CHEM 242 – Lecture 8 *24/01/2014*

Overheads: - Outline

Recap Monday: Predicting S_N2 *vs* S_N1 Reactions

1° R-Br
2° R-Br
3° R-Br

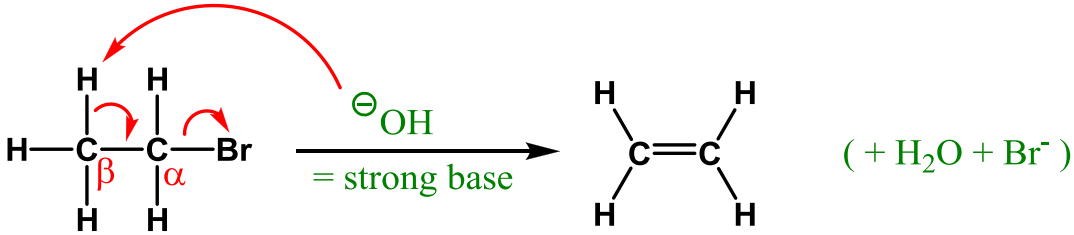
S_N2 only

both reactions possible → S_N2: strong Nu^-, aprotic solvent; S_N1: weak Nu^-, protic solvent

S_N1 only

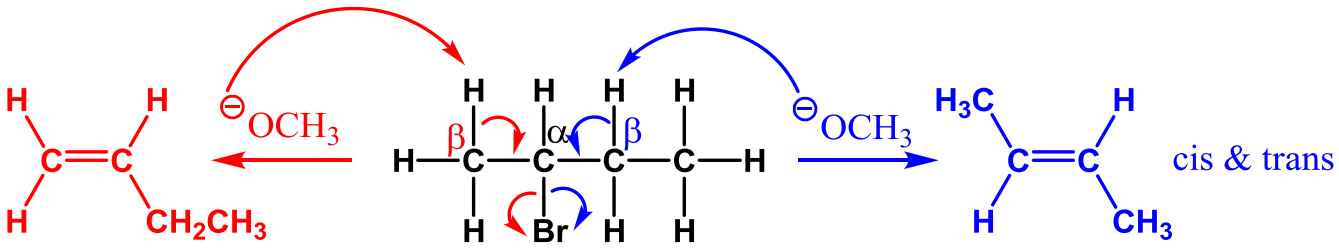
Elimination Reactions

Nu^- ⇨ also a base



⇨ Base removes H^+ from β-C as LG leaves (concerted ⇨ one step)
Rate = k[R-Br][OH^-] = bimolecular ∴ E2 reaction

What if there is more than one β-H?



20%

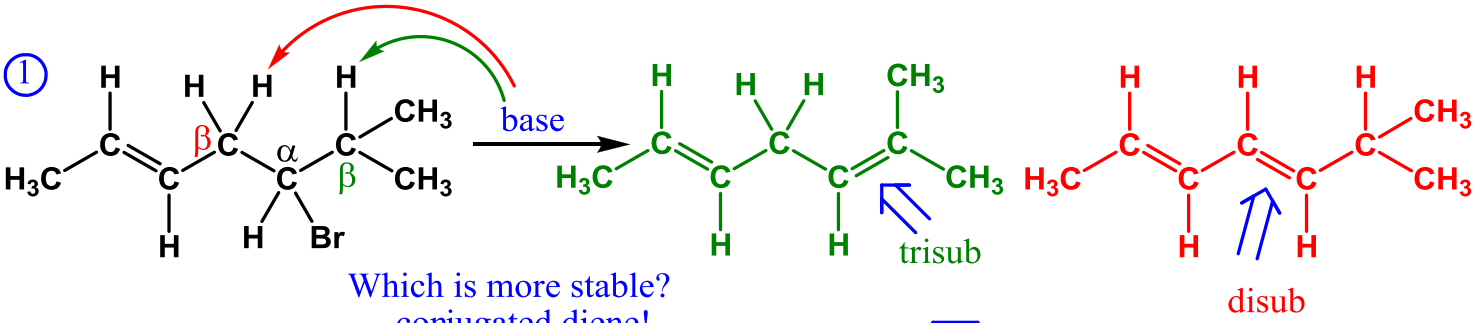
Which is major?
More stable?

80%

⇨ form most stable alkene = most substituted
⇨ E2 = regioselective

Zaitsev's Rule: Most substituted alkene is favored

Exceptions to Zaitsev's rule:

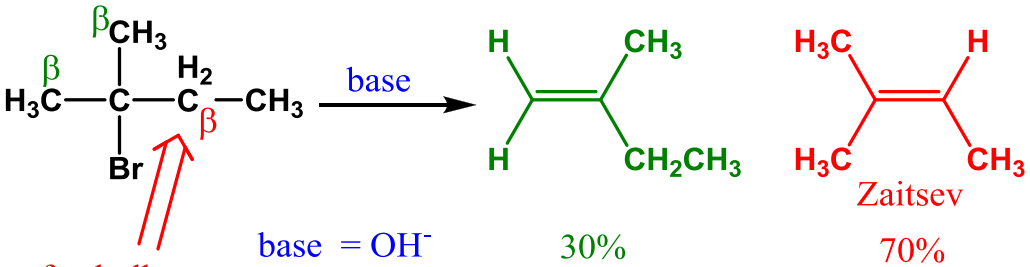
① 

Which is more stable?
- conjugated diene!

⇒ if "new" C=C can be conjugated to C=C or  more stable

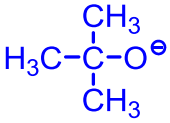
Zaitsev: most stable alkene formed (usually = most sub'd)

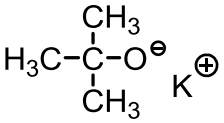
② If a very bulky base is used, steric hinderance leads to formation of less substituted alkene



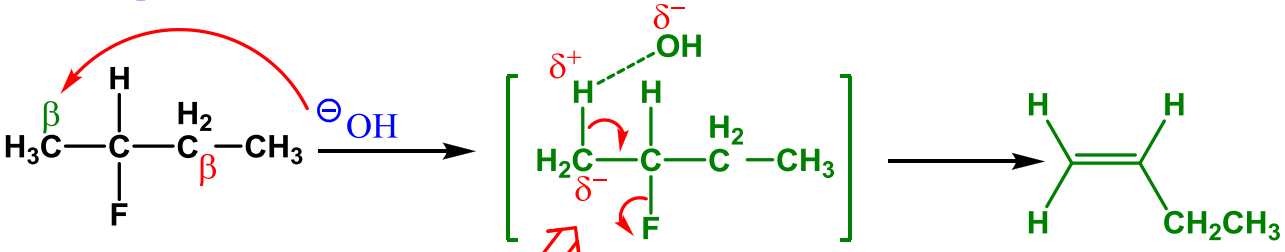
harder for bulky base to get here (steric hinderance)

base = OH^- 30% 70%

base =  72% 28%

 = potassium tert-butoxide = great bulky base = bad Nu-
best base for E2, but gives less sub. C=C

③ If there is a poor LG, base starts to remove H^+ before LG starts to leave:



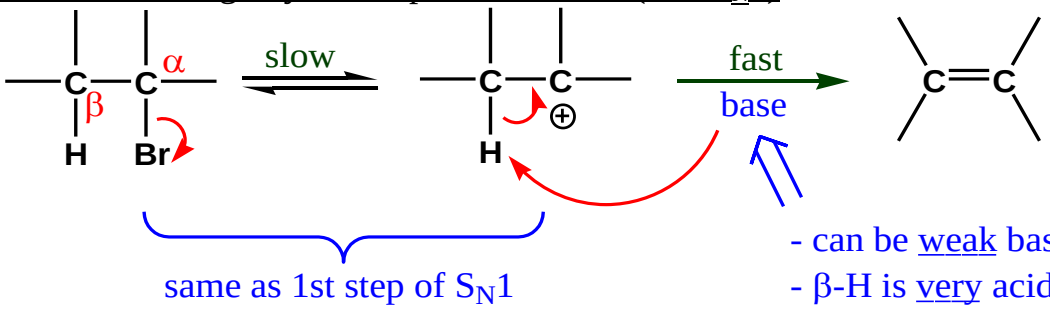
what would be most stable carbanion (C^-)?

$1° > 2° > 3°$ reverse of C^+ stability because R_3C- wants less e^-s.

∴ get less substituted alkene if poor LG

⇒ reverse of C^+ stability because R_3C- wants less e^-s.

Elimination can also go by a 2-step mechanism: (like S_N1)



same as 1st step of S_N1

- can be weak base
- β-H is very acidic since next to C^+

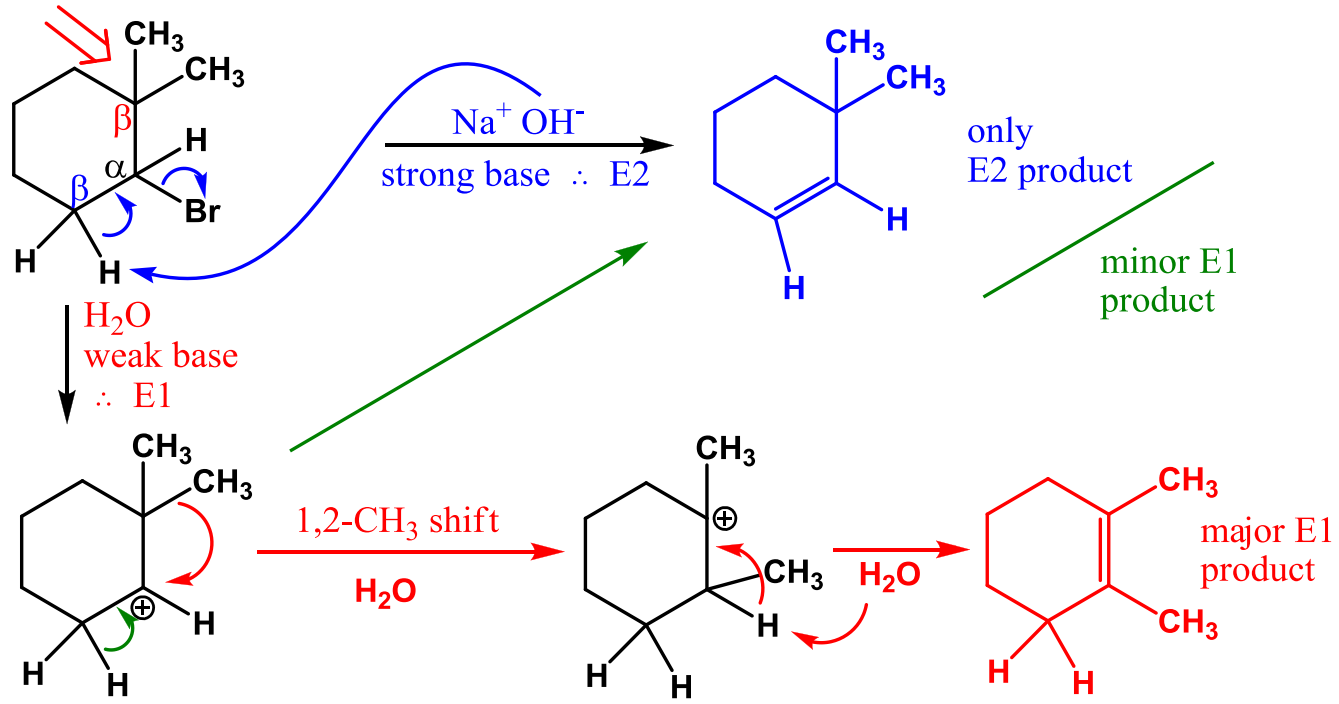
Rate = k[R-Br] ⇨ base not in RDStep, unimolecular ∴ E1

⇨ E1 favored if C+ stable: 3° R-Br > 2° >> ~~1~~° no E1 for 1°
Regiochemistry: Zaitsev still rules

which β-C will OH- attack?

no β-H here ∴ can't go

e.g.

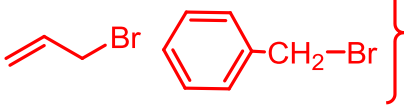


Competition between E1 & E2
- similar factors to S_N1/S_N2

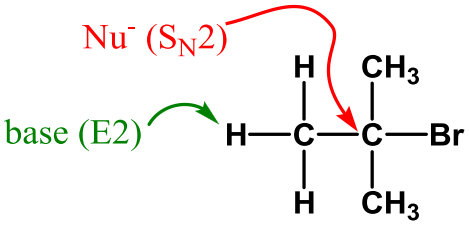
1) Degree of Substitution:

1° R-Br — E2 only (no C^+)

2° R-Br / 3° R-Br — E1 or E2



NOTE: Unlike S_N2, E2 <u>can</u> go with 3° R-Br since base goes to β-H, not to sterically hindered α-C ∴ ALL can do E2 (as long as there is a β-H!)



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