Course CH 343 Lecturer Sam Gellman

Day Friday 1:20 Date 11/11/11

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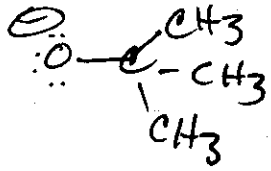
Recall: S_N2 vs E_2

1) Structure of alkyl halide (Bulk favors E_2)

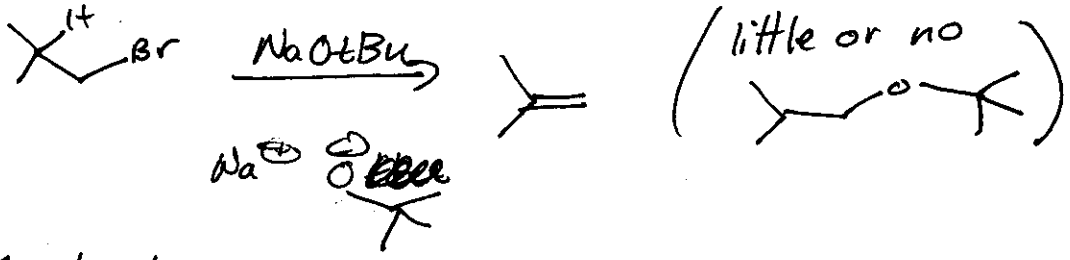
2) Structure of nucleophile/base



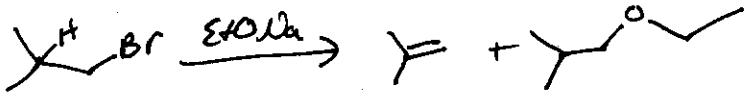
⇒ steric bulk favors E_2 vs S_N2

(a) Bulk favors E_2

Ex:



Contrast:



(b) If a nucleophile is a weak base, then S_N2 favored.

Ex: 

No elimination
(H–I is a strong acid)

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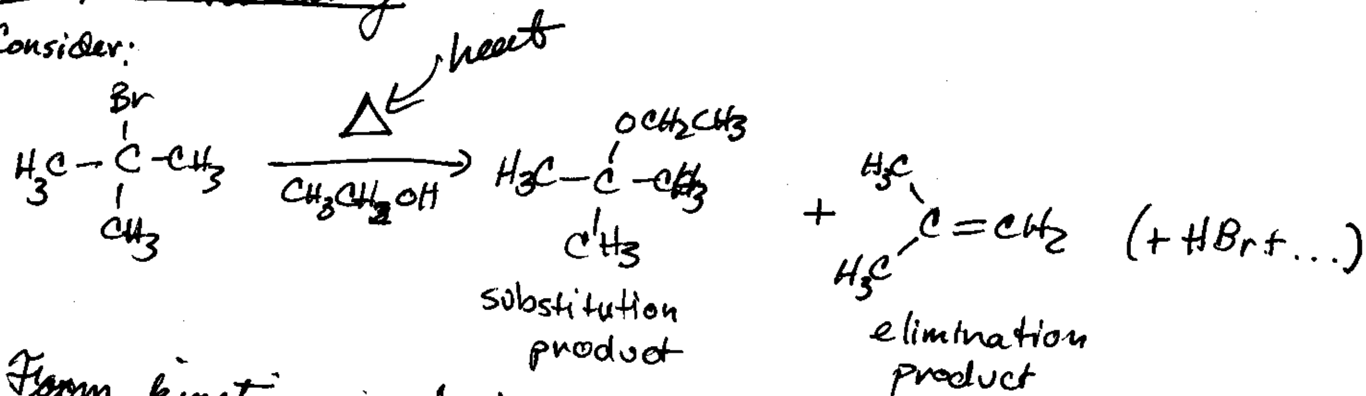
$S_N1/E1$ Pathway

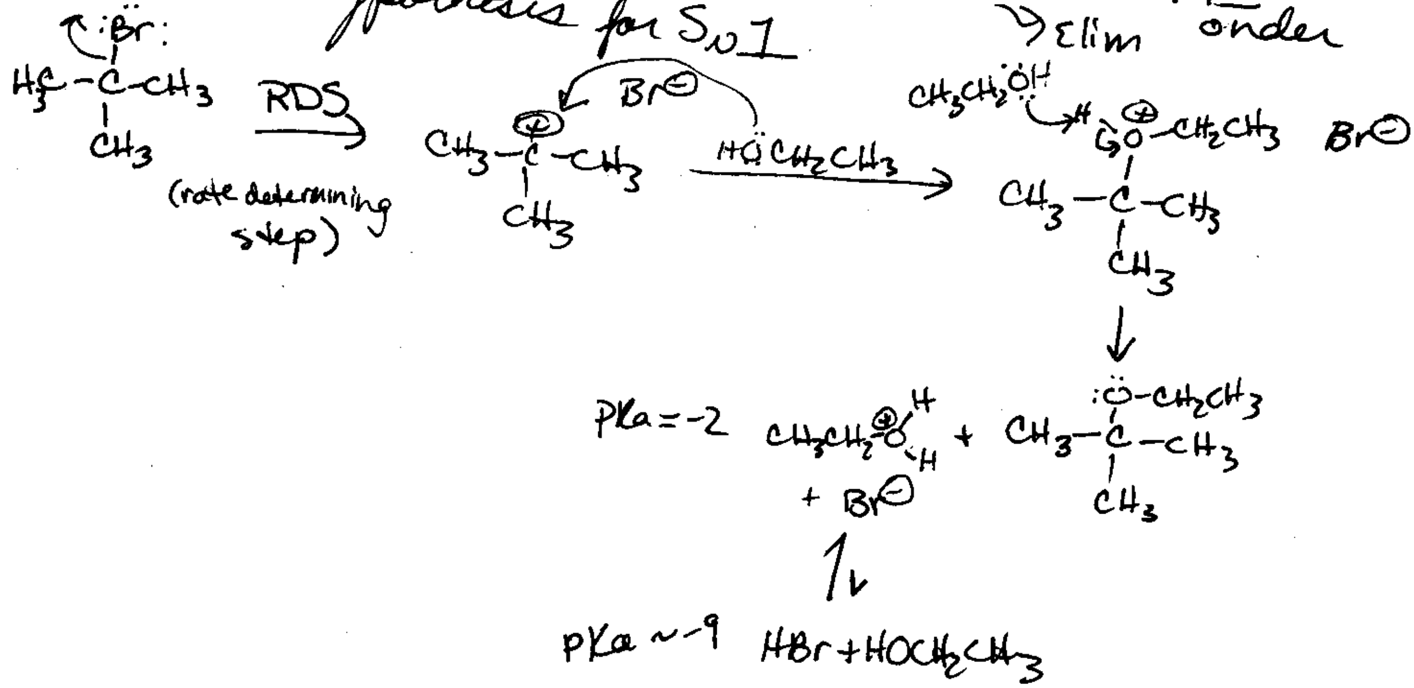
Consider:



From kinetics analysis: rate $= k[C(CH_3)_3CBr]$
- First order process

⇒ S_N1 → sub. nuc. 1st order
+ E1 → 1st order
→ Elim

Mechanistic hypothesis for S_N1



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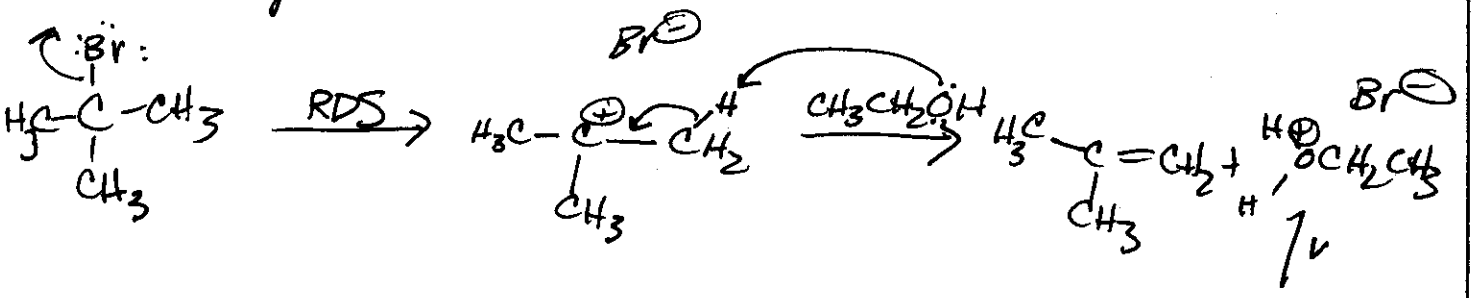
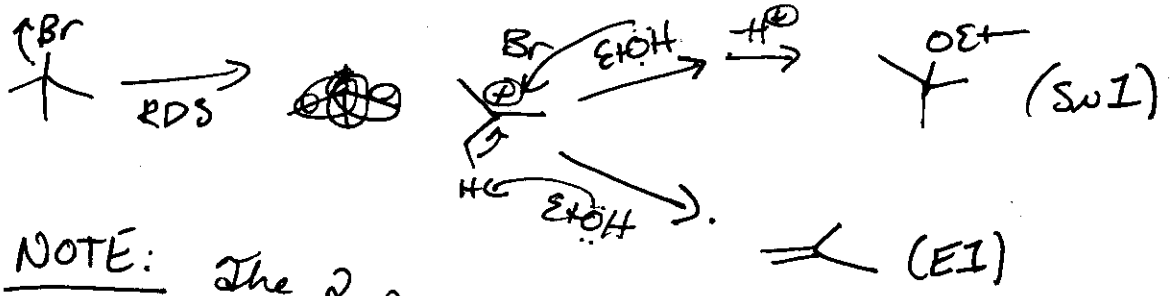
Mechanism for E1



Comprehensive View



NOTE: The 2 processes proceed via a common intermediate (carbocation). Product determining step happens after rate determining step

Apply previously learned concepts....

1) 3° alkyl halides are more reactive (SN1/E1) than 2°. 1° do not react in this way.

Rationale:

3° $C^{\oplus}$ more stable than 2° $C^{\oplus}$ (1° $C^{\oplus}$ usually not invoked..)

2) Better leaving group, greater SN1/E1 reactivity

R-I > R-Br > R-Cl (R-F does not react)

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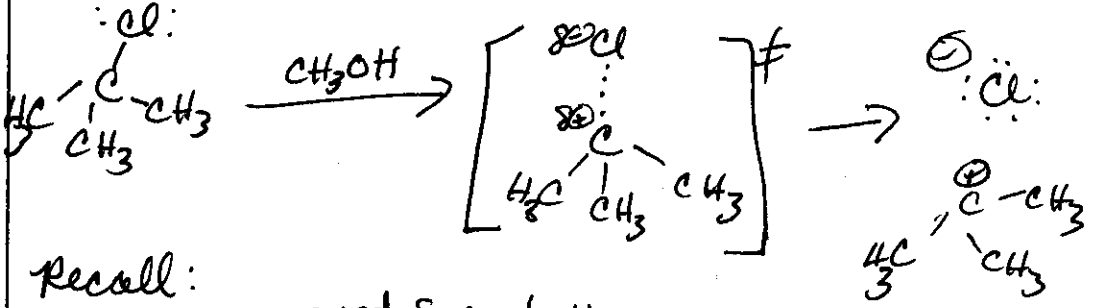
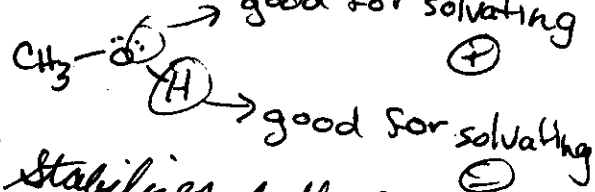
3. ~~Solvation~~ Solvation Effects: Polar protic solvents (eg. H_2O, CH_3OH, CH_3CH_2OH) strongly promote S_N1/E1 pathway

Focus in on RDS:

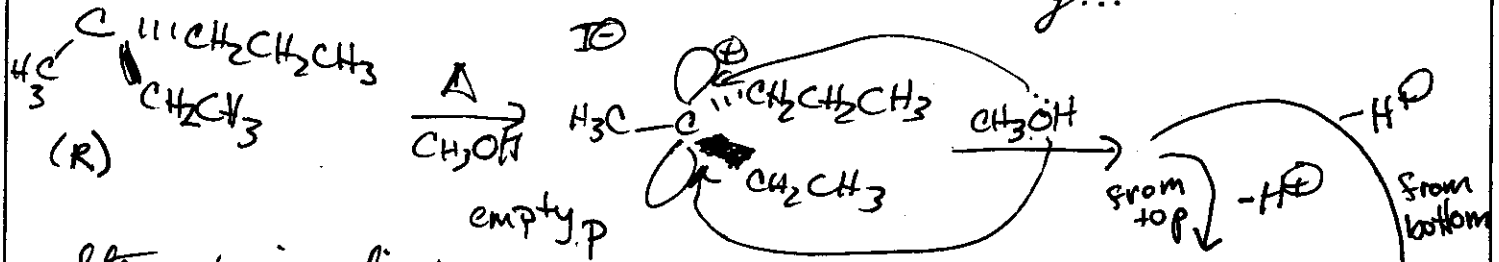


Recall:



∴ Stabilizes both δ⊕ and δ⊖ at key T.S. (ie RDS)

Stereochemistry is revealing mechanistically...



- Stereochemical information is lost in the carbocation

Note: carbocation is planar & thus achiral