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Course: Chem 345 — Lecturer: Gellman

Day: Friday — Date: 2-12

Notes Taken by: Liz — Page: 1 of 5 (Total Pages)

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Exam 1 locations — Students A-M = Bascom 165

N-Z = Here

Recall: EAS — effects of pre-existing substituents —

1) Reactivity (activating vs. deactivating)

2) New sub. position ("regiochemistry")

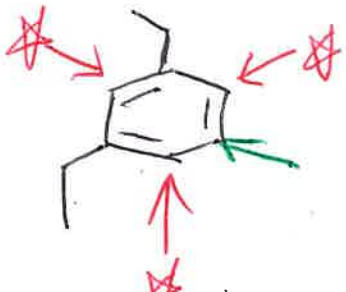
## MECHANISM

Multiple substituents...? (Directing effects?)

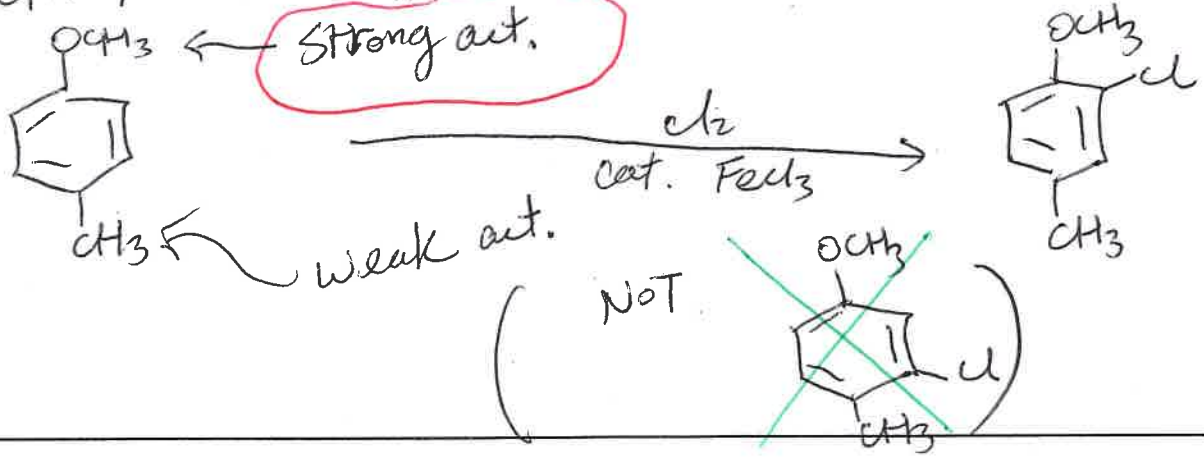
→ 2 substituents

(i) substituents direct in parallel

Ex:



(ii) substituents have different directing effect — strongest activator "wins"



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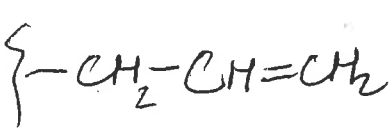
Read § 16.6 on hydrogenation of aromatic rings.

Chap 17

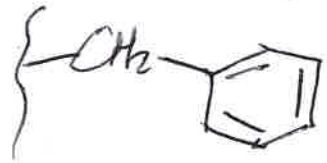
Rec. Problems: 1-12, 15-16, 22, 23, 26-35, 37, 44-49, 53-59

## Benzylic & Allylic Reactivity

Recall: Terms



"allyl group" &

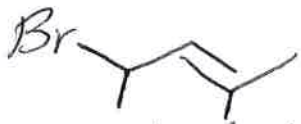


"benzyl group"

Allylic is a general term – a type of location within a molecule

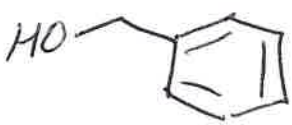
Ex:

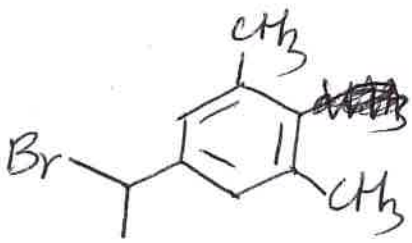
An "allylic hydroxyl"



An "allylic bromide"

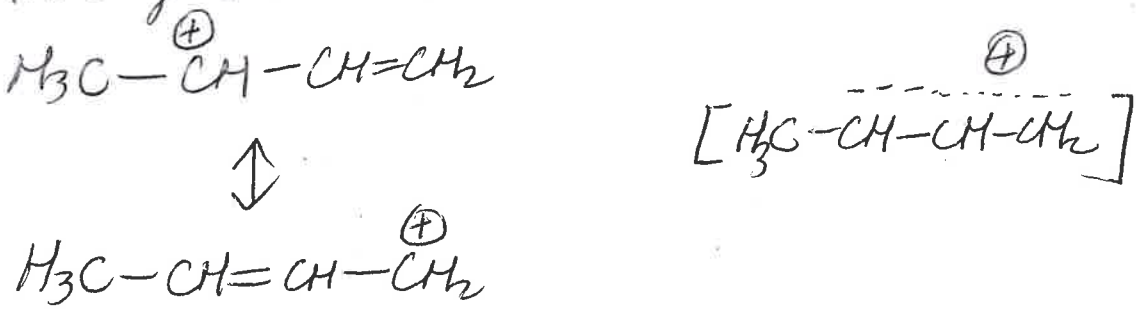
Benzylic ... (analogous)



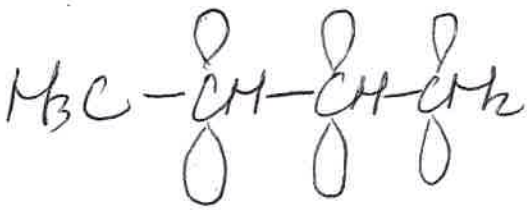


Origin of terminology - special reactivity @ allylic and benzylic sites. Arises from resonance stabilization of ⊕, ⊖, or • (radicals).

Ex: An allylic cation:



M.O. Consideration - π M.O.s



3 x C, 2p A.O.'s that form allylic π MOs

2e⁻s shared over the 3 Cs (⊕)

Review:

Alkene π bonding (§4.1 B)

Conj. diene π-bonding (§15.1 A)

∴ 3 allylic π MOs (from 3 p A.O.s)

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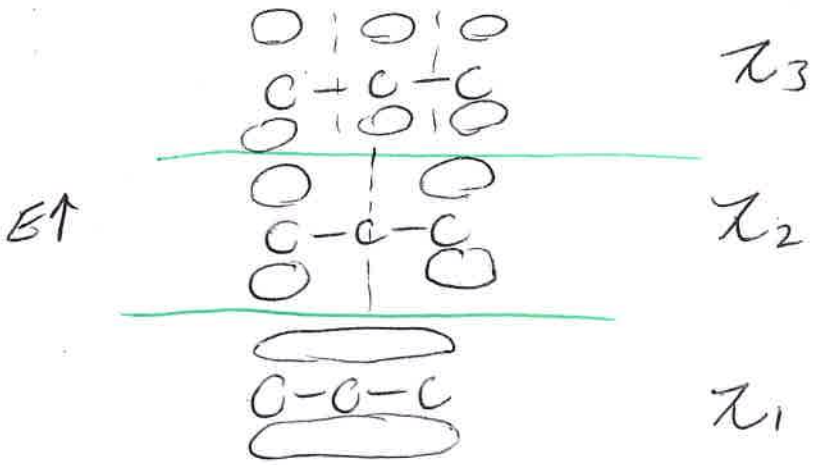


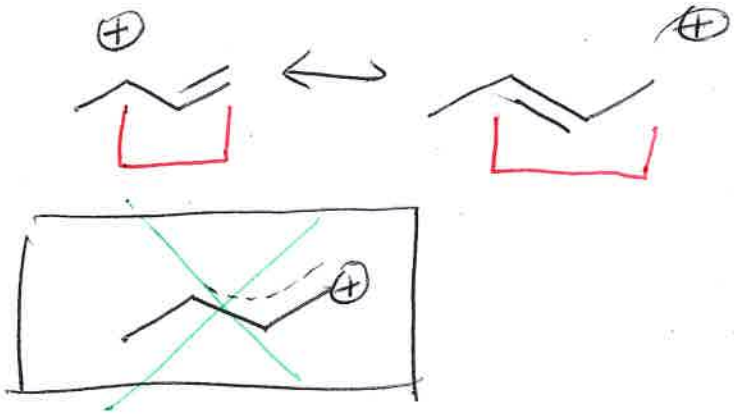

e⁻ occupancy (ground state)

— $\pi_3$

E↑ — $\pi_2$ ←

⇅ $\pi_1$

$\pi_2$ spatial distribution is reflected in the rs. structures.



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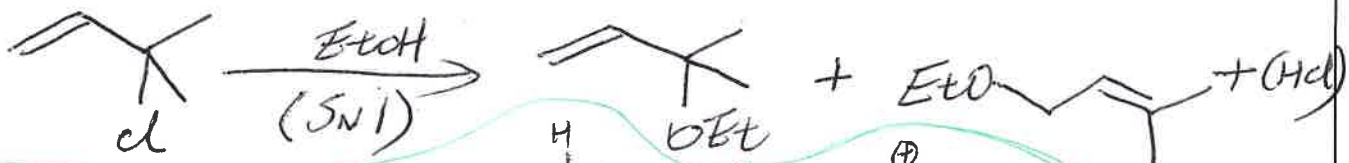
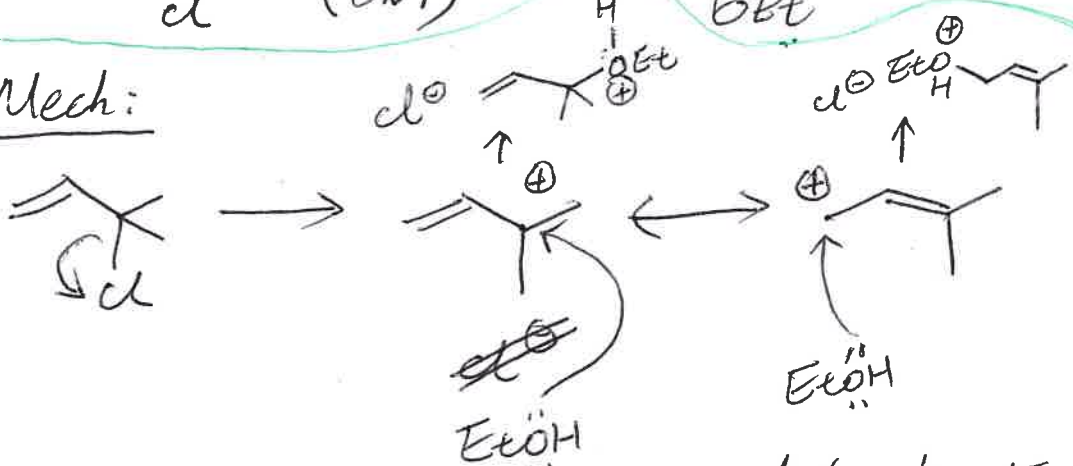
This analysis explains product mixture identity for rxns involving allylic cations as intermediates.

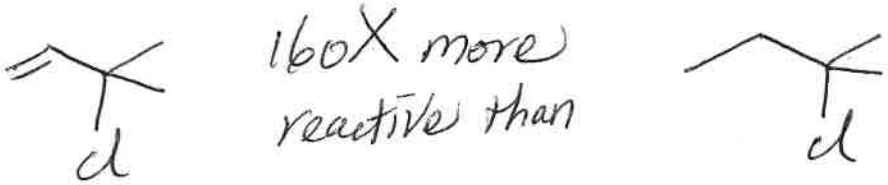



Mech:




Stabilization of ⊕ by res. delocalization leads to enhanced SN1 reactivity.

Ex: [Table 17.1]




Comparable reactivity effects observed for benzylic systems