Course CHEM 345 Instructor GELLMAN
Day FRIDAY Date 2/21/2014
Notes Taken By ELLIOT Total # of Pages 3

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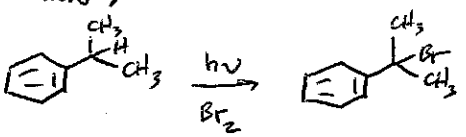
PLEASE COMPLETE NOTES IN INK AND DO NOT STAPLE.

RECALL: SPECIAL REACTIVITY PATTERNS AT ALLYL & BENZYLIC POSITIONS
→ STABILIZATION OF ⊕ etc...

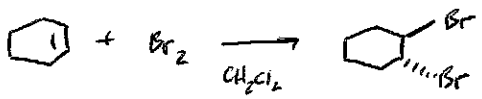
BENZYLIC STABILIZATION OF RADICAL INTERMEDIATE LEADS TO SITE-SELECTIVE BROMINATION:



(+ HBr)

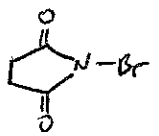
ANALOGOUS SELECTIVITY CAN BE ACHIEVED AT ALLYLIC POSITIONS, BUT WE NEED A SPECIAL REAGENT TO AVOID Br_2 RXN WITH ALKENE... (π-BOND)

RECALL:



MUST AVOID THIS REACTION FOR ALLYLIC BROMINATION

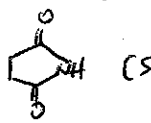
ALTERNATE REAGENT FOR ALLYLIC BROMINATION (RADICAL MECHANISM):



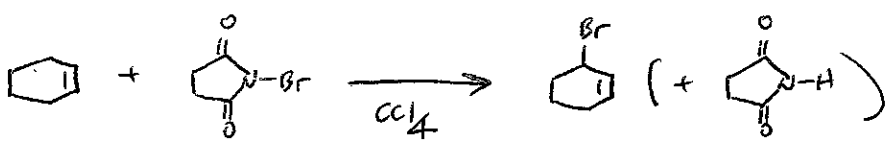
"N-BROMOSUCCINIMIDE" (NBS)

HAS A WEAK BOND BETWEEN TWO ELECTRONEGATIVE ATOMS (N–Br) AND CARBONYL GROUPS WITHDRAW e⁻ DENSITY

ROLE OF NBS – GENERATE LOW CONCENTRATION OF Br_2 UNDER RXN CONDITIONS

(BY-PRODUCT =  (SUCCINIMIDE))

THUS,



CONDITIONS THAT FAVOR RADICAL FORMATION: hν or Δ, peroxides

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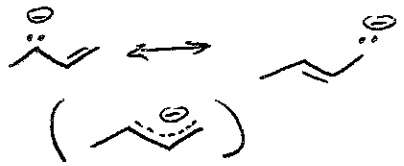
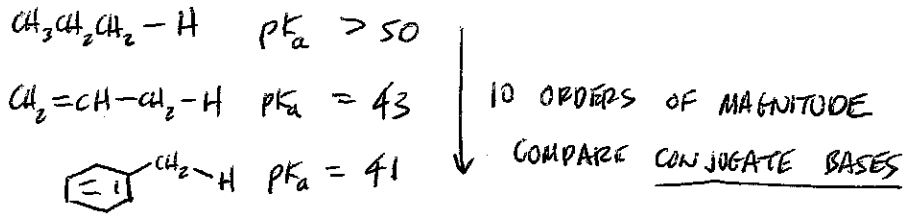
ALLYLIC / BENZYLIC STABILIZATION OF CARBANIONS. E.g.,



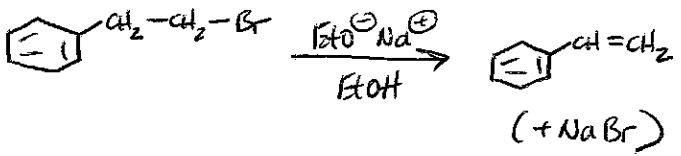
YOU FILL IN NO DIAGRAM

CHEMICAL MANIFESTATION OF ALLYLIC / BENZYLIC DELOCALIZATION OF CARBANIONS

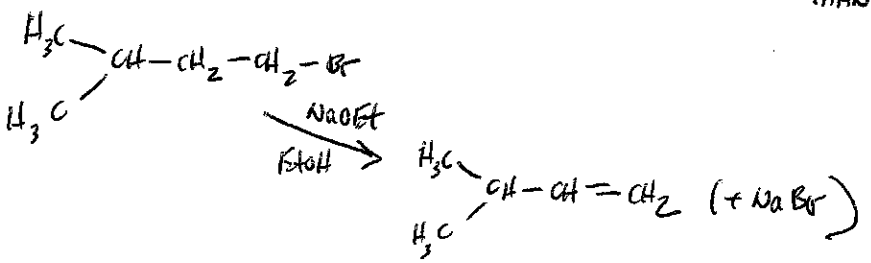


SEE DISTINCTIVE REACTIVITY WITHOUT DISCRETE ⊕, ⊖, OR ⊙ INTERMEDIATE

EX 1 – E2



THIS RXN IS ~100× FASTER THAN...



RATIONALE – CONSIDER T.S.

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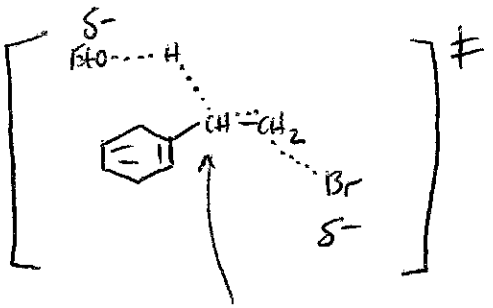
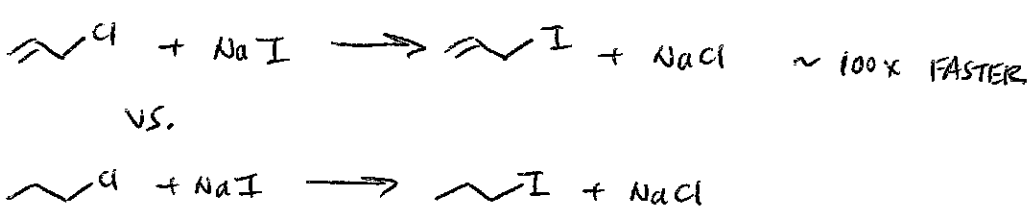


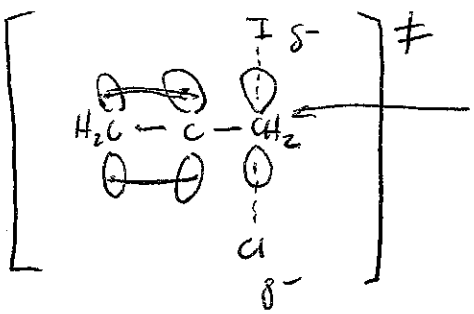
PARTIAL π-BONDING, CONJUGATED TO AROMATIC π-SYSTEM

TRANSIENT δ⁻ AT THIS POSITION ?

Ex #2 – S_N2 RXNS



- EVEN LARGER BENEFIT FOR BENZYLIC POSITIONS!
- RATIONALE – BASED ON TS (NO INTERMEDIATE)



THIS C IS sp^2 AT THE TRANSITION STATE; CONJUGATION TO π-SYSTEM @ T.S. (BUT NOT AT STARTING MATERIAL OR PRODUCT)