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

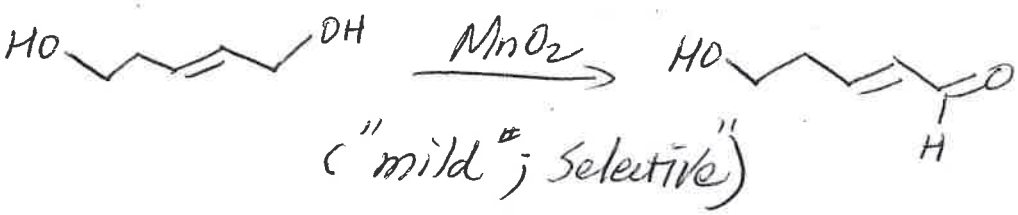
Course Chem 345 Lecturer Gellman

Day Monday Date 2-22-16

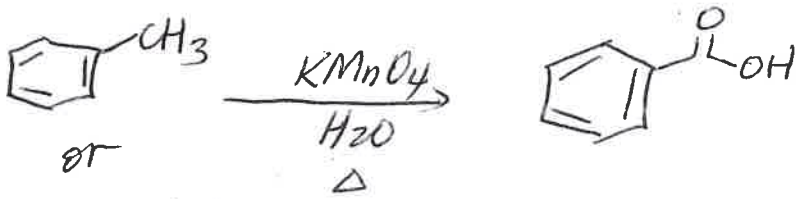
Notes Taken by Lu Liu Page 1 of 5 (Total Pages)

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

Recall Mn oxides for oxidations



("mild"; selective)



or

("Harsh")

Perspective — varying Mn oxidation state — Mn(+4) → MnO_2

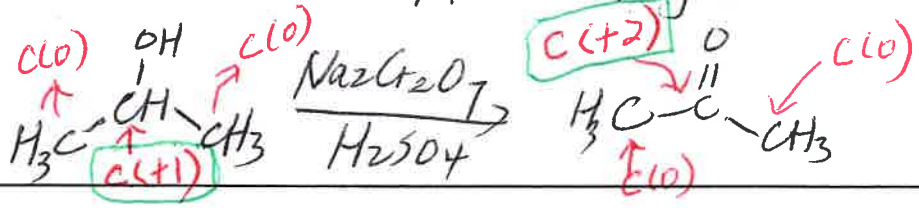
vs. Mn(+7) → MnO_4^-

Higher oxidation state of the metal ⇒ more reactive agent ⇒ less selective

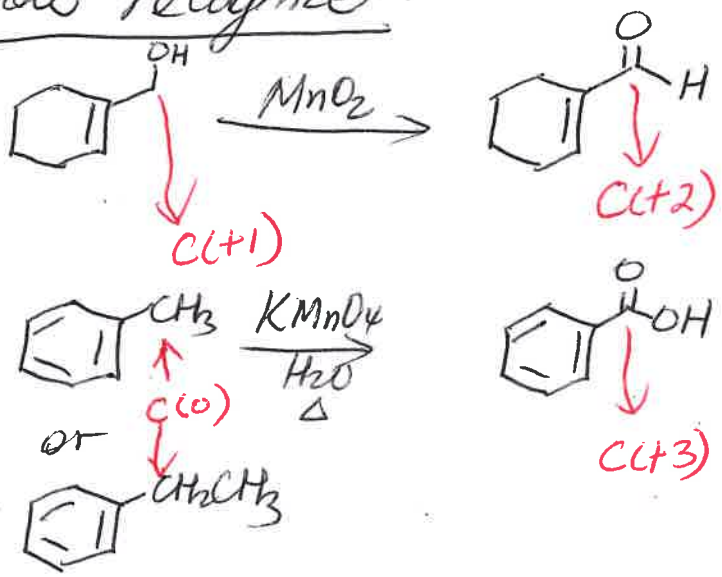
Carbon oxidation states — simplistic scheme (vs. Chap. 10)

For a given C, every bond to a more electronegative atom leads to an increment of +1.

Ex:



Now recognize:



Cannot use $KMnO_4$ for allylic alcohols – π bond reacts

Chap. 18 (Partial) §18.1-4, 18.7 & 18.9

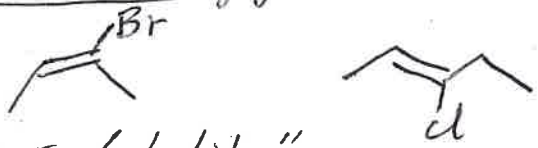
Aryl & vinyl halides & phenols. [No metal catalyzed rxns]

Rec. Problems: 1, 3-5, 30, ~~35~~ 31, 40, 41, 46a-d, 47a-g, ~~52, 56~~, 50-52, 53a-e, 54-58, 60, 62, 67, 68, 69a-i, 70a-d, g, l-n, 73-75, 78, 82.

#51 — "Warfarin"

Wisconsin Alumni Research Foundation.

Terminology:



"vinyl halide"

"aryl halide"

phenol

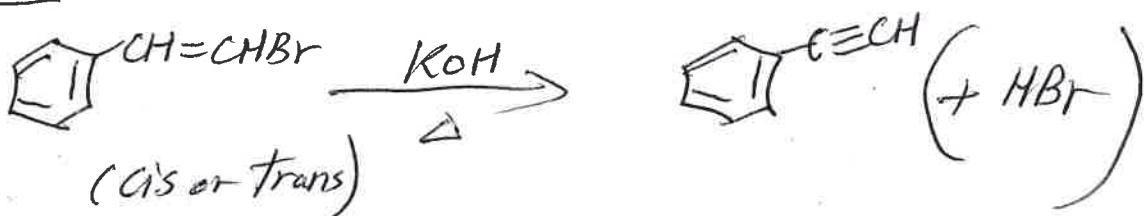
Recall: "X" ("leaving group") on sp^3 carbon

– SN1 / SN2 / E1 / E2

rxn manifold ⇒ Now X on sp^2 carbon

Most of these (SN1, SN2, E1, E2) rxns do not occur for C(sp^2)–X bonds

E2 Can occur under harsh conditions.

Ex. 

(Cis or trans)

(Vinyl halides only!)

SN2 – Steric Problems!

Ex 

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

Course Chem 345 Lecturer Gellman

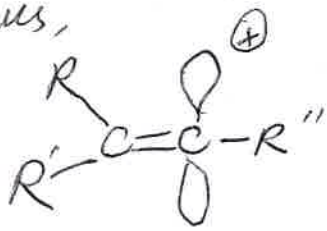
Day Monday Date 2-22-16

Notes Taken by JL Page 4 of 5 (Total Pages)

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

SN1 / E1 rxns — very unstable cations would be formed!

Thus,

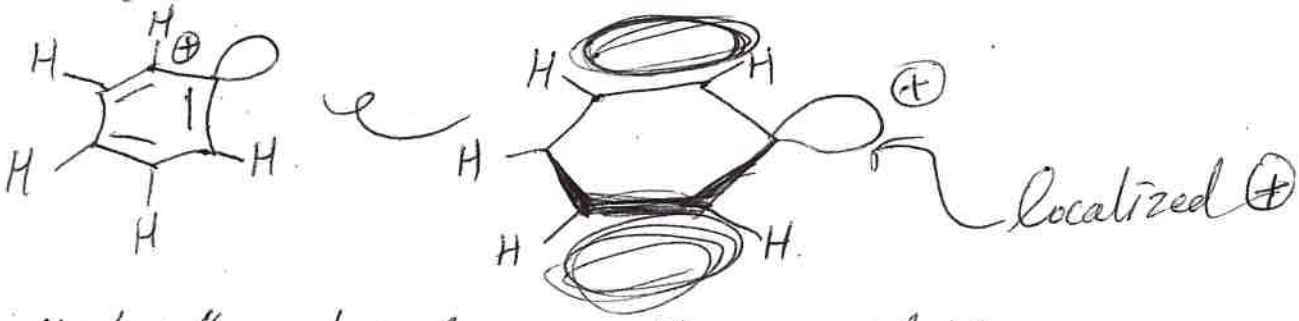


"vinyl cation"

⊕ on sp^2 C (localized)

sp^2 C is effectively more electronegative than sp^3 carbon

Analogous problem w/ aryl cation



"New" mode of reactivity available to some aryl halides

Nucleophilic Aromatic Substitution (NAS)

→ Not as broad rxn scope as EAS.

→ Require a LG, for NAS.

(halides, etc.)
tosylates

→ Also require an electron-withdrawing group ortho

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

Course Chem 345 Lecturer Gellman

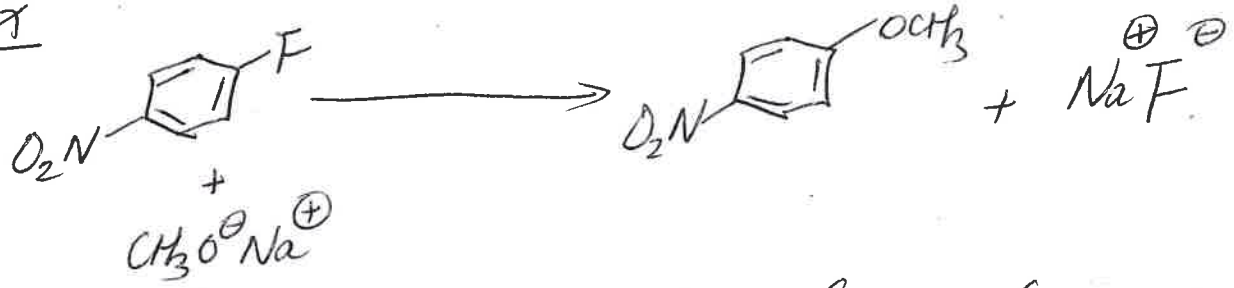
Day Monday Date Monday

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

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

para to LG

Ex



Note: $F^{\ominus}$ is an excellent LG for NAS (in contrast to SN1 / SN2 / E1 / E2)

Mech: