Course 3432 Lecturer Gellman

Day Friday Date 11/9/12

Notes Taken By Marlies Hoger Total # of Pages 3

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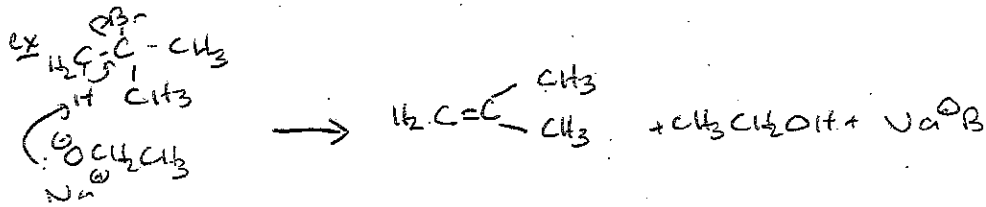
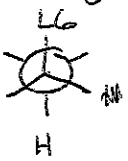
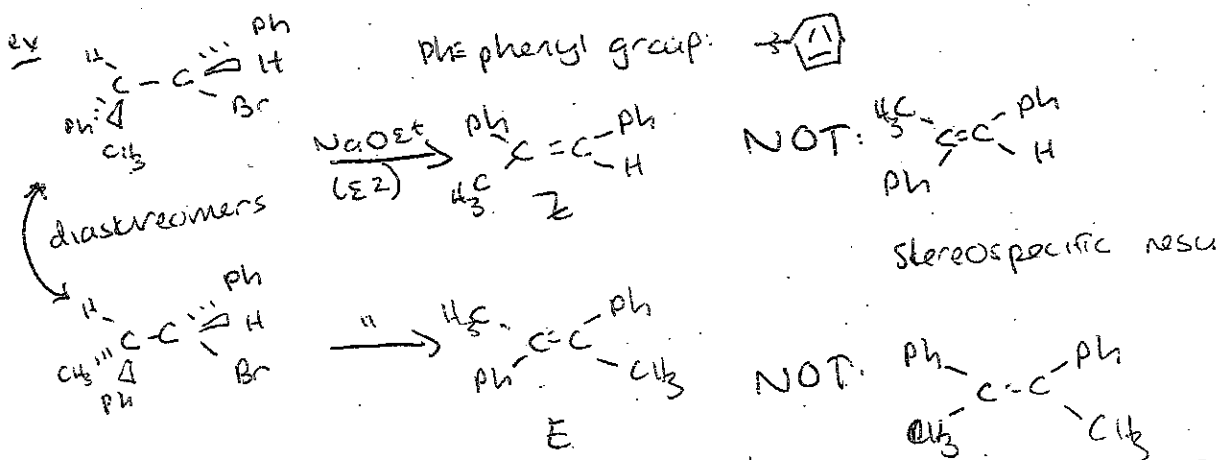
Recall: Elimination - E2 Mech.



stereochemical analysis provides mechanistic insight...
⇒ H & LG must be anti to one another

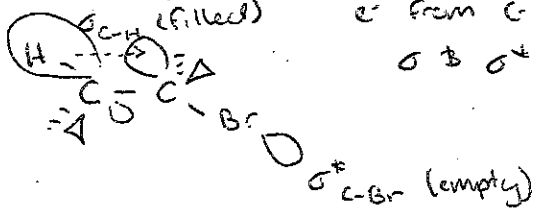




Stereospecific result

These results demonstrate requirement that H & Br be anti for E2

MO Rationale:



e⁻ from C-H bond flow into σ*, pushes off Br⊖
σ & σ* are only aligned if H & Br are anti

requires proper MO alignment, which requires H & Br to be anti

Regioselectivity?
→ generally not. If multiple alkene products are possible via E2, they are all usually observed

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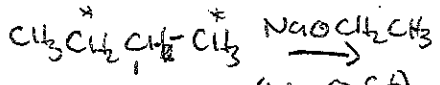
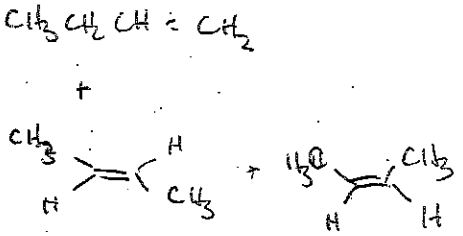




note: two potential sites for H loss

Note:
Zaitsev's Rule

⇒ don't be concerned with this rule
Dual view of synthetic reactions: mechanistic insight vs synthetic utility

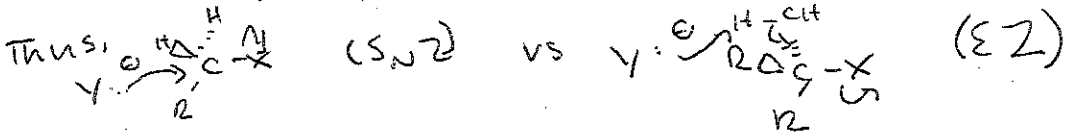
S_N2 vs E2

- potentially competing pathway
general challenge: species that can act as nucleophiles often can also act as Brosted bases (& vice versa)

∴ Recognize when
- S_N2 dominates
- E2 dominates
- both pathways significant (product mixture)

Key Considerations:

1) alkyl halide structure
- more alkyl substituents on C bearing LG ⇒ stronger pref. E2 rel. to S_N2
rationale: increased substitution makes it harder for nucleophile to access back side of electrophilic carbon, β Hs (for E2) always more accessible



1° - often favors S_N2 over E2

cis blocked. It isn't 3° - S_N2 impossible, so E2 likely

note: 2° alkyl halides often give product mixtures!

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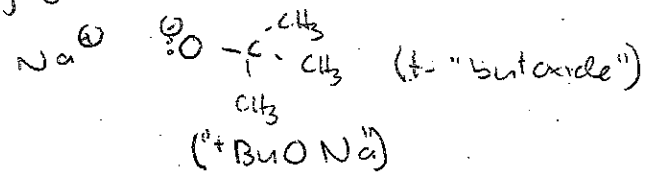
2) Structure of nucleophile/ base
- steric bulk favors E2 vs S_N2

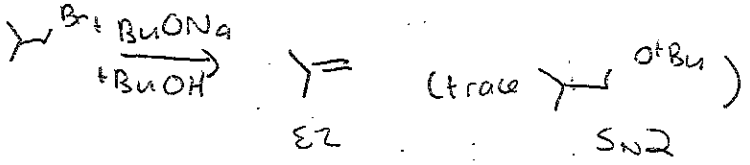
∴ common choice for a species that prefers "base" vs "nucleophile" ("bulky base")

conjugate base of t-butanol:



("^tBuONa")

eg



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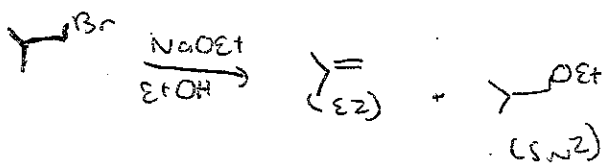

both products substantial

F avor S_N2 w/ species that are good nucleophiles but poor bases