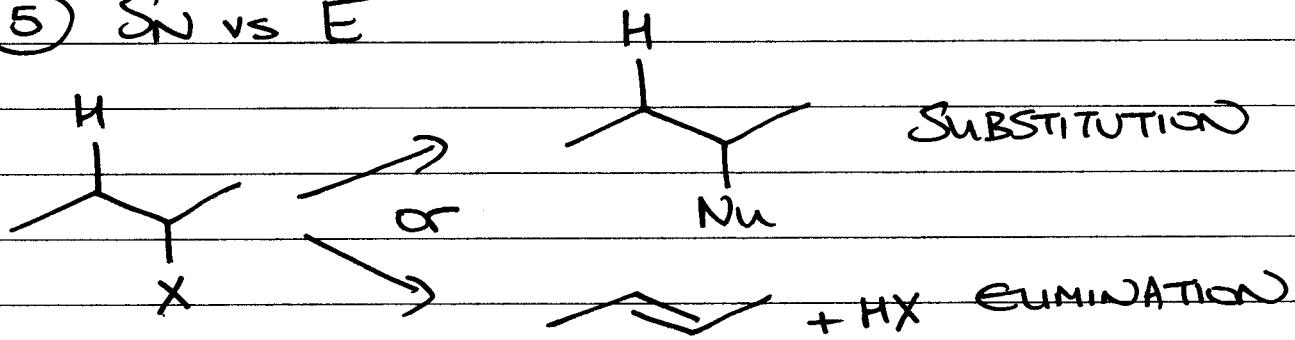
ALKYL HALIDE	E1	E2
methyl	— ELIMINATION IMPOSSIBLE —	
1° (RCH_2X)	DOES NOT HAPPEN (1°C+)	FAVORED ELIMINATION MODE
2° (R_2CHX)	H_2O/ROH (weak bases) ALLYLIC/BENZYLIC	STRONG BASES ($RO^\ominus$ / $HO^\ominus$)
3° (R_3CX)	WEAK BASES	STRONG BASES

- can also depend upon reaction conditions



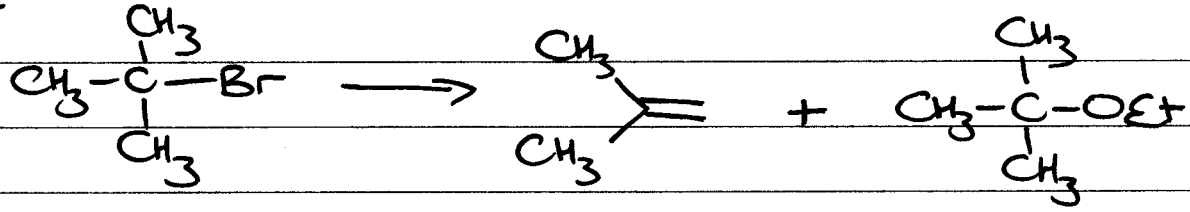


(5) S_N vs E



(i) S_N1 vs E1

e.g.



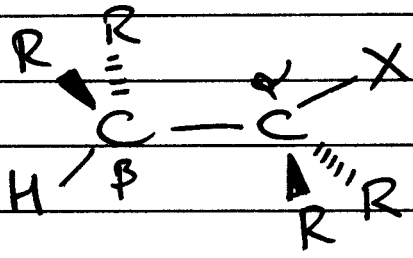
affinity for proton vs carbon ⇒ stronger base

EtOH/EtONa → 90%** (↳ E2 mechanism) 10%

Generally S_N1 is favored over E1 except at higher temperatures (more later)

(ii) S_N2 vs E2

- structure of substrate

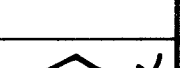
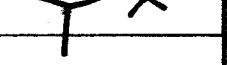
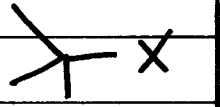


BRANCHING AT α / β
slows S_N2 (STERICS)
speeds up E2 (more stable alkene)

- nucleophile

as nucleophilicity ↑ ratio $S_N2/E2$ ↑
as basicity ↑ ratio $E2/S_N2$ ↑

- SUMMARY

	Poor Nuc (H_2O/ROH)	Weakly BASIC Nuc (I^-; RS^-; RCO_2^-)	(Unhindered) Strongly BASIC Nuc (RO^-/HO^-)	(Hindered) Strongly BASIC Nuc ($^+O^\ominus$)
CH_3X	NR	S_N2	S_N2	S_N2
	NR	S_N2	S_N2	E2
	NR	S_N2	E2	E2
	S_N1/E1 (slow)	S_N2	E2	E2
	S_N1/E1	S_N1/E1	E2	E2

- 2° SUBSTRATES

attacking Nuc → pka conjugate acid ≥ 11 → ELIMINATION

attacking Nuc → pka conjugate acid < 11 → SUBSTITUTION

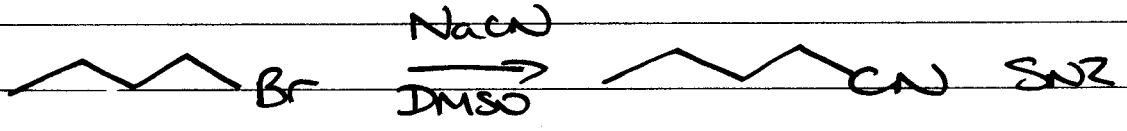
Also higher temp favors ELIMINATION

$\Delta G = \Delta H - T\Delta S$

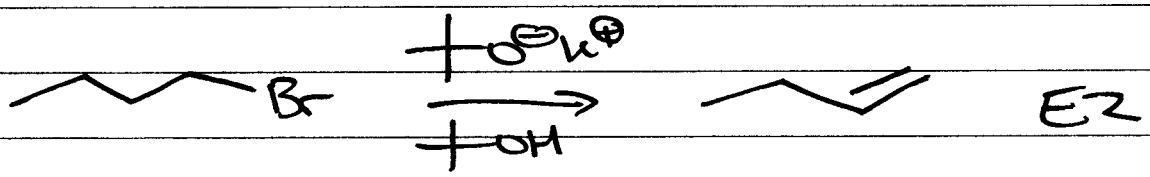
S_N2 2 molecules → 2 molecules

E 2 molecules → 3 molecules $+\Delta S$

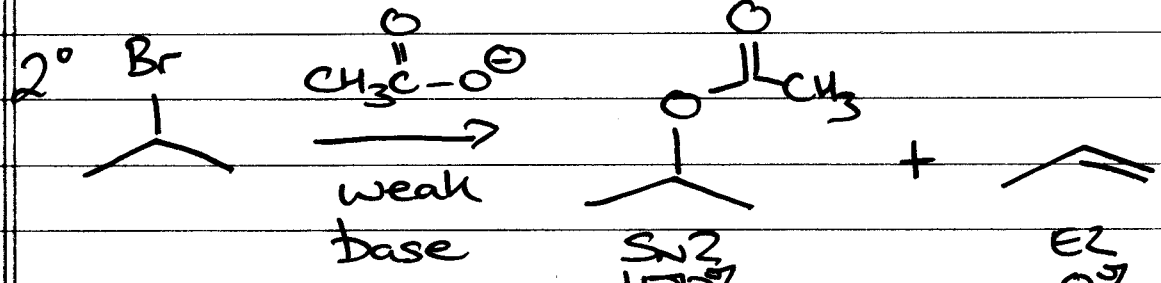
- examples

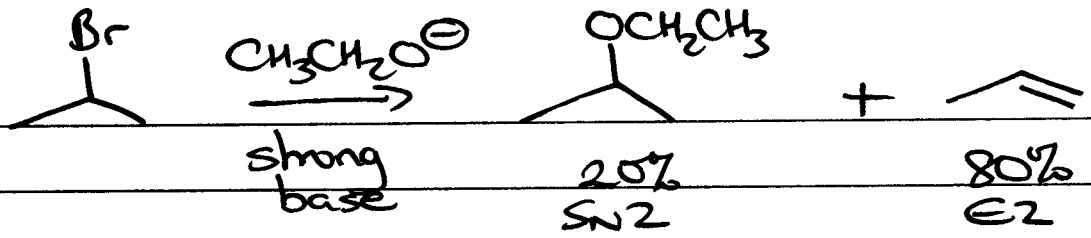
1° 

(CN^-, RS^-, N_3^-, NH_3, Br^-, I^-) GOOD NUC



strong hindered bases

2° 



2° BENZYLIC/ALLYLIC substrates can do E1/SN1 with weakly basic Nuc in polar protic solvents