

Course Chem 345

Instructor Gellman

Day Monday

Date 24 Feb 2014

Notes Taken By Kaz Skub:

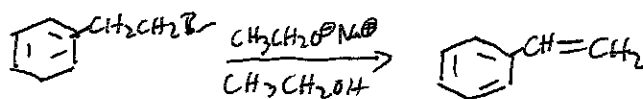
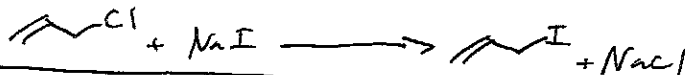
Total # of Pages 5

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PLEASE COMPLETE NOTES IN INK AND DO NOT STAPLE.

Guest Lecturer: Dr. Cheri Barta

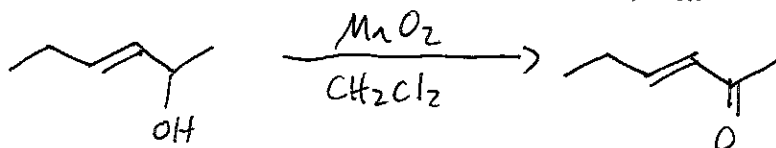
Allylic & Benzylic Reactivity:

Example #1: E2 Reactions

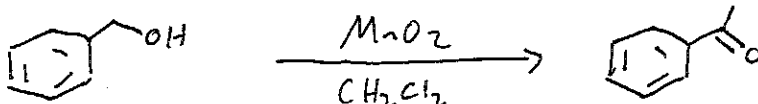
Example #2: S_N2 Reactions

Example #3: Selective Oxidation of allylic or benzylic alcohols to ketones or aldehydes using MnO₂

2° allylic alcohol

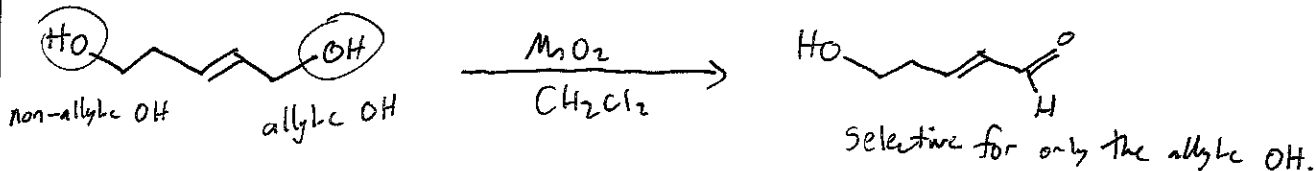


1° benzylic alcohol

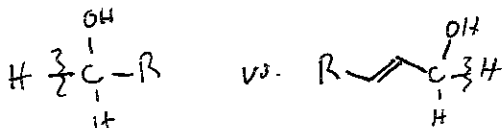


(Note that MnO₂ has Mn in the +4 oxidation state)

Consider

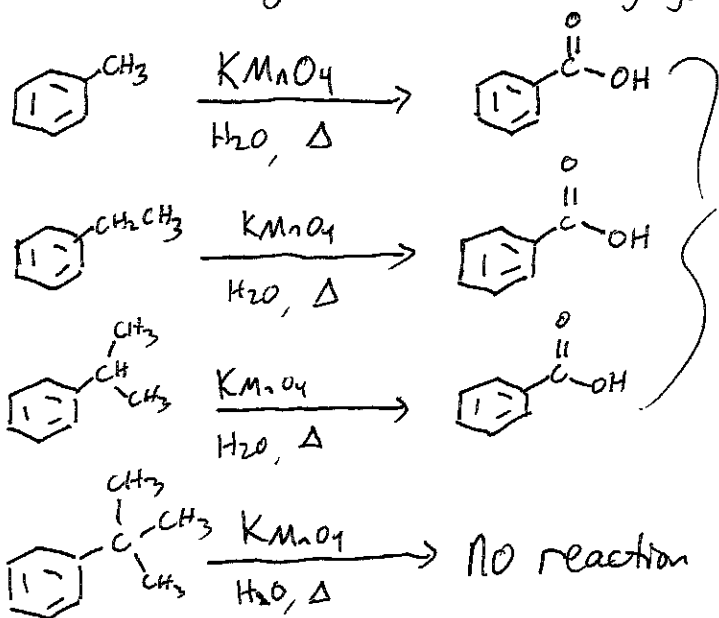


* Allylic stabilization of the intermediate favors oxidation at that site.



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Example #4: Benzylic oxidation of alkyl groups on benzene rings



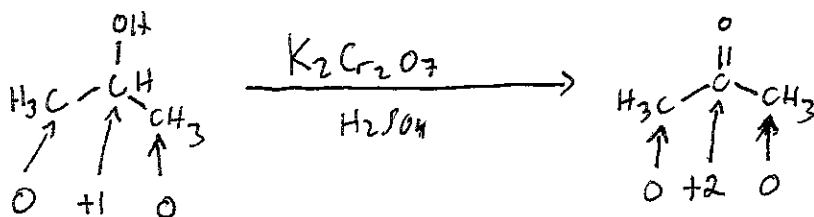
Same product regardless of alkyl group. But the group must have at least one hydrogen

stronger oxidant
 Note: this Mn is +7, ~~+2~~

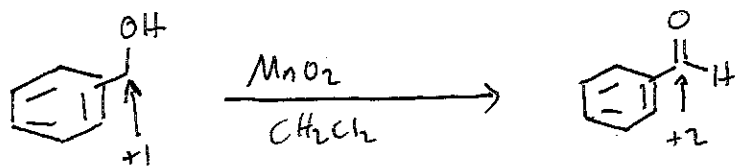
"Carbon Oxidation State" analysis

* Simple rule: every C-X bond, where X is something more electronegative than C (e.g. O, N, halogen, etc.).

Causes +1 increase in oxidation state of that carbon



Overall result is +1 \rightarrow +2, so this was an oxidation



also oxidation

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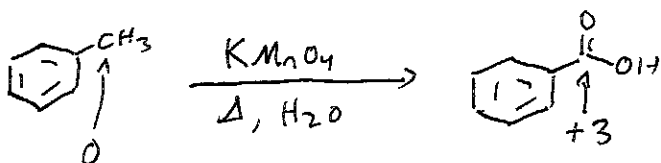
Day Monday

Date 29 Feb 2014

Notes Taken By Karz Skub:

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Note, this capacity of KMnO_4 is unique to benzylic groups. Does not work with allylic or alkyl groups.

Ch. 18: Aryl & Vinyl Halides and Phenols

(no metal-catalysis)

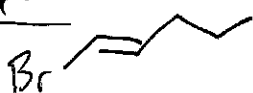
18.1 - 18.4, 18.7, 18.9

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.

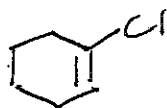
Terminology

aryl halide and vinyl halide - bonded to sp^2 -hybridized carbon

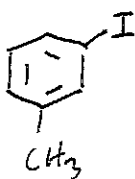
examples



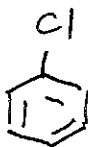
or



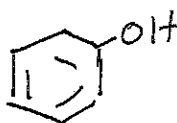
Vinyl halides



or



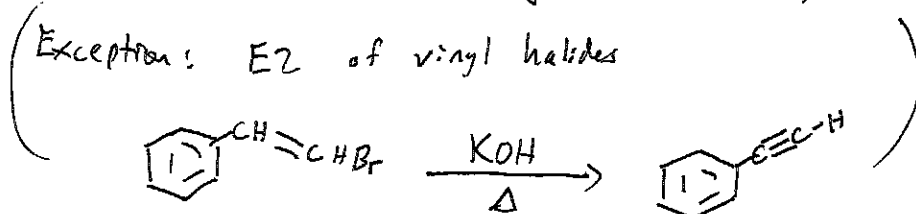
aryl halides



Phenol

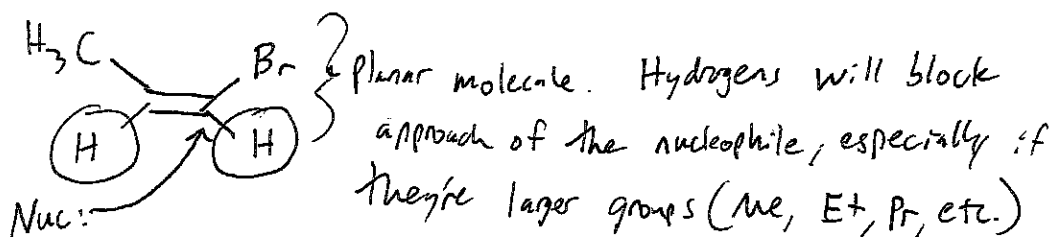
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* Most of the $S_N1/S_N2/E1/E2$ reaction mechanisms do not occur for halogens on sp^2 -hybridized carbons.

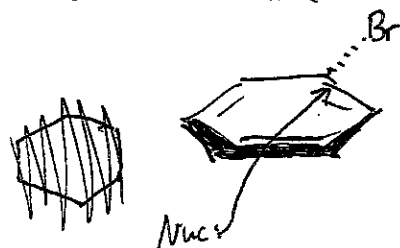


Why can't we do most other reactions of this type?

S_N2 : vinyl halides are not able to have the ~~correct~~ correct nucleophilic approach (backside attack)

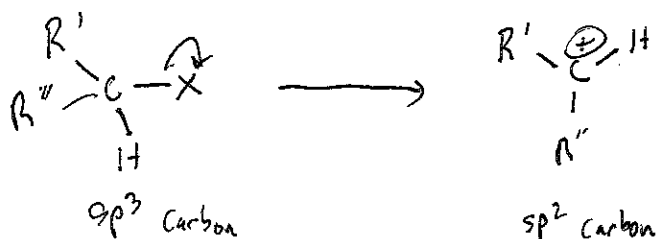


Same argument for aryl halides:

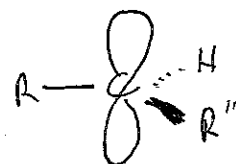


The ring now blocks approach of the nucleophile.

Why don't S_N1 and $E1$ reactions occur?

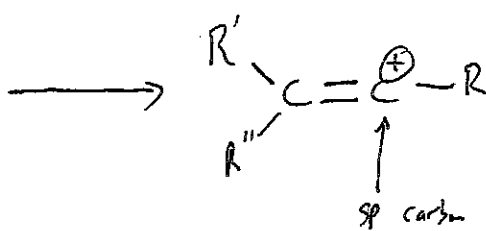
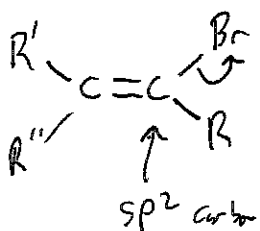


empty p-orbital above & below the plane

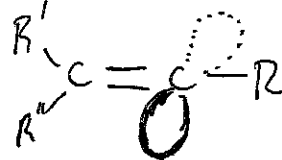


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But, for a vinyl halides

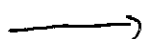
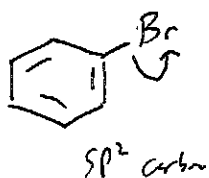


empty p-orbital
 coming at us

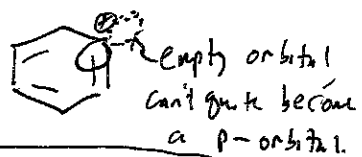


The carbocation intermediate is too unstable to form, so these reactions typically do not occur

Similar for aryl halides:



Reality:



ring constraint prevents it from
 being linear — would be unstable