LEC (23) CHEM 30A Mar 9th

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

Review Ch 8 PROBLEMS 8.42 – 8.50 (NOT 8.46 f, g, h)

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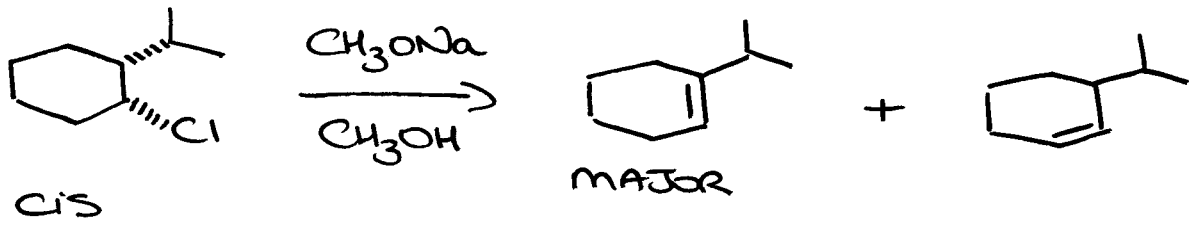
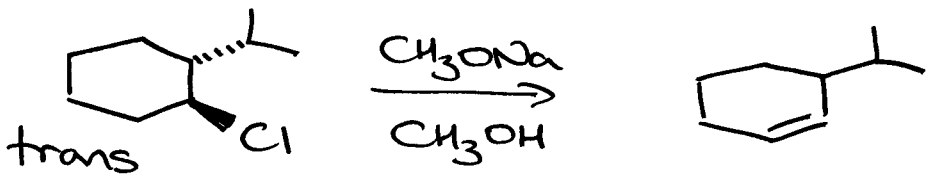
(1) STEREOCHEM cont...

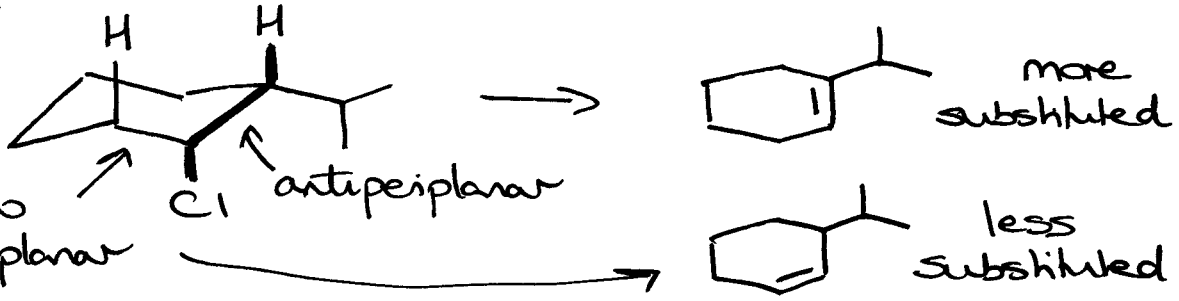


BUT

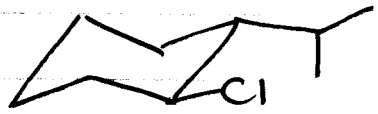


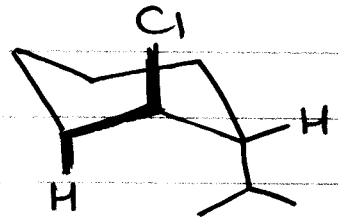
also: cis reaction FASTER than trans – WHY?

– cis



-trans



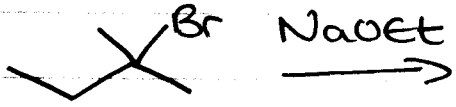


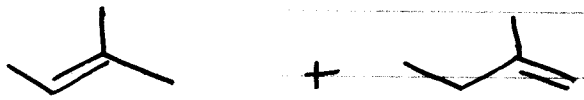
most stable chair (no Hs antiperiplanar to Cl)

only one H antiperiplanar

SLOWER b/c reacts thru LESS STABLE chair

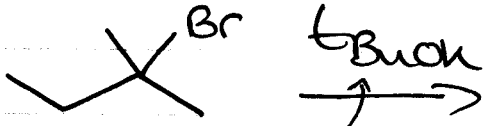
(2) REGIOSELECTIVITY

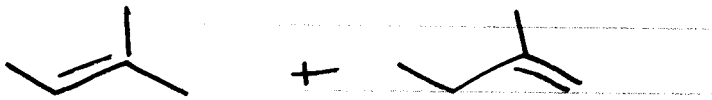




MAJOR (70%) + MINOR (30%)

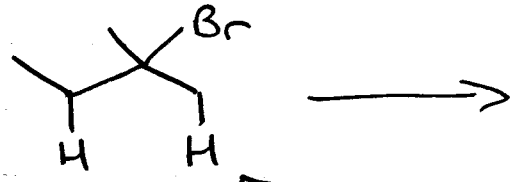
ZAITSEV selectivity → more substituted, more stable alkene

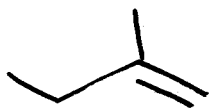




MINOR (30%) + MAJOR (70%)

HOFMANN → least substituted alkene preferred

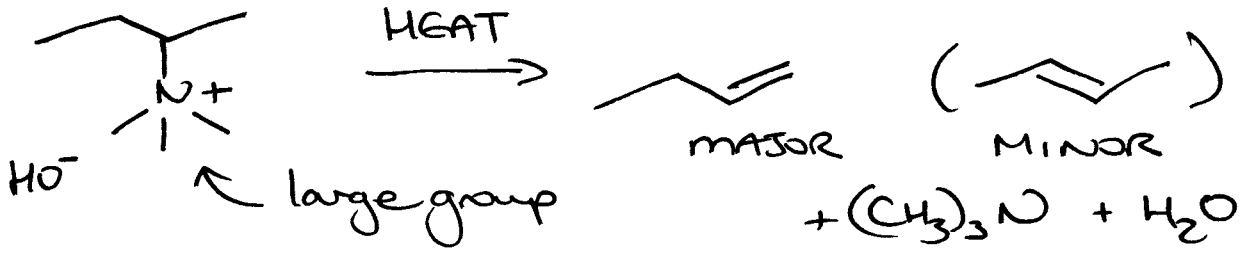




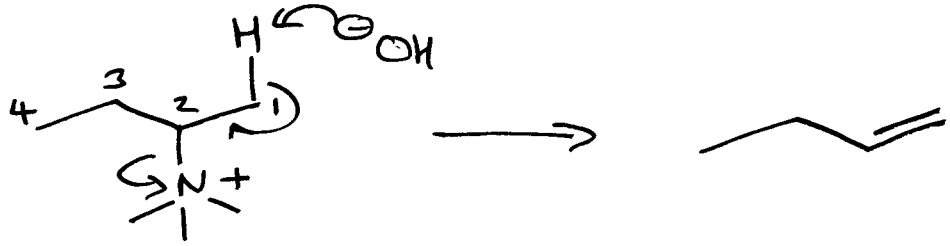
MAJOR

↖ most accesible β-H

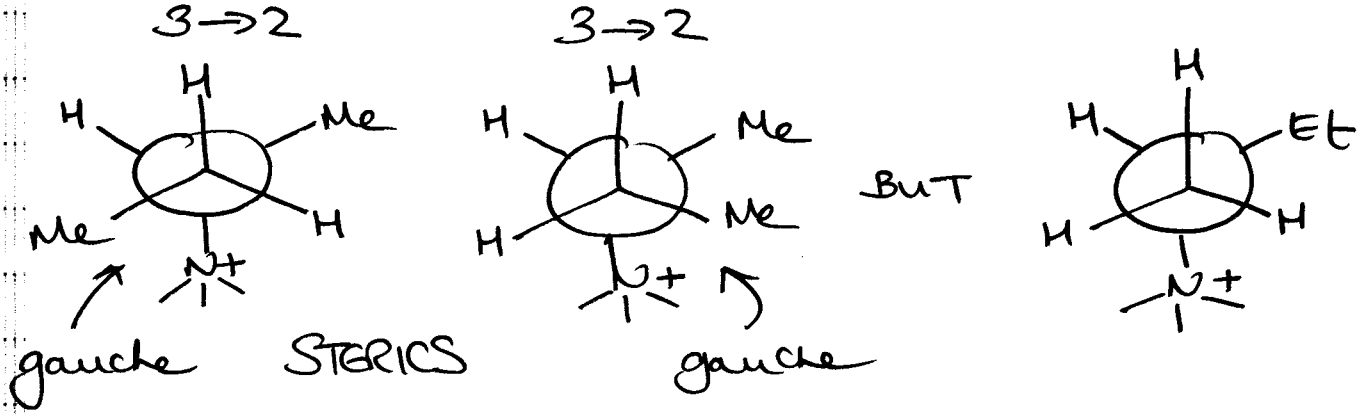
Common reaction w/ QUATERNARY AMMONIUM SALTS



Proceeds w/ ANTISTEREOSPECIFICITY

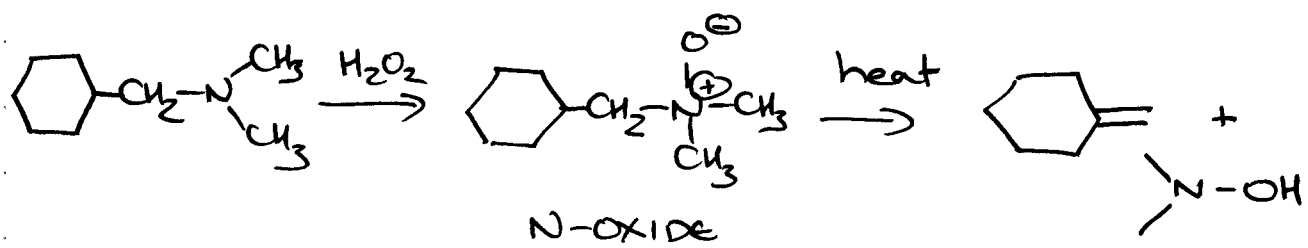


Consider NEWMAN projections

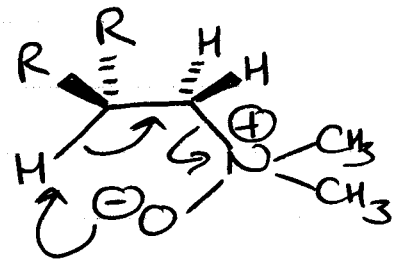


... also electronic effects

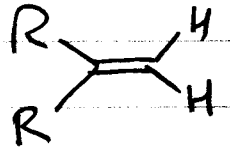
(3) SYN ELIMINATION (cope elimination)



mechanism

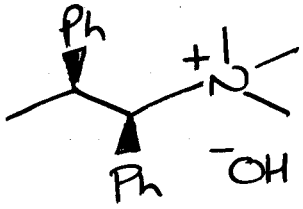


concerted rxn →

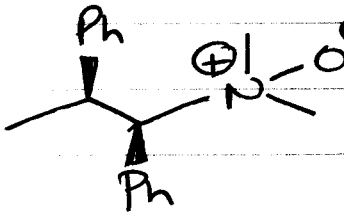


SYN

FIGURE out the PRODUCTS of these reactions

(i) 

heat → ?

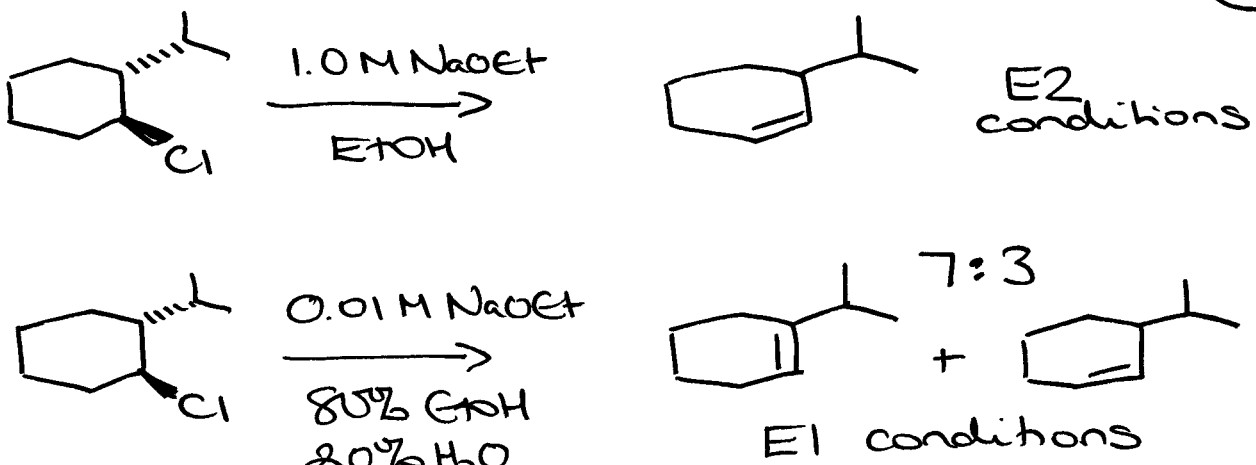
(ii) 

heat → ?

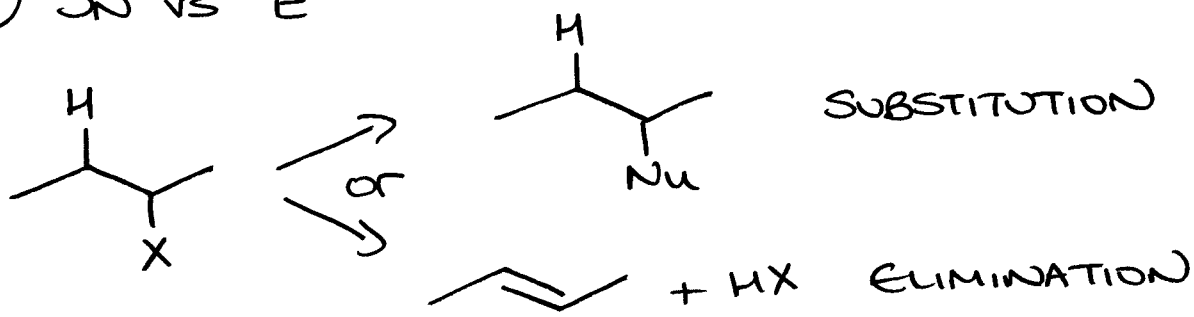
④ E1 vs E2

alkyl halide	E1	E2
methyl	– ELIMINATION IMPOSSIBLE –	
1° (RCH_2X)	DOES NOT HAPPEN ($1°C^+$)	FAVORED ELIM MODE
2° (R_2CHX)	H_2O/ROH (WEAK BASES) ALLYLIC/BENZYLIC	STRONG BASES ($RO^\ominus$/$OH^\ominus$)
3° (R_3CX)	WEAK BASES	STRONG BASES

– can also depend on reaction conditions

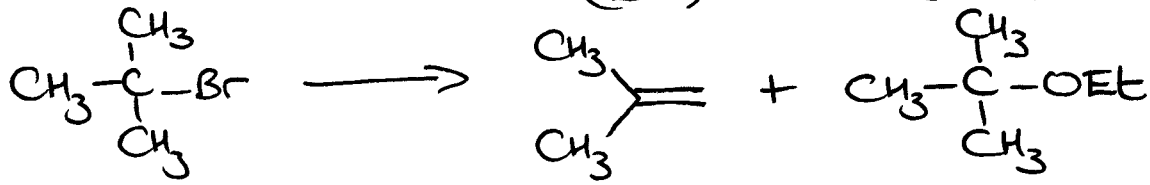


(5) S_N vs E



(i) S_N1 vs E1

e.g.



	(E1)	(S_N1)
EtOH	20%	80%

affinity for proton vs carbon ⇒ stronger base

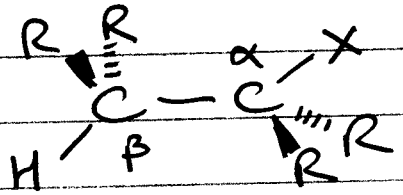
EtOH/EtONa	90%*	10%

↳ E2 mechanism

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

(ii) SN2 vs E2

- structure of substrate

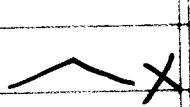
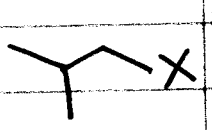
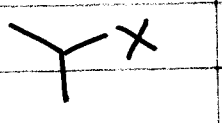


BRANCHING at α/β =>
SLOWS DOWN SN2 (Sterics)
SPEEDS UP E2 → more stable alkene

- Nucleophile

as nucleophilicity ↑ ratio SN2:E2 ↑
as basicity ↑ ratio E2:SN2 ↑

- SUMMARY

	Poor Nuc (H_2O, ROH)	Weakly basic Nuc (I^-, RS^-, RCO_2^-)	(UNHINDERED) Strongly basic Nuc (RO^-, HO^-)	(HINDERED) Strongly basic Nuc ($tBuO^-$)
CH_3X	NR	SN2	SN2	SN2
	NR	SN2	SN2	E2
	NR	SN2	E2	E2
	SN1/E1 (slow)	SN2	E2	E2
	SN1/E1	SN1/E1	E2	E2

- 2° SUBSTRATES

attacking Nuc → pka conjugate acid ≥ 11 ELIMINATION

attacking Nuc → pka conjugate acid < 11 SUBSTITUTION

Also Higher temp favors ELIMINATION

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

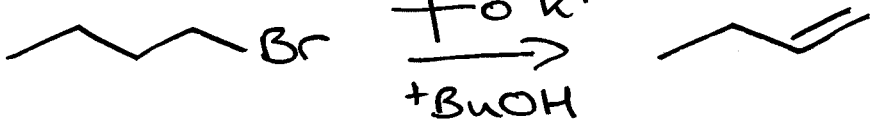
SN 2 molecules → 2 molecules

E 2 " → 3 " $+\Delta S$

- EXAMPLES

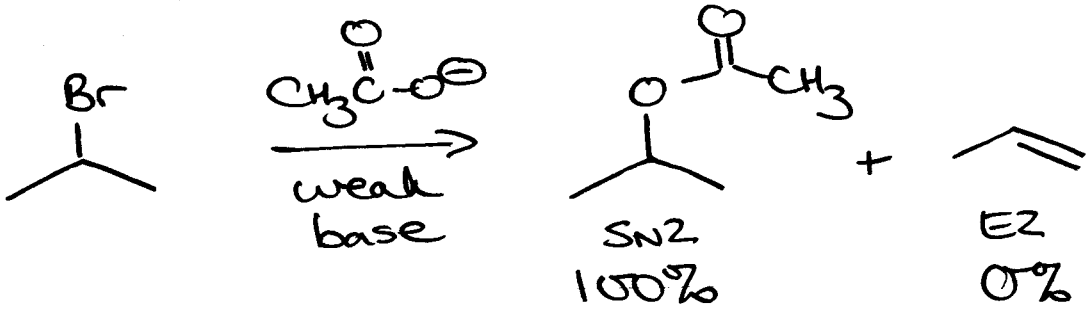
1°  SN2

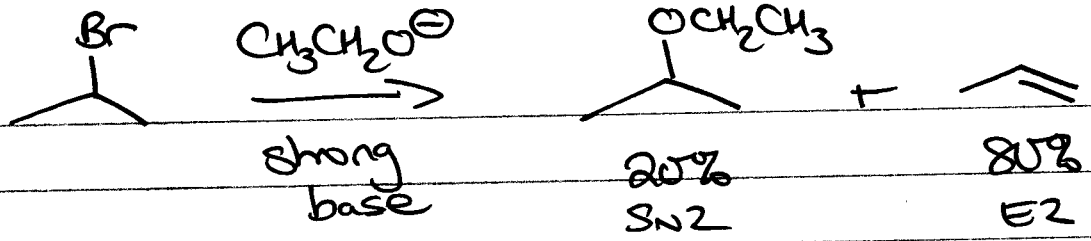
(CN⁻, RS⁻, N_3^-, NH_3, Br^-, I^-) good nucleophiles



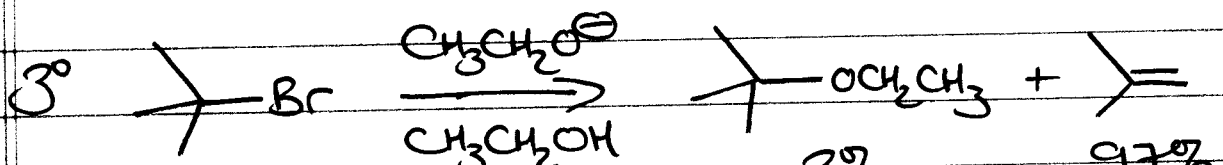
E2

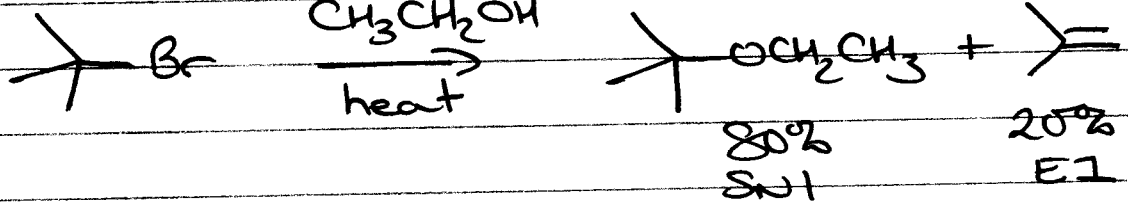
strong hindered bases

2° 

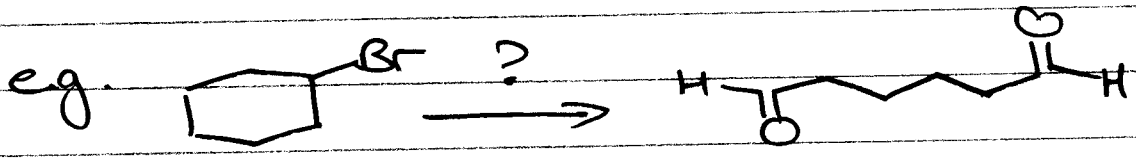


2° BENZYLIC/ALLYLIC SUBSTRATES can do SN1/E1 with weakly basic NuX in polar protic solvents



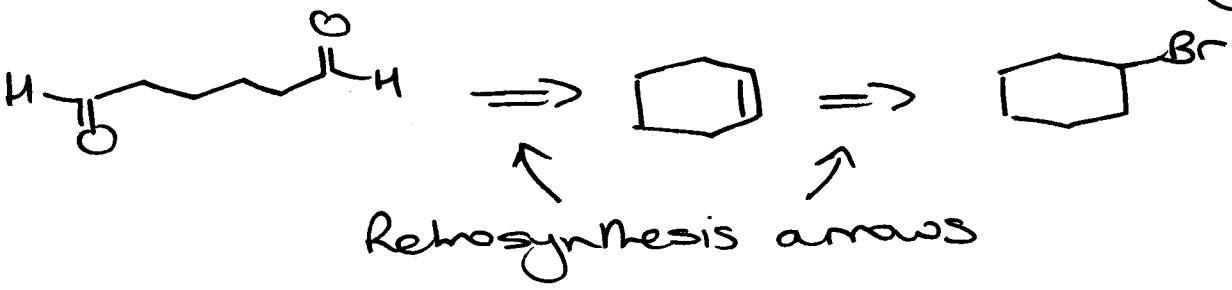


(6) SYNTHESIS
- sequences of reactions



usually told if you need more than ONE STEP (here you do)

RETROSYNTHESIS → work backwards



So, forward synthesis: