Do Not Use Pencil — Do Not Staple, Please!

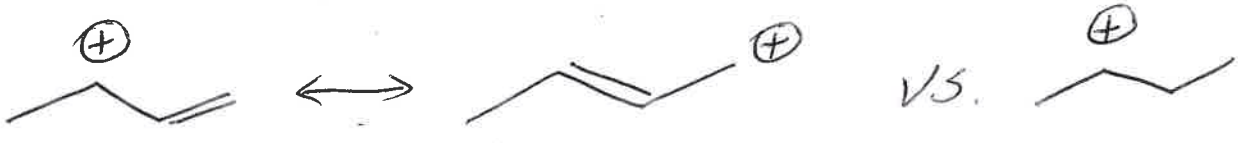
Course Chem 345 — Lecturer Gellman

Day Friday — Date 2-19-16

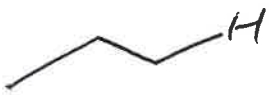
Notes Taken by Lu Liu — Page 1 of 5 (Total Pages)

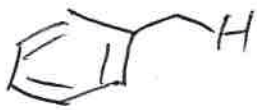
Submit a **COPY** of these notes for posting, please.

Recall: Stabilization of carbocations, carbanions & carbon radicals via resonance (delocalization).



Various manifestations, e.g. pKa (carbanions)

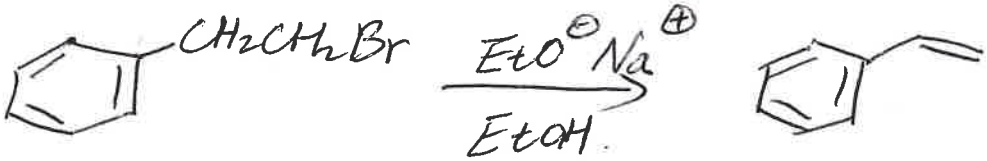




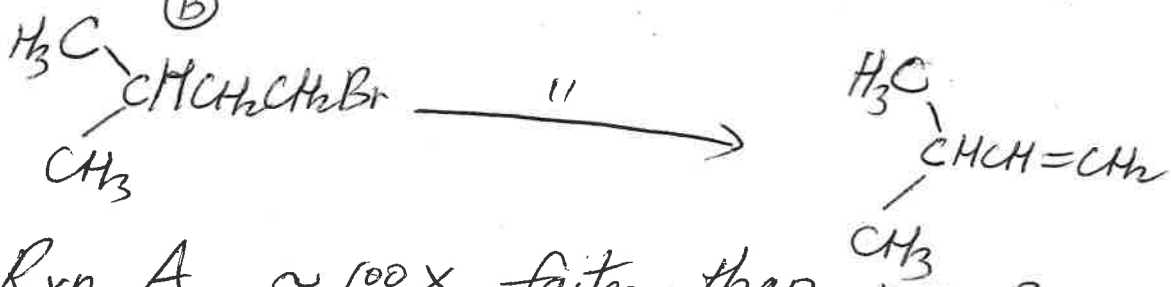
Manifestation of heightened reactivity @ allylic/benzylic sites even when no ionic or radical intermediate is formed.

Ex: E2 rxns

(A)

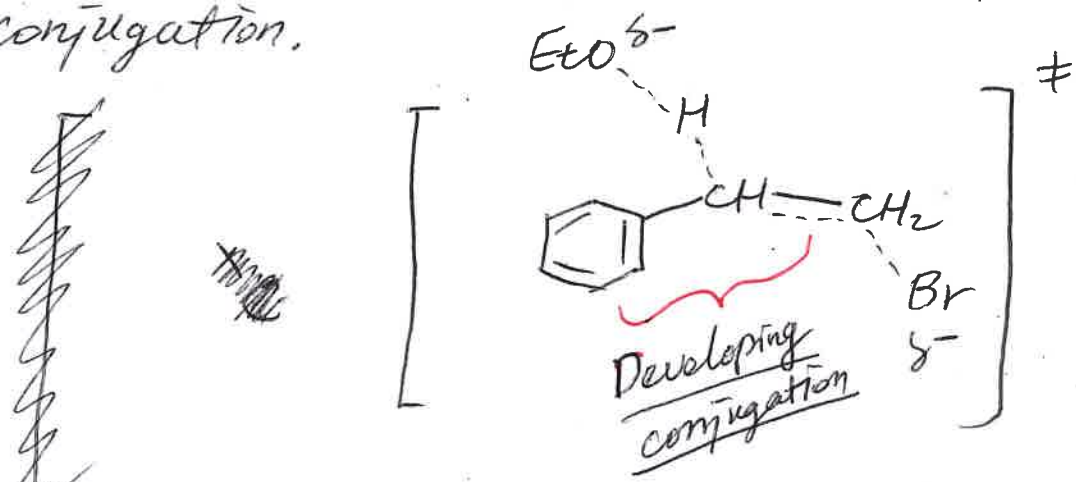


(B)



Rxn A ~100× faster than rxn B.

Rationale? Consider E2 TS; effect of developing conjugation.

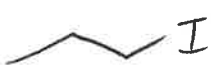


Example: SN2.

Ex:

(C)  + NaI ⟶  + NaCl

vs.

(D)  + NaI ⟶  + NaCl

(C) is 100,000× faster than (D)

Do Not Use Pencil *Do Not Staple, Please!*

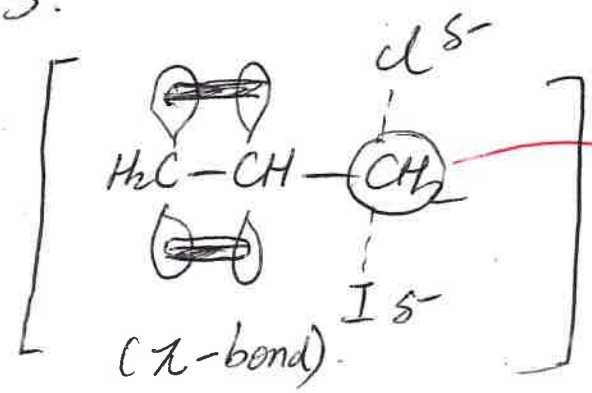
Course Chem 345 Lecturer Gellman

Day Friday Date 2-19-16

Notes Taken by LL Page 3 of 5 (Total Pages)

Submit a ***COPY*** of these notes for posting, please.

TS:

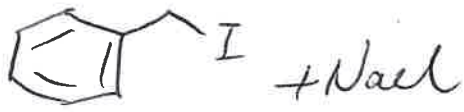


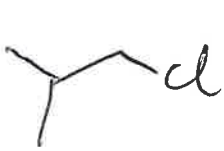
@ TS, this carbon is sp^2 (transient)

this carbon is sp^3 in SM & in product.

Transient conjugation w/ alkene π @ TS.

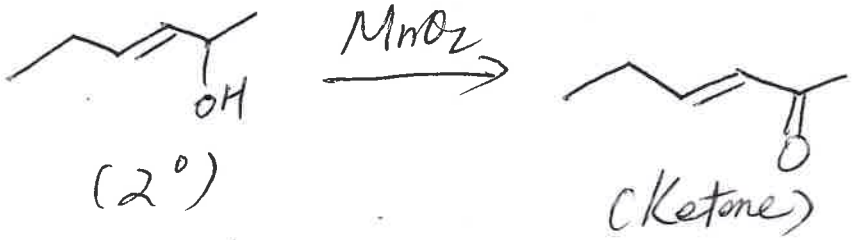
Comparable (& larger) effects for benzylic halides

(E)  + NaI →  + NaCl

(F)  + NaI →  + NaCl

(E) 100,000 × faster than (F)

Example #3 – Selective oxidization of allylic & benzylic alcohols



(2°) (Ketone)

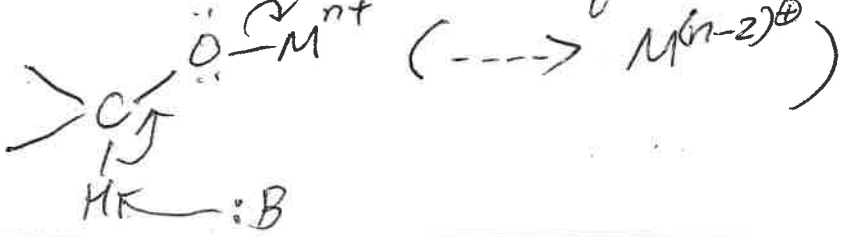
(1°) (aldehyde)

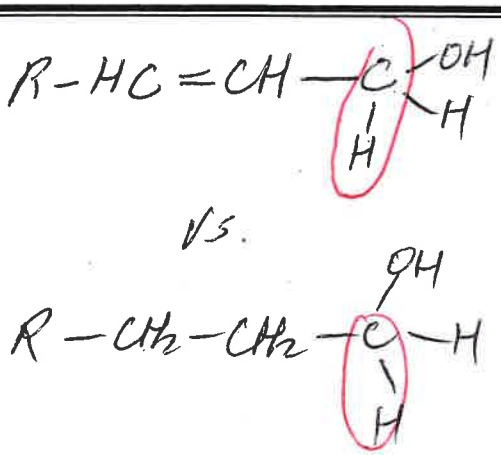
Selectivity possible w/ MnO_2, but not Cr(VI) reagents. (e.g., $K_2Cr_2O_7$, CrO_3, PCC)

Ex.

Origin of Selectivity – variations in C-H bond strengths

(See pp. 484–486, on mech of Cr(VI) oxidations)



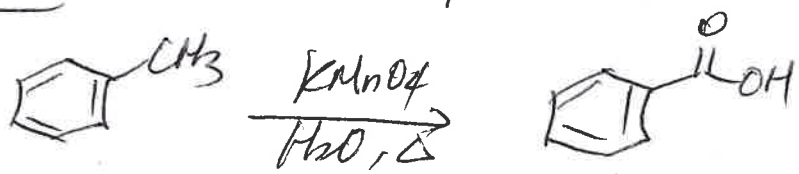


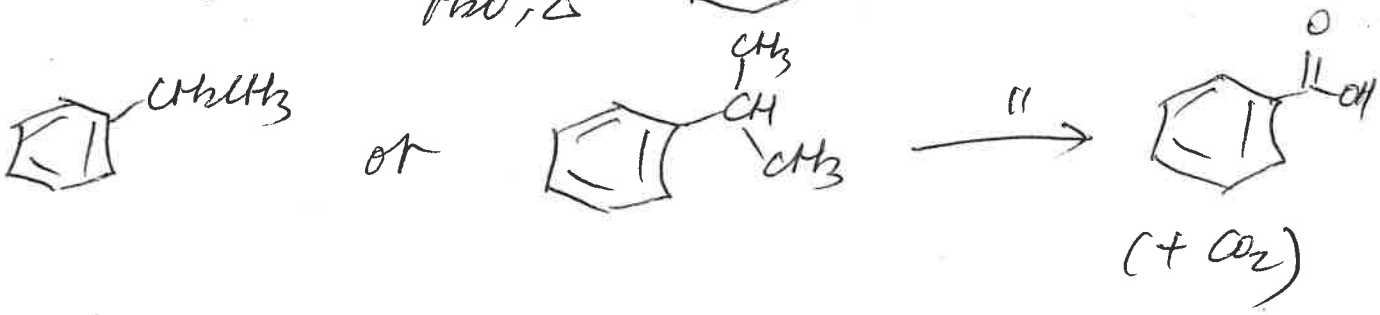
Allylic C-H weaker than non-allylic.

(Similar for benzylic vs. non-benzylic

Example 4 – oxidation of benzylic alkyl groups.

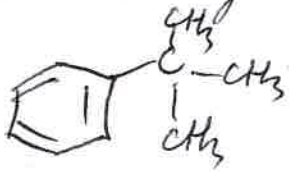
Ex:





(+ CO_2)

This type of rxn requires that there be at least one benzylic C-H. Thus,



No rxn. (or ring destruction)