Course Chem 345 Lecturer Gellman

Day ~~Class~~ Monday Date 2/23/15

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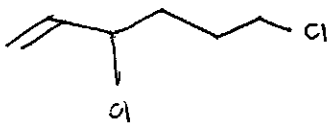
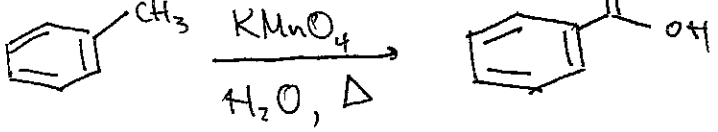
Recall: Special Reactivity patterns @ allylic & benzylic positions w/in molecules ...

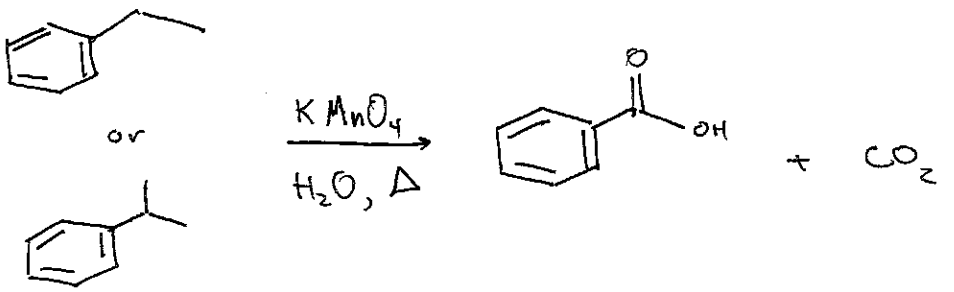


Example #4: Benzylic oxidation of alkyl groups

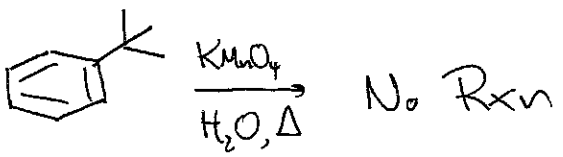
Ex:



Longer alkyl groups show comparable reactivity...



Limit:



→ Need one or more benzylic C-H bond

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Note: Harsh conditions! Limited applicability for more complex molecules.

Cannot apply to allylic oxidation b/c π-bond reacts.

Compare:

$MnO_2 \rightsquigarrow Mn(+4)$ vs. $KMnO_4 \rightsquigarrow Mn(+7)$

$\therefore KMnO_4$ is stronger oxidant (more reactant).

Carbon oxidation state analysis - "organize" organic reactions conceptually + recognize relationships.

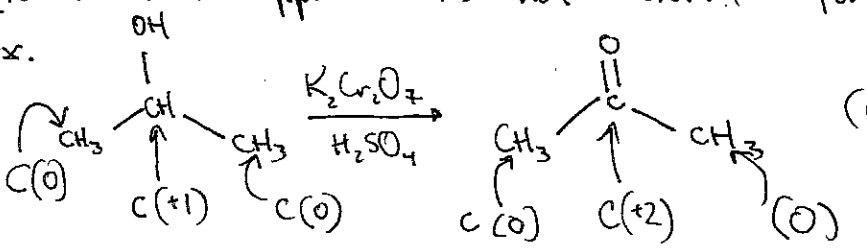
Note: This approach is simpler than approaches in the text (Ch 10). This approach is less general, but perhaps more useful than text's approach.

General: For a given carbon bond, each bond to a more electronegative atom "X" (halogen, O, N), increment carbon ox. state by +1.

No change for C or H as bonding partners.

(Note: This approach is not useful for alkenes or alkynes)

Ex.



(Chem 343)

"oxidation"

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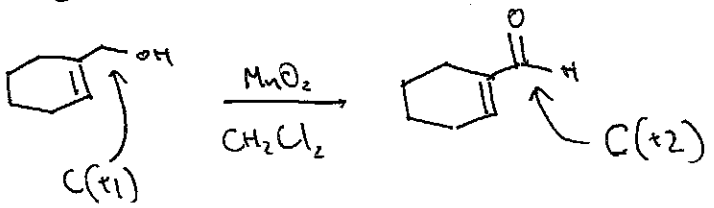
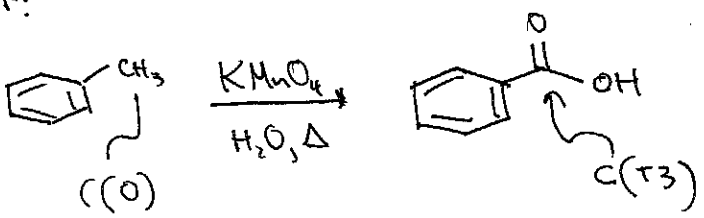
Now recognize:



Contrast:



∴ Multi-stage oxidation.

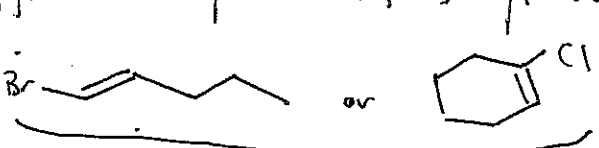
Ch. 18 (partial)

§§ 18.1 - 18.4, 18.7, 18.9

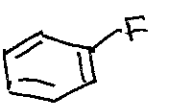
Aryl & vinyl halides, phenols (not metal-catalyzed reactions)

Rec. problems: 1-5, 30, 31, 38-40, 44a-d, 45a-g, 47-49, 51-55, 59, 62, 63, 64a-f, h, i, 69, 70, 73, 75-77

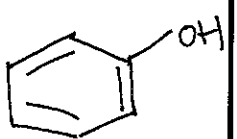
Terminology - "Aryl halide," "vinyl halide" - halogen bound to sp^2 carbon.



vinyl halides



aryl halide



phenol

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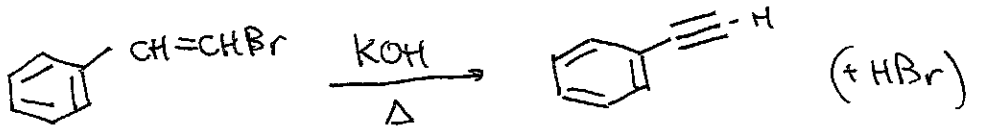
Recall from Chem 343 -

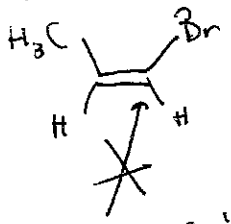
S_N1 / S_N2 / E_1 / E_2 - molecules w/ halogen bonded to sp^3 carbon.

Most of these reactions don't occur for $C_{(sp^2)} \rightarrow X$ bonds

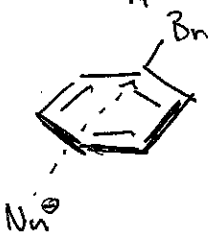
Exception: E2, for some vinyl halides,

Ex. 

Why no S_N2 for $C_{(sp^2)} - X$?



Can't approach → steric hindrance to back side attack prevents S_N2.



Approach blocked by ring.

S_N1 / E1 - $C_{(sp^2)}$ is much worse at allowing carbocation formation relative to $C_{(sp^3)}$. $C_{(sp^2)}$ is more electronegative effectively than $C_{(sp^3)}$.

Vinyl & aryl carbocations are very unstable. (See next page.)

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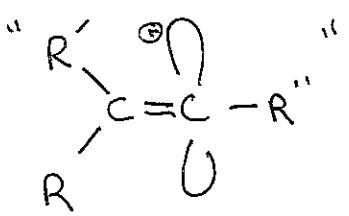
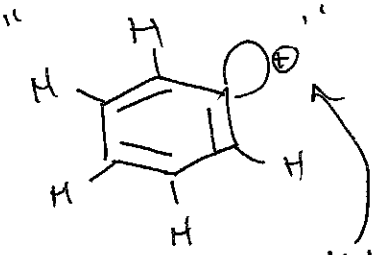
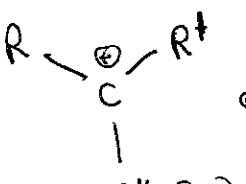


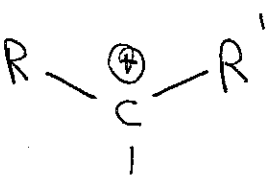


Not delocalized

Much less stable than sp^3 analogues.



or



(2°)

New mechanism allows nucleophilic substitution on aromatic rings. (aryl halides) – nucleophilic aromatic substitution (NAS).

(It's illmatic. on reaction)