Course Chem 343 11 AM Lecturer Gellman

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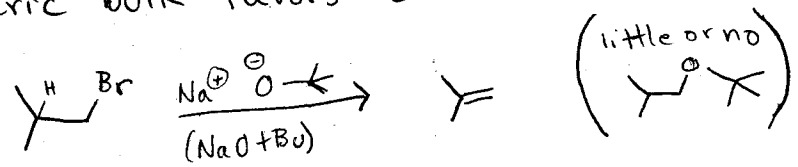
Recall: S_N2 vs E2 - in many cases, both pathways are possible (nucleophilic vs basic reactivity...)

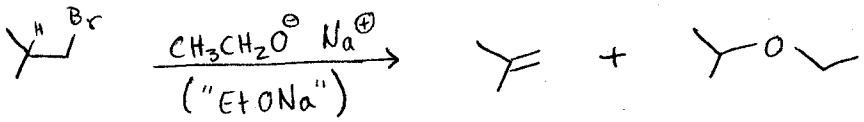
Factors:

1) Structure of alkyl halide - steric bulk favors E2 rel. to S_N2

2) Structure of base/nucleophile

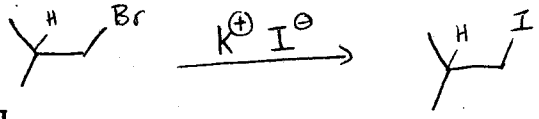
(a) Steric bulk favors E2 rel to S_N2





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

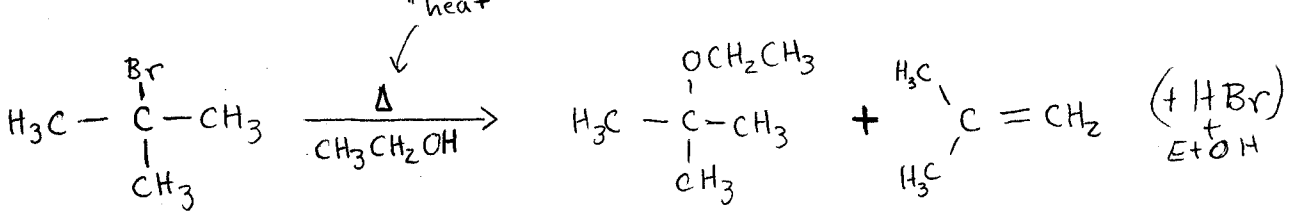
Ex:



S_N1 + E1

- often both active simultaneously

Ex:



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* both substitution and elimination

→ side note: $HBr + HOCH_2CH_3 \rightleftharpoons Br^{\ominus} + EtOH_2^{\oplus}$

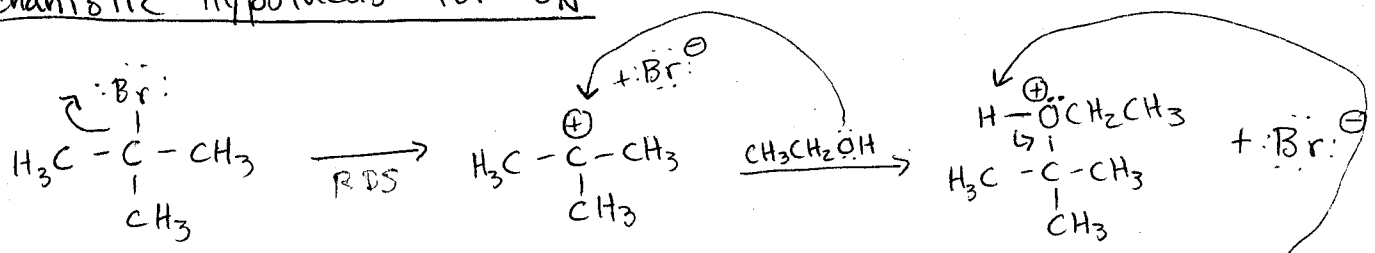
Rate law:

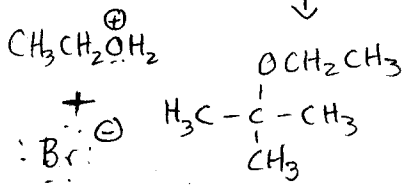
rate = $k[(CH_3)_3CBr]$

First-order processes! therefore mechanisms diff from S_N2 + ~~E2~~

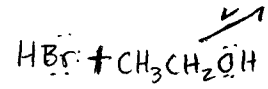
S_N1 ↖ 1st order (↗ sub, ↑ nuc) $\quad$ E1 ↖ 1st order (↗ elim)

Mechanistic Hypothesis for S_N1:





* Note: $CH_3CH_2\ddot{O}H$ stronger base than $:\ddot{B}r:^{\ominus}$ so $CH_3CH_2\ddot{O}H$ deprotonates



For this to satisfy the rate law, the Rate-Determining Step (RDS) and therefore slowest step must be the first step- formation of the carbocation

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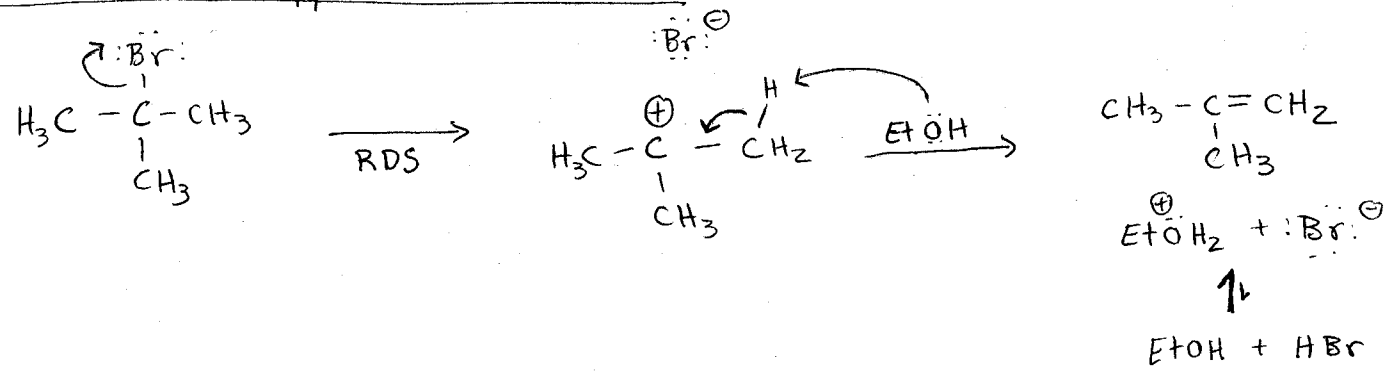
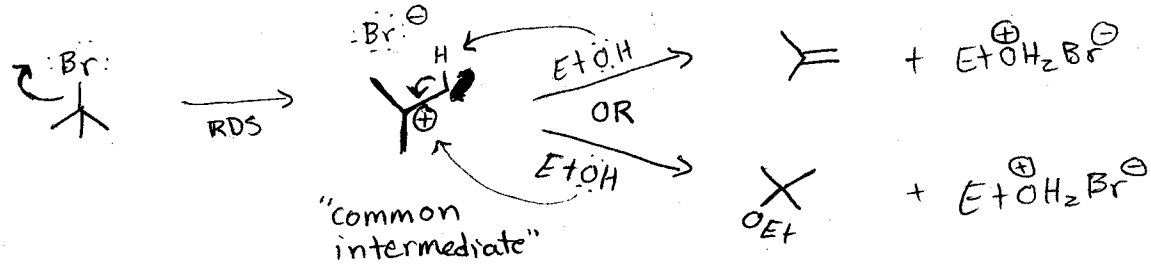
Mechanistic Hypothesis for E1



Comprehensive view - S_N1 & E1



Thus, this process involves a "common intermediate," the carbocation

Note: The product-determining step occurs <u>after</u> the RDS

S_N1 / E1 reactivity: influences of rxn parameters

1) Alkyl halide - 3° > 2° (NOT 1°) b/c of carbocation stability - follows trend for C^+ stability

2) Better leaving group ⇒ higher S_N1/E1 reactivity

Thus, R-I > R-Br > R-Cl

(no rxn for R-F)

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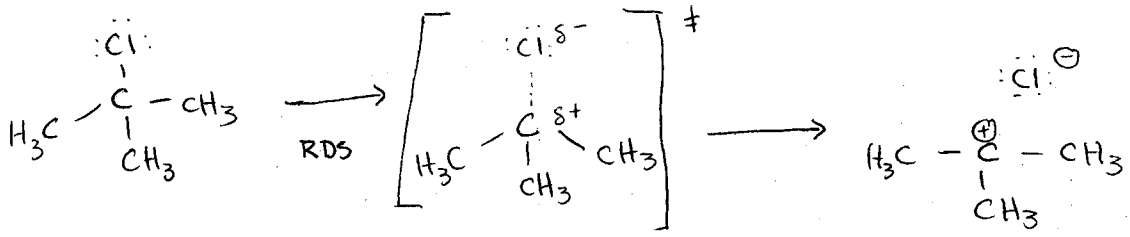
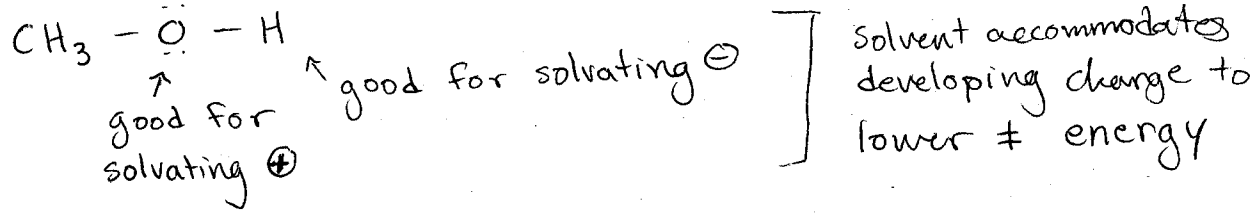
3) Solvents: For alkyl halides, $S_N1/E1$ pathway favored by polar protic solvents (H_2O, MeOH, EtOH, etc.)

Rationale: rate-determining TS has charge developing - both ⊕ and ⊖ - need to be solvated → stabilize

Consider:



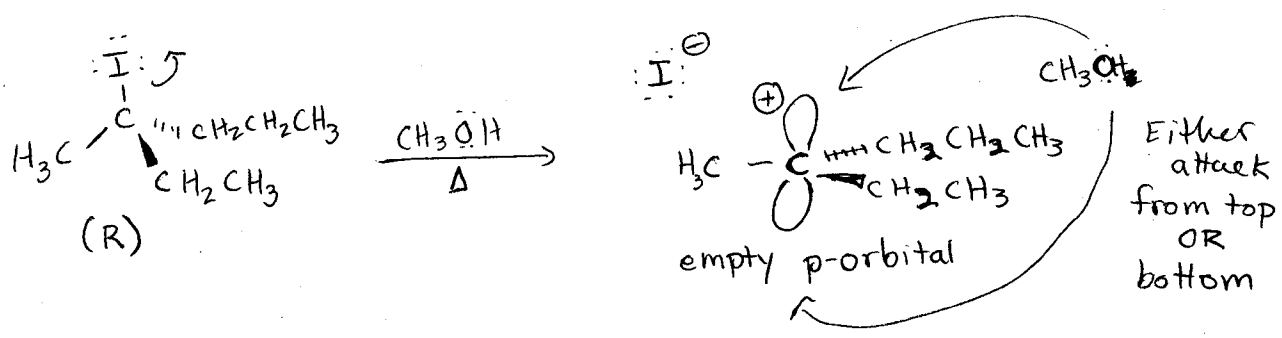


Stereochemistry in $S_N1/E1$ pathway...

New stereochemistry from C^+ intermediate

Key consideration - carbocation carbon is sp^2, i.e. planar

Ex:



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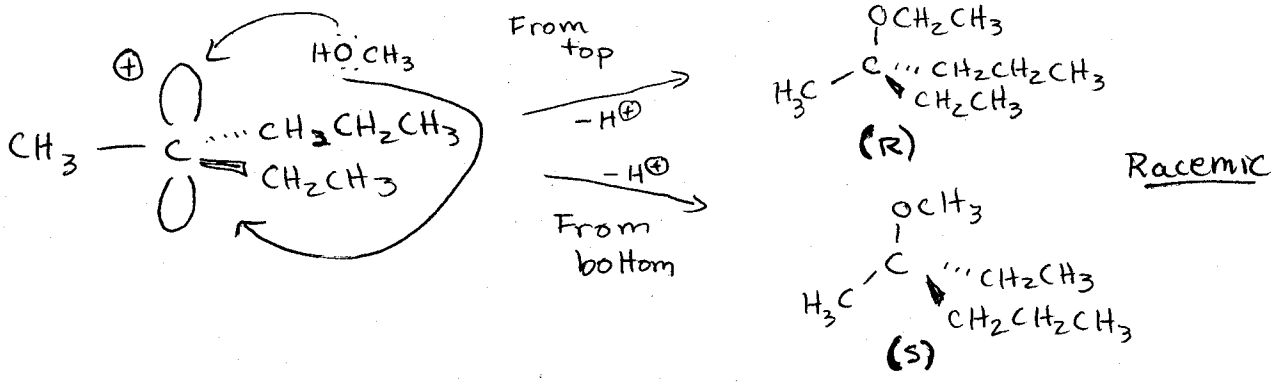
Carbocation is achiral- when achiral material gives chiral product, must be racemic.



+ elimination products