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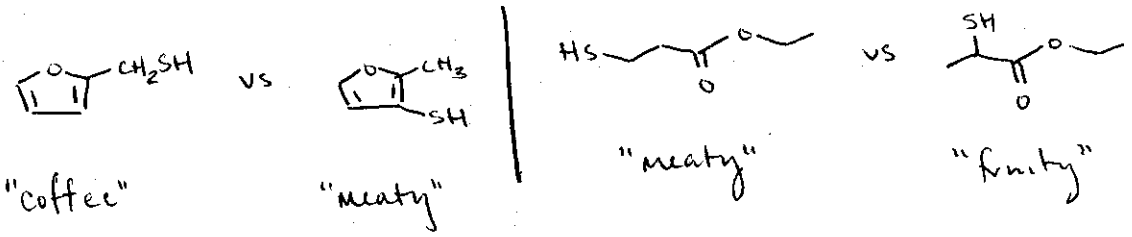
Aside: Fun fact - Aroma producing thiols in wine

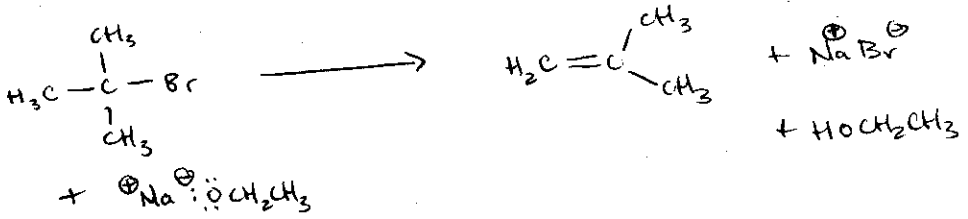


"coffee" "meaty" "meaty" "fruity"

perception: < 1 ng/L

Elimination

Recall:



Rate Law:

rate = k [NaOEt][$(CH_3)_3CBr$]

- * 2nd order overall
- * 1st order in base
- * 1st order in alkyl halide

E2 Reaction

Elimination

bimolecular rate law (2 molecules involved in rate-limiting transition state)

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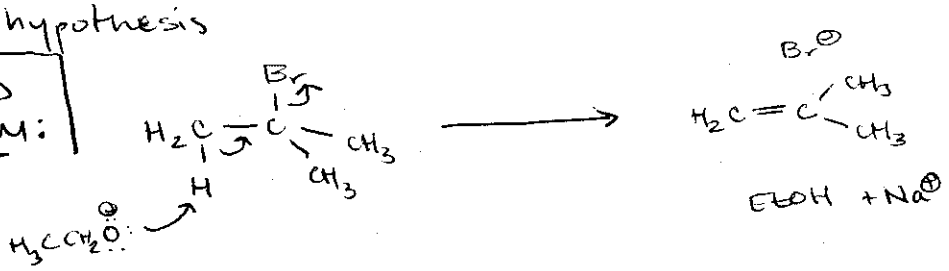
→ Rate Law is consistent with the standard mechanistic hypothesis

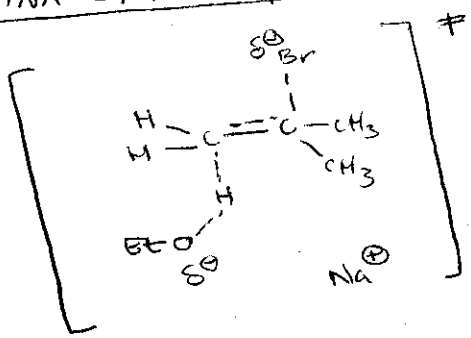
CONCERTED MECHANISM:



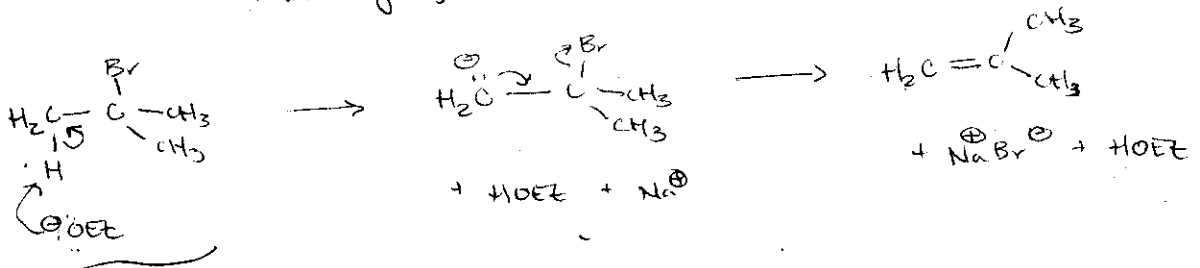
EtOH + $Na^{\oplus}$

Converted process
↳ Electrons flow at one time

Transition State Proposal:



* Alternative Mechanistic Hypothesis (has been disproven)
↳ unlikely by pka consideration



+ HOEt + $Na^{\oplus}$

+ $NaBr^{\ominus}$ + HOEt

this step is consistent with kinetic data

This mechanism has been disproven by stereochemical data

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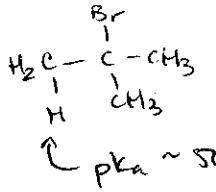
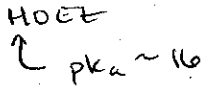
Alt. Mechanism is also unlikely based on pk_a values





* $\ominus$:$\ddot{O}$Et is unlikely to deprotonate alkyl halide to generate a carbanion intermediate

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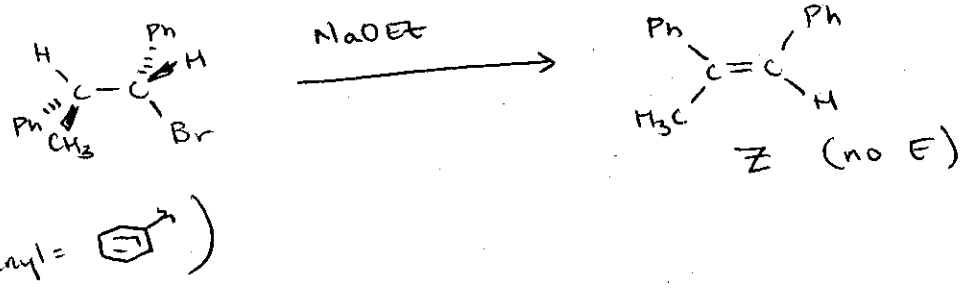
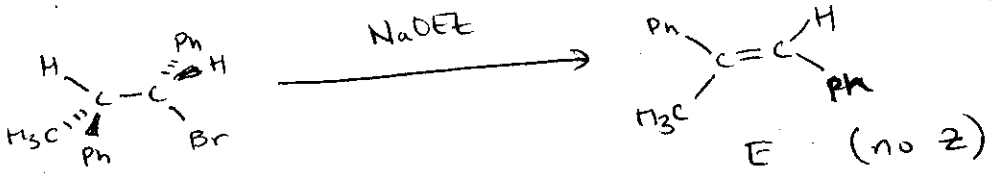
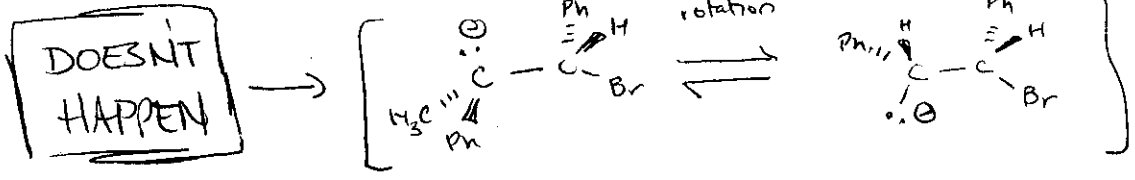
Stereochemical Correlations - observed between SM & product
*Consistent with concerted mechanism



(Ph = Phenyl =)



*Rules out 2-step mechanism via carbanion - would give both E & Z



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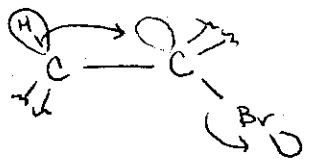
Stereochemical Correlation supports concerted Mechanism

* Based on Alignment of CH bond & C-Br σ^* orbital



* Reaction requires a particular conformation which gives specific isomer products for the example reaction

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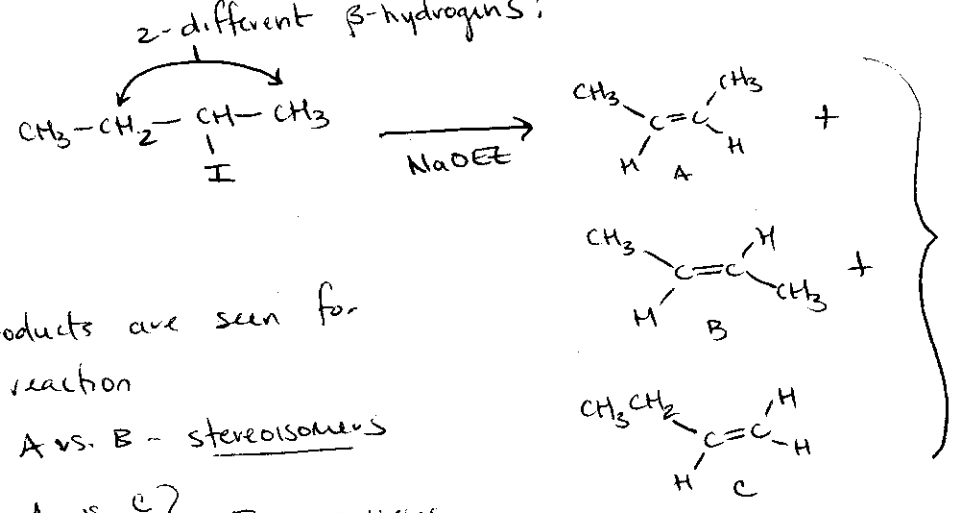
Regioselectivity vs. E2

* If multiple elimination products are possible, they are usually observed.

Example:



All products are seen for this reaction

A vs. B – stereoisomers

A vs. C
B vs. C } – Regioisomers

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Text: Zaitsev's Rule → Don't worry about it.

KNOW: Eliminations on compounds with multiple kinds of β hydrogens will give mixtures

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S_N2 vs. E2

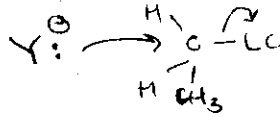
↳ POTENTIALLY COMPETING PROCESSES!

[Which cases will be selective?
Which cases will give MIXTURES?]

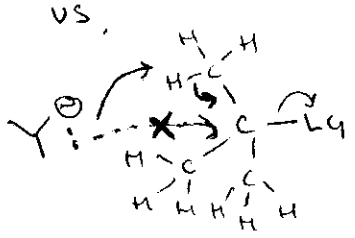
Key Considerations:

① Structure of the Alkyl Halide

↳ More alkyl groups on the carbon bearing the leaving group — Less-likely S_N2 / More-likely E2

1°  S_N2

vs.

3°  E2 (Substitution blocked)

2° → Ambivalent: Undergo both S_N2 & E_2

($Y:^{\ominus}$ = generic electron rich species (could be base or nucleophile))

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(2) Structure of Base/Nucleophile

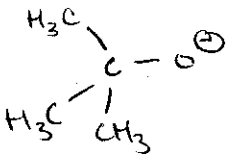
Steric bulk discourages S_N2

↳ favors E2

- Prototypical "Bulky Base"

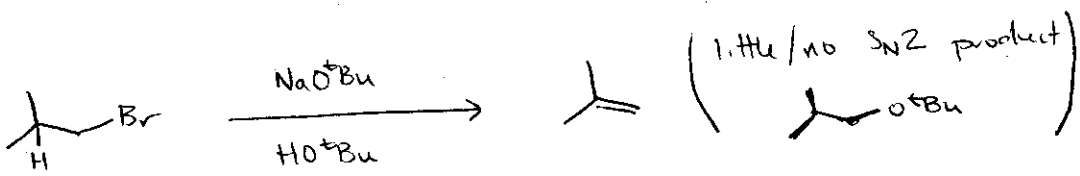
tert-butoxide

($^tBuO^\ominus$)

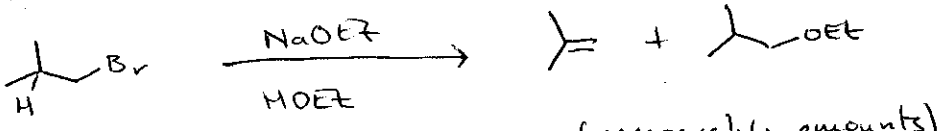


Used to favor E2 over S_N2

* Good base, bad nucleophile *



VS.



(comparable amounts)