Course Chem 345 Lecturer Gellman

Day Monday Date 2/16/2015

Notes Taken By Leslie Rank Total # of Pages 4

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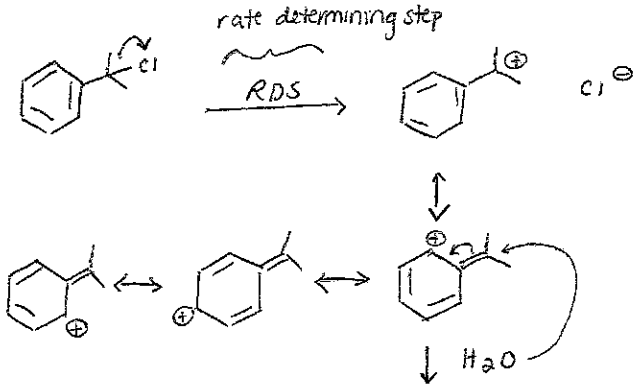
Recall: Special Reactivity at allylic & benzylic positions

⟹ S_N1 rxns . . . .



Exam locations:

Student last names:

A - L: 1125 Biochem

M - Z: Chem 1361

Office hours:

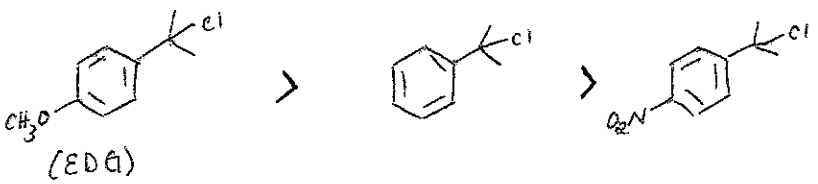
Office hour TODAY

- after lecture 4:00 PM

Review session TOMORROW

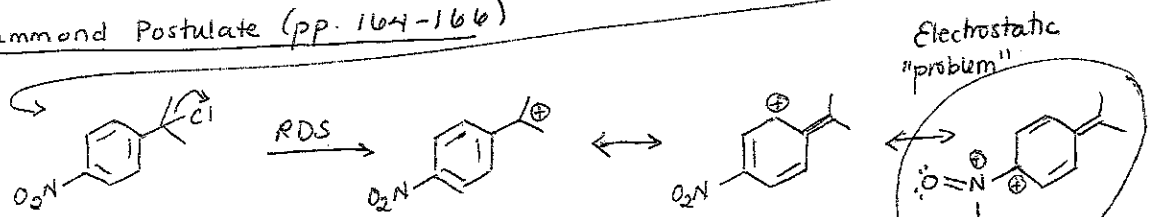
B371, 5:15 PM

- Substituents on aromatic ring influence reactivity among benzylic alkyl halides relative rxn rates:

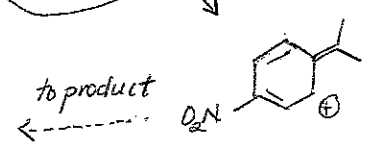


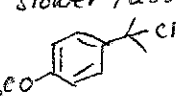
- Consider nitro case (e⁻ withdrawing group (EWG)).

Hammond Postulate (pp. 164-166)



invoking Hammond's Postulate: circled intermediate is higher in energy, therefore transition state energy is higher ⟹ reaction is slower/less reactive



* You fill in logic for 

Course Chem 345 Lecturer Bellman

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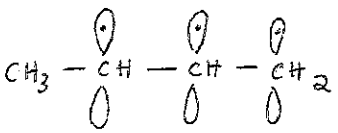
Allylic and Benzylic radicals are stabilized by resonance

→ Reactivity patterns

Ex: 

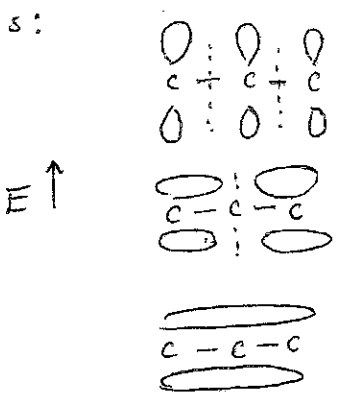
sp² hybridized carbons have unhybridized p orbital



3 adjacent unhybridized p orbitals, 3 e⁻'s ....

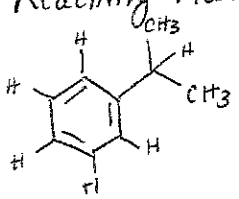
atomic orbitals

Form 3 π MOs:

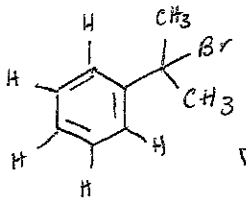


SOMO: singly occupied Molecular Orbital

Reactivity Manifestation:



+ Br_2 $\xrightarrow{h\nu}$



+ (HBr)

selective introduction of Br at benzylic position!

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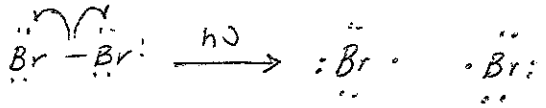
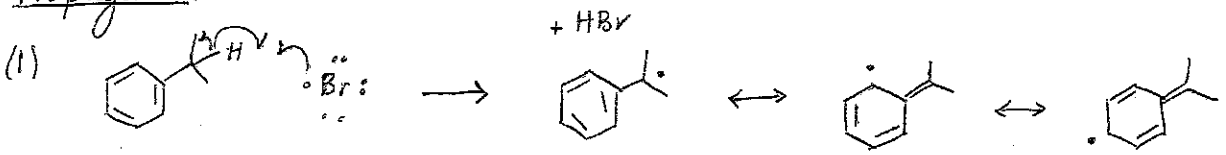
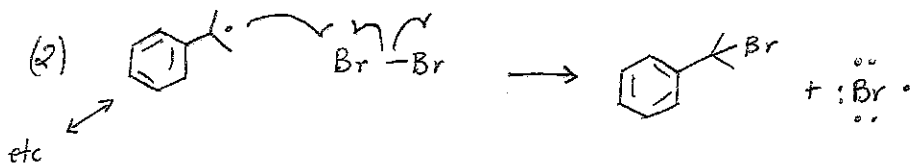
Mechanistic explanation for this selectivity.

Initiation: 

Propagation:

(1) 

(2) 

- Step (1) is the product-determining step

Selectivity because benzylic C-H weaker than other C-H in starting material

- Benzylic C-H is weaker because as H breaks the radical is delocalized.

Course Chem 345 Lecturer Hellman

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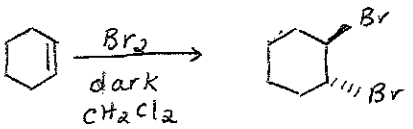
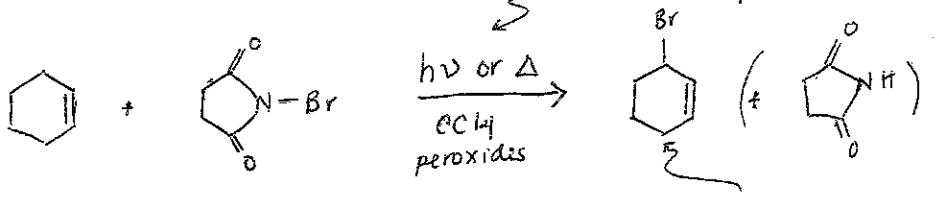
Expect comparable bromination selectivity for allylic C–H; however, must circumvent ionic addition of Br_2 to alkene (π bond).

Recall, 

alternative: 

N-bromosuccinimide (NBS)

allylic bromination

– See text – NBS leads to formation of Br_2, but $[Br_2]$ remains low

allylic and benzylic anions also benefit from resonance delocalization

→ you fill in MO analysis for an allylic anion

E.g. $CH_3-\overset{\ominus}{\underset{\cdot\cdot}{C}}H-CH=CH_2 \leftrightarrow CH_3-CH=CH-\overset{\ominus}{\underset{\cdot\cdot}{C}}H_2$

Manifestation: pKa values $CH_3CH_2CH_2-H$ pKa 50-60