

Course Chem 345Instructor GellmanDay MondayDate 17 Feb 2014Notes Taken By Kaz SkubiTotal # of Pages 5

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PLEASE COMPLETE NOTES IN INK AND DO NOT STAPLE.

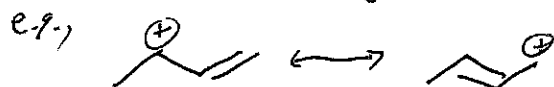
Exam 1 Locations:

Last name A-N — Biochemistry 1125

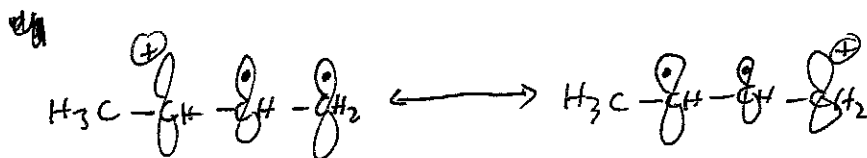
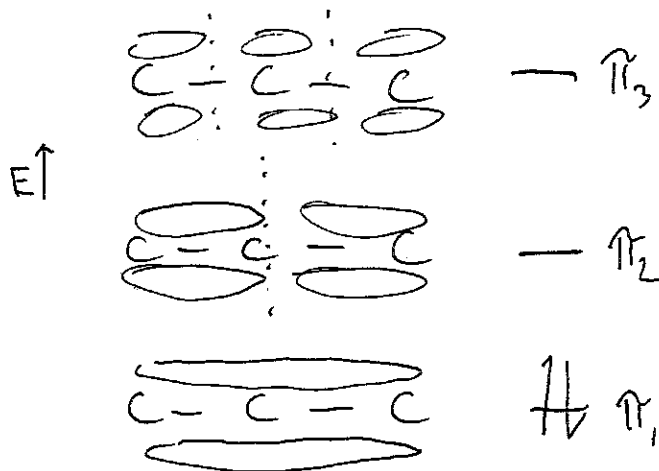
Last name O-Z — Here

Recall: Distinctive reactivity @ allylic & benzylic positions

Example - rxns involving carbocation intermediate

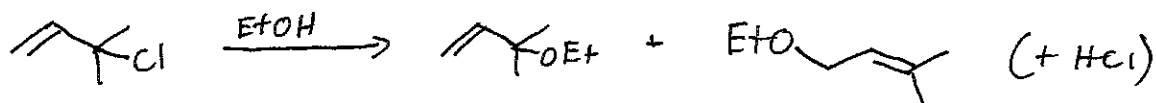


another depiction:

Molecular Orbitals (allylic cation)

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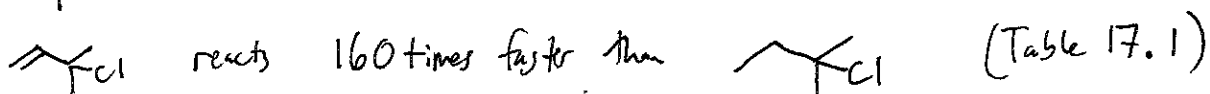
Representative Reaction (S_N1):



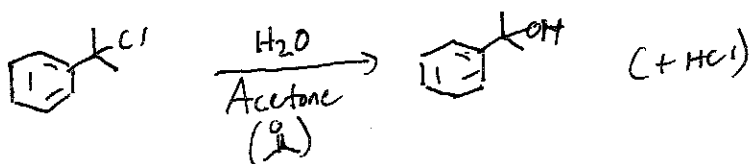
Via



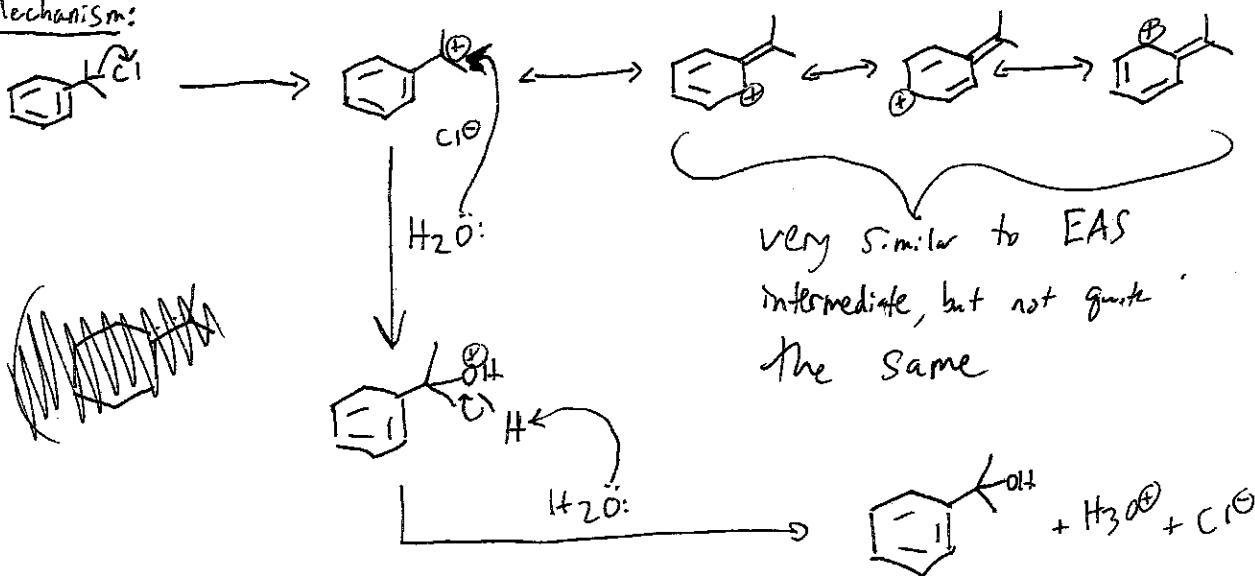
Compare:



Analogous reactivity boost from benzylic positioning of leaving group



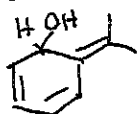
Mechanism:



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S_N1 reactivity @ benzylic position is greater than S_N1 at analogous but non-benzylic position.

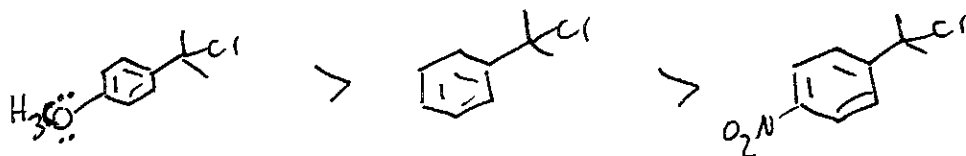
Why not other products?



, etc. are not aromatic

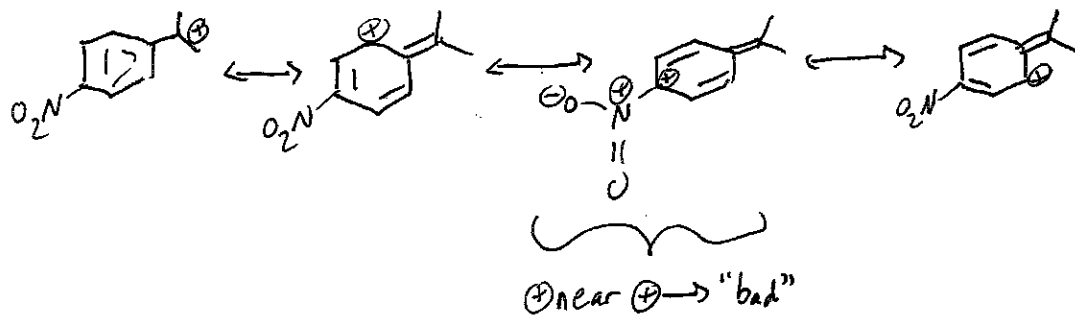
Substituents on ring influence benzylic S_N1 reactivity (cf. EAS effects)

Thus, reactivity order (S_N1):



Rationale: effect of substituents on cationic intermediate.

~~Not~~ e.g.,



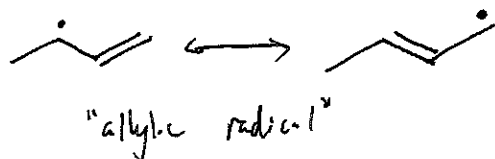
Thus, this cation is less stable than the analog with H instead of NO_2 .

\therefore will be more reactive than in an S_N1 reaction.

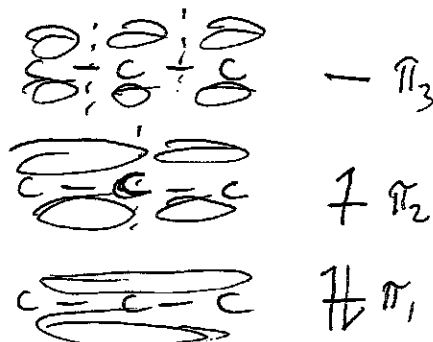
Recall Hammond Postulate. You fill in argument for

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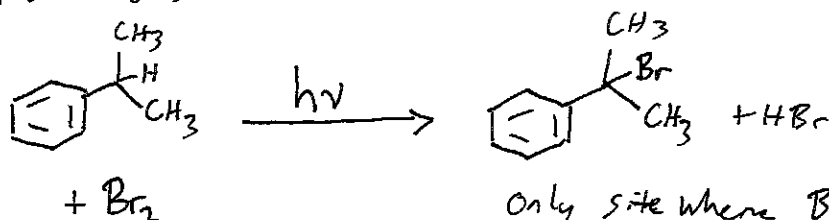
Also see special reactivity patterns for processes involving allylic or benzylic radicals.



MOs



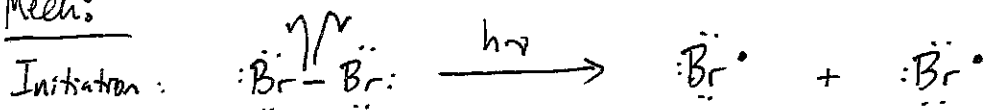
Reactivity manifestation of benzylic radical stabilization



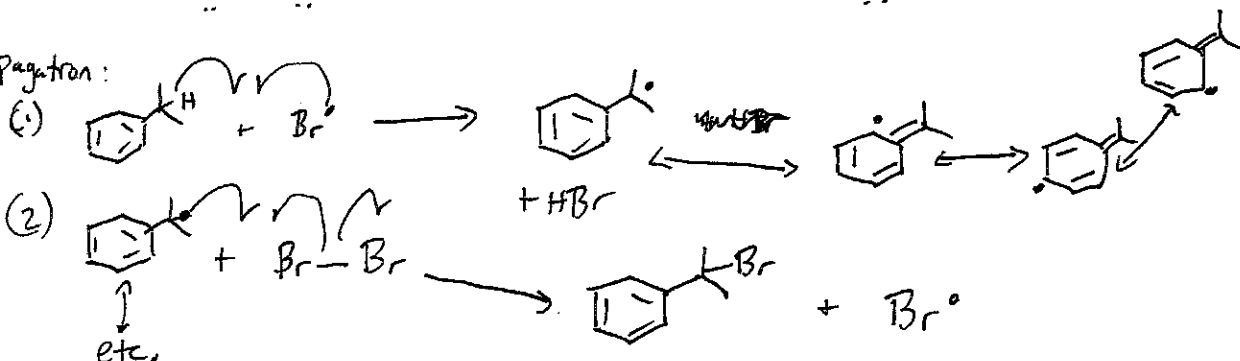
Extra electron beyond the cation

Only site where Br ends up. This is a highly selective bromination reaction.

Mech:



Propagation:



~~Termination~~

Step (1) is the "product-determining step." This is where we "select" which C-H bond is going to break.

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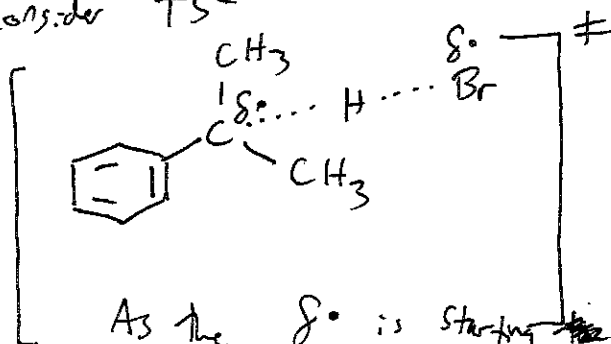
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Why the selectivity for benzylic C-H (~~vs.~~ ^{vs.} other C-H)

Consider TS^\ddagger



As the δ^\bullet is starting ~~to~~ to build on the carbon, there is a benefit from benzylic delocalization. That makes the benzylic C-H bond the weakest (and most reactive) C-H bond in the molecule

Allylic Analogy — Similar "benefit" for allylic C-H, but we have to worry about competing reaction of Br_2 + alkene

