

Do Not Use Pencil

Do Not Staple, Please!

Course Chem 345.

Lecturer Gellman

Day Monday

Date 2-15-16

Notes Taken by Zu Liu

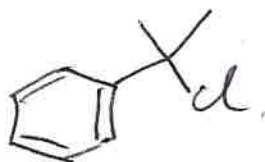
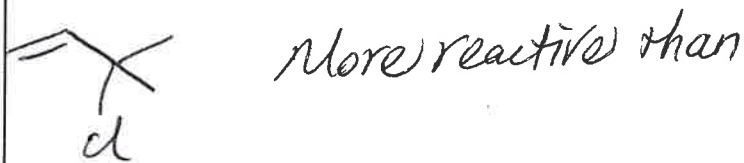
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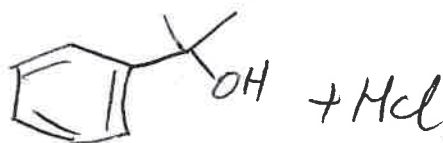
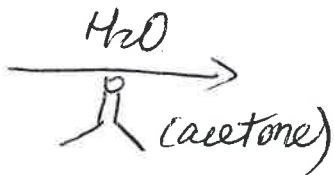
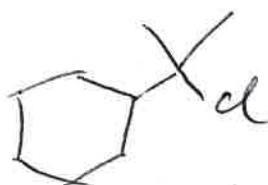
Exam 1 on Wednesday (165 Bascom & Here)  
~~Office hour after class today.~~

Review session @ 5 PM, B371.

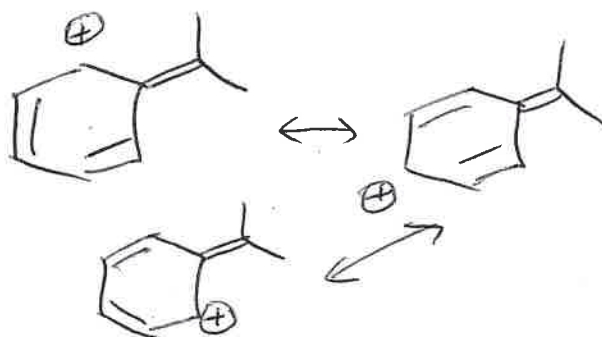
Recall: Allylic & benzylic halides. highly reactive  
via  $S_N1$ ; stabilization of carbocation implies  
stabilization of preceding TS.



''



Mech



next  
page

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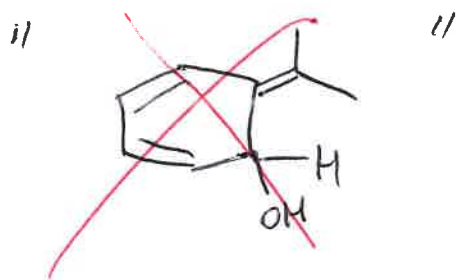
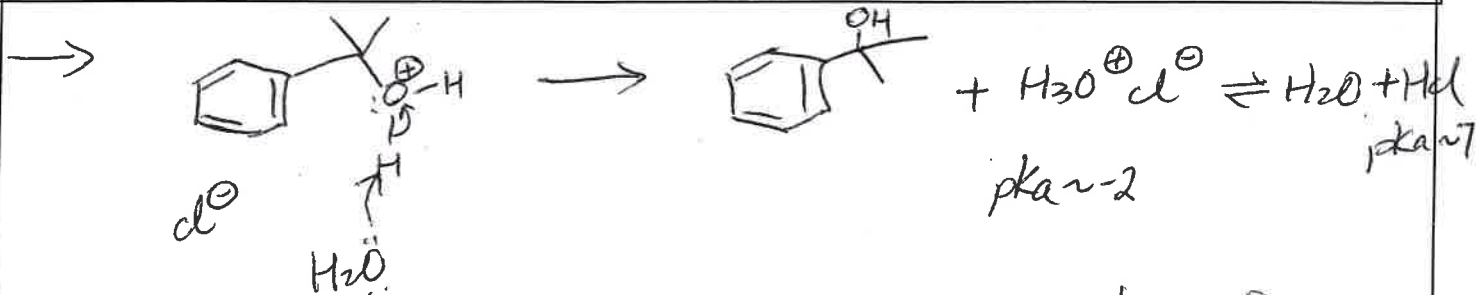
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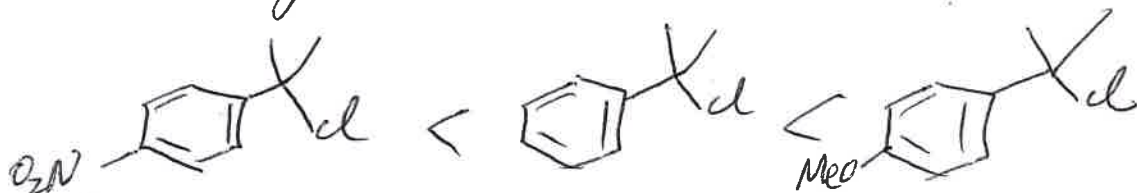
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We can extrapolate from EAS "wisdom" to understand (or predict) effects aromatic ring substituents on benzylic halide S<sub>N</sub>1 rxns.

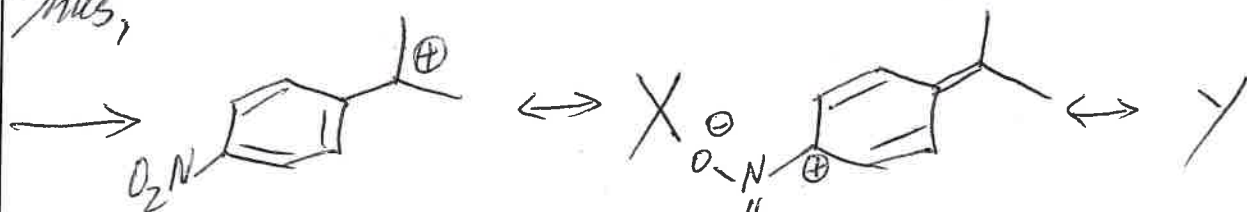
E.g., reactivity order



Rationale:

- Impact of substituent on carbocation stability
- Hammond postulate (pp 168-170)

Thus,



→ observe - NO<sub>2</sub> destab. rel. to H.

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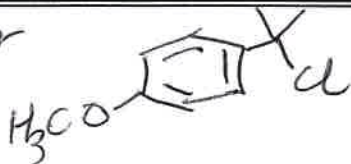
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you fill in argument for

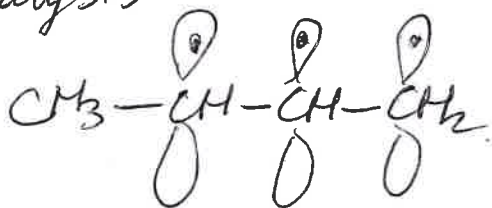


Radicals are stabilized by allylic or benzylic delocalization.

Ex:



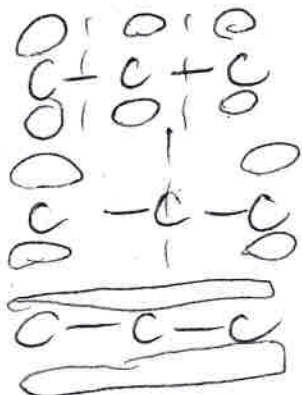
MO analysis



3  $\sigma$ 's + 3 p-orbitals to combine

$\pi$  MOs

E↑



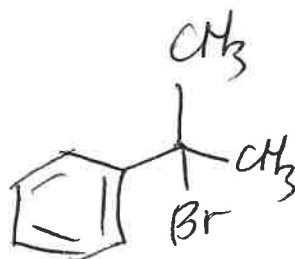
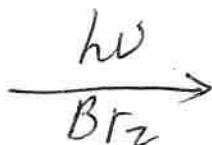
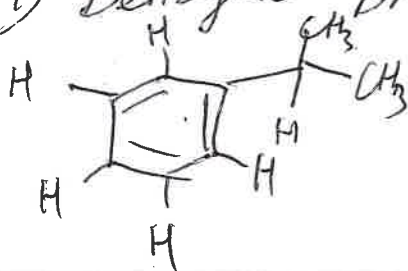
$\pi_3$  —

$\pi_2$  |

$\pi_1$  ||

Reactivity manifestations:

1) Benzylic bromination



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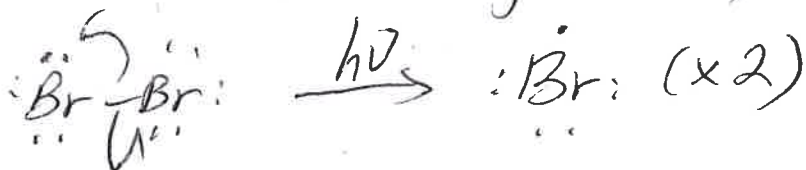
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## Note Selectivity!

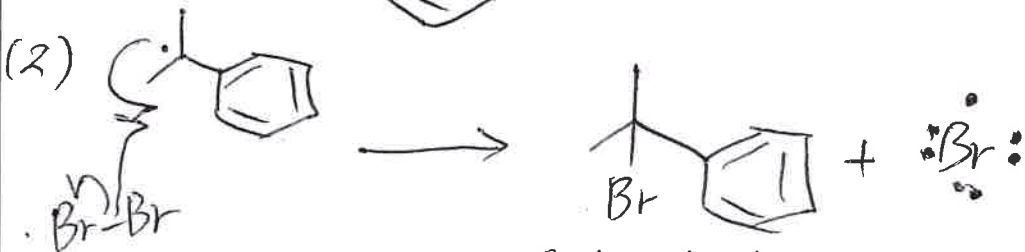
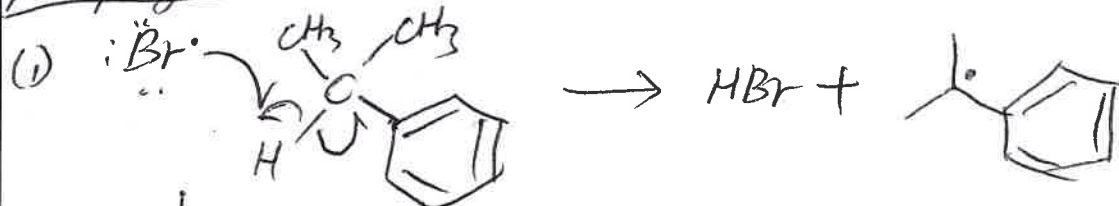
Origin?

Consider mechanism...

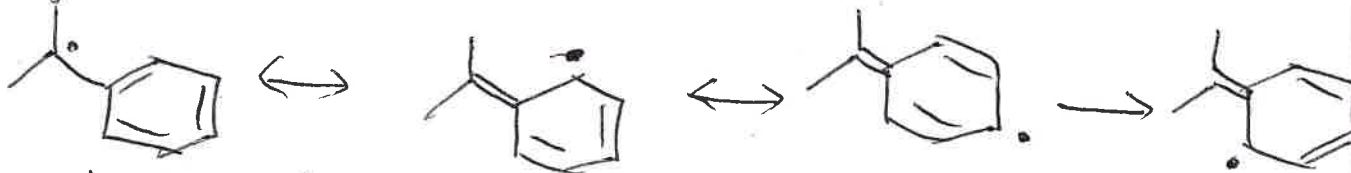
Initiation (creation of radicals)



propagation:



Benzylic radical stabilized by resonance:



Step (i) "product-determining step". Why is benzylic H removed in preference to the other H's.



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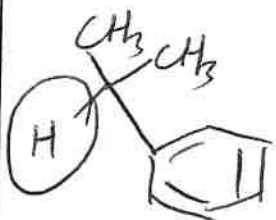
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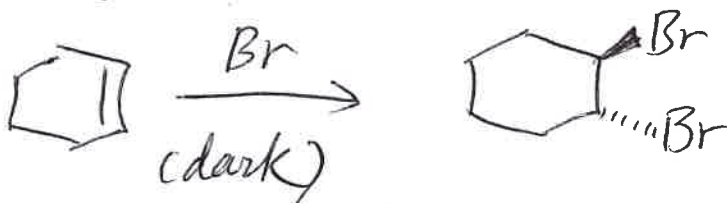
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Because of benzylic radical stabilization via resonance

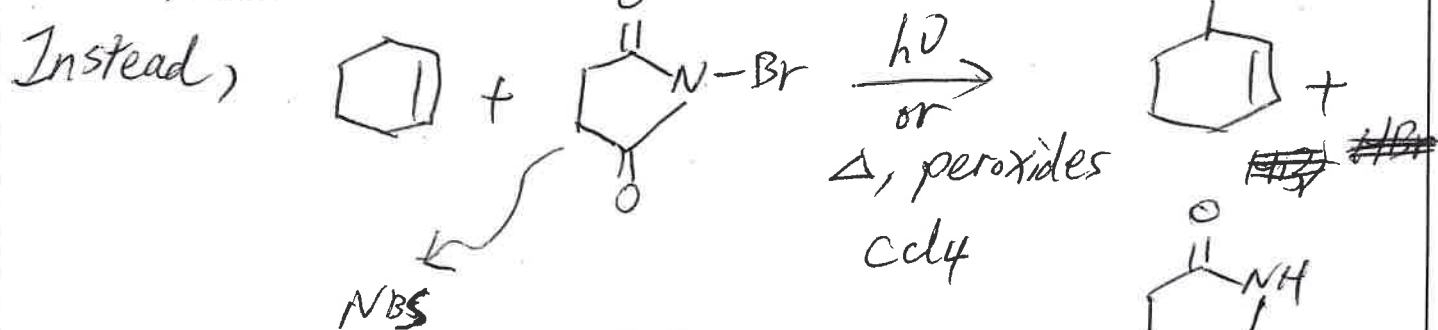


Similar selectivity possible for allylic C-H, but must avoid alternative rxn...

Recall:



Not radical mech...



see text — use of NBS ensures a low conc. of Br<sub>2</sub> at all times; avoids addition across  $\pi$ -bond.

Allylic & benzylic anions are stabilized by res. deloc. (... stabilized relative to localized anions)



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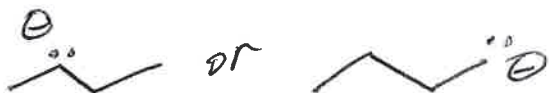
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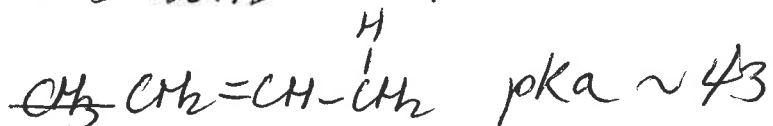
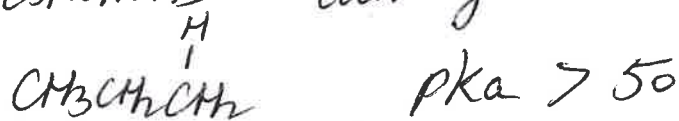
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You fill in  $\pi$  MO analysis  
manifestations - acidity



pKa  $\sim 41$