Course 343 Lecturer Hackenberger

Day Wed Date 11/13/2013

Notes Taken By Adams Total # of Pages 7

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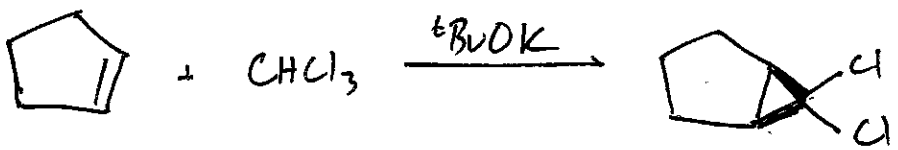
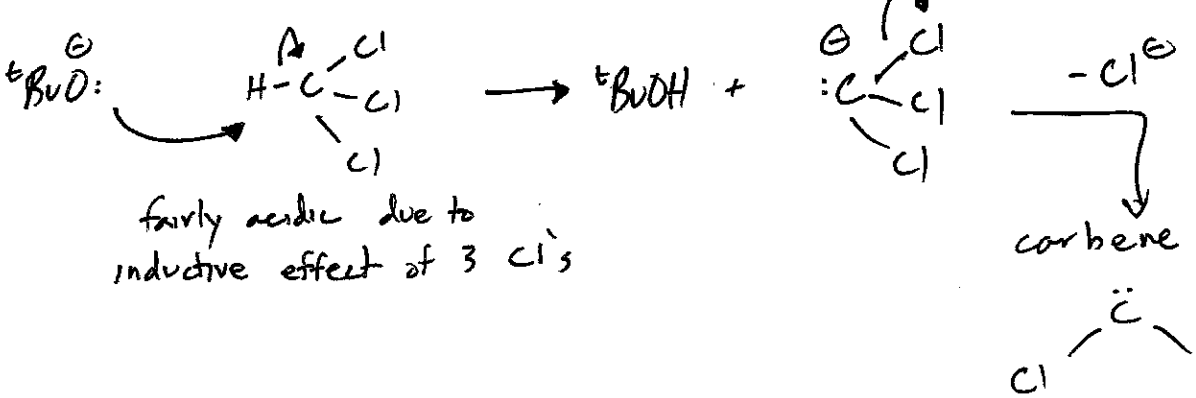
- Upcoming office hours
  - Fri, Nov 15th (12-1 pm)
  - Mon 18th, Wed 20th normal
  - Mon 25th normal, Tue 26th 12-1 pm
  - Wed 27th normal lecture but no office hours
  - Dec 2nd: no lecture or office hr
  - Dec 4th: 3rd exam

- Carbenes:



- Mechanism: two steps

Step 1



fairly acidic due to inductive effect of 3 Cl's

Course 343 Lecturer Hackenberger

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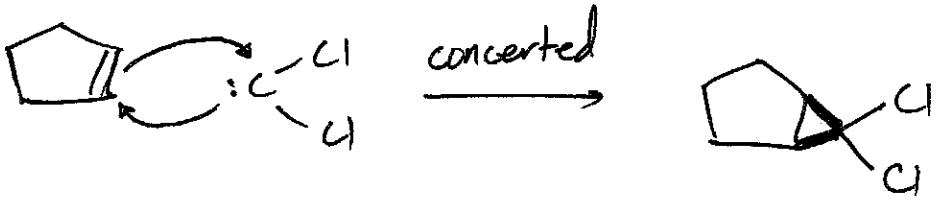
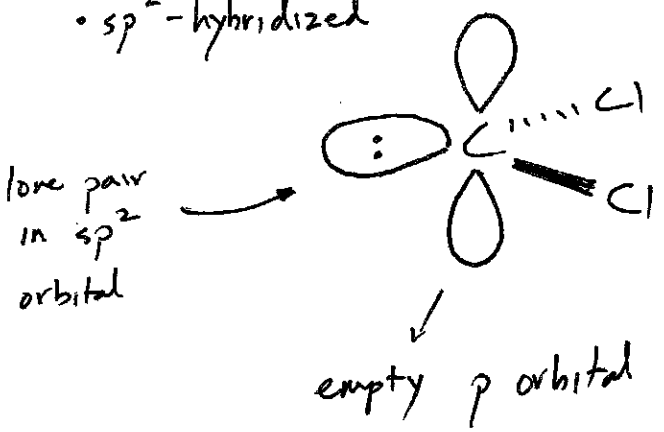
step 2



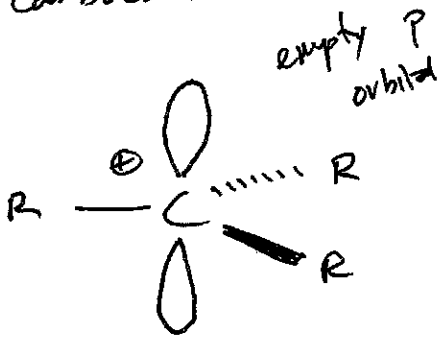
· A closer look at carbene

· sp^2-hybridized

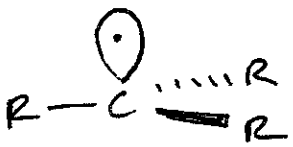


· Compare to:

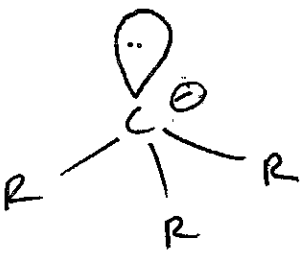
- carbocation



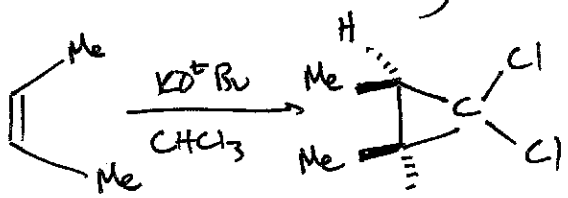
- carbon radical



- carbanion



· Evidence for concerted ring formation



cis cis only

trans

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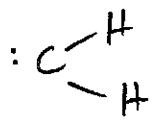
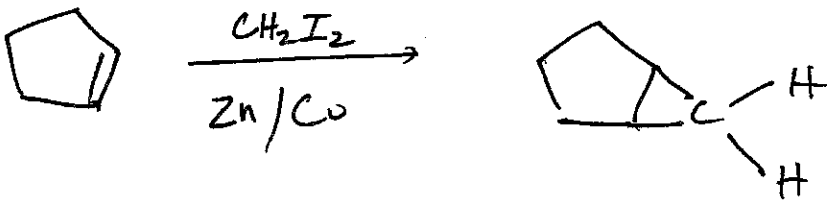


methylene

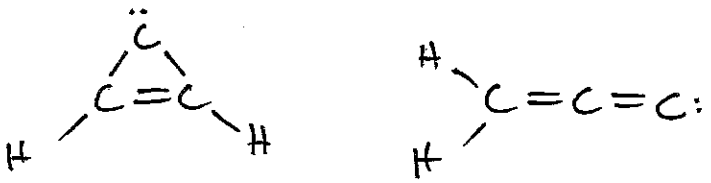
- methylene is too reactive to give useful products
- useful alternative: use metal atom to "tame" reactivity of the carbene
- metal-carbene species called a "carbenoid"

Example: Simmons-Smith reaction with Zn/Cu alloy



Key intermediate: $\left[I\text{-}CH_2\text{-}Zn\text{-}I \right]$

- Another interesting aspect: carbenes are observed in space



very high-energy species (requires cold temp. and "diluted" conditions of space)

Course 343 Lecturer Hackenberger

Day _____ Date 11/13

Notes Taken By _____ Total # of Pages _____

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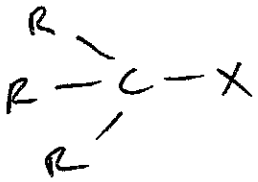
Chapter 10: Alcohols and Thiols

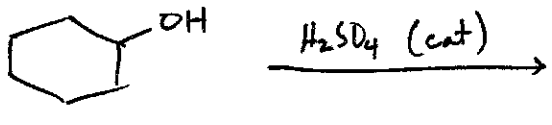


X = Cl, Br, I (Chapter 9)

X = OH/SH (Ch 10)

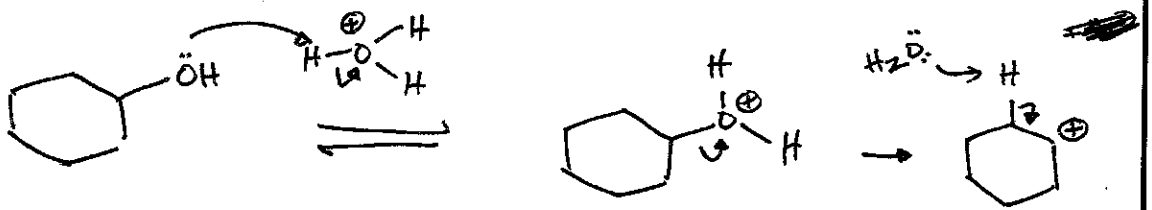
Prob: 1-21, 23, 26, 27, 33, 35-37, 41-46, 52-55, 56c, 57-61

- Dehydration of alcohols to form alkenes



("reverse" of H^+-catalyzed hydration of alkenes)

Mechanism:

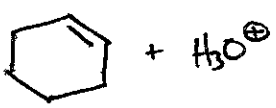


E1-type mechanism (~~reacts~~ for 2°/3° alcohol)

E1

H_2O is good leaving group

H_3O^+ regenerated, ∴ catalyst



Course 343 Lecturer Hackenberger

Day _____ Date 11/13

Notes Taken By _____ Total # of Pages _____

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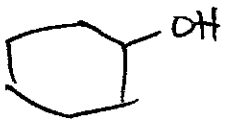
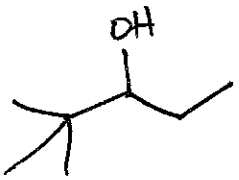
- If this is just the reverse of alkene hydration, how do we favor formation of the alkene?
  - use low concentration of H_2O (LeChatelier's)
  - boil off alkene product (LeChatelier's)

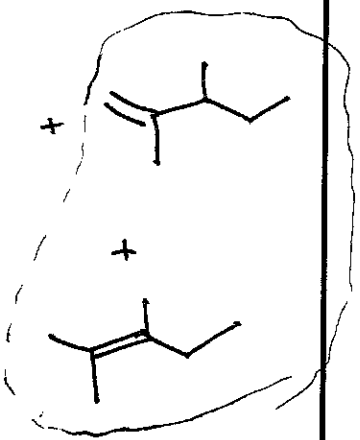
 is lower boiling than 

- Rearrangements are possible once C⊕ are formed!

↑ carbocations

ex: 

$\xrightarrow[H_2O]{H_2SO_4\ (cat)}$  (+ 2 alkene)



2° alcohol

formed from methyl shift of carbocation

Course 343 Lecturer Hackenberger

Day _____ Date 11/13

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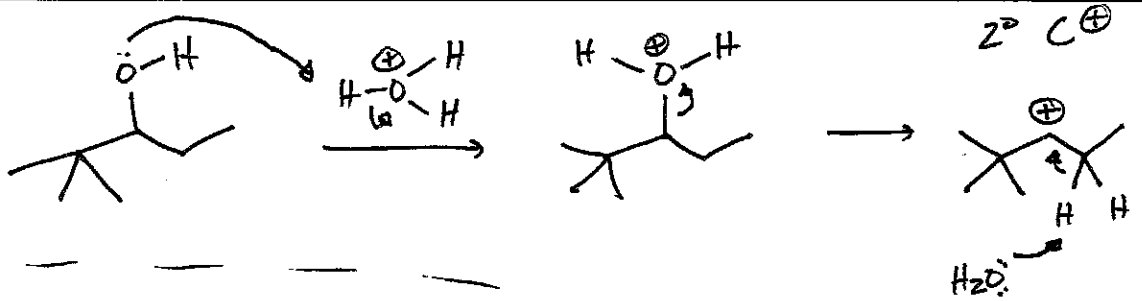
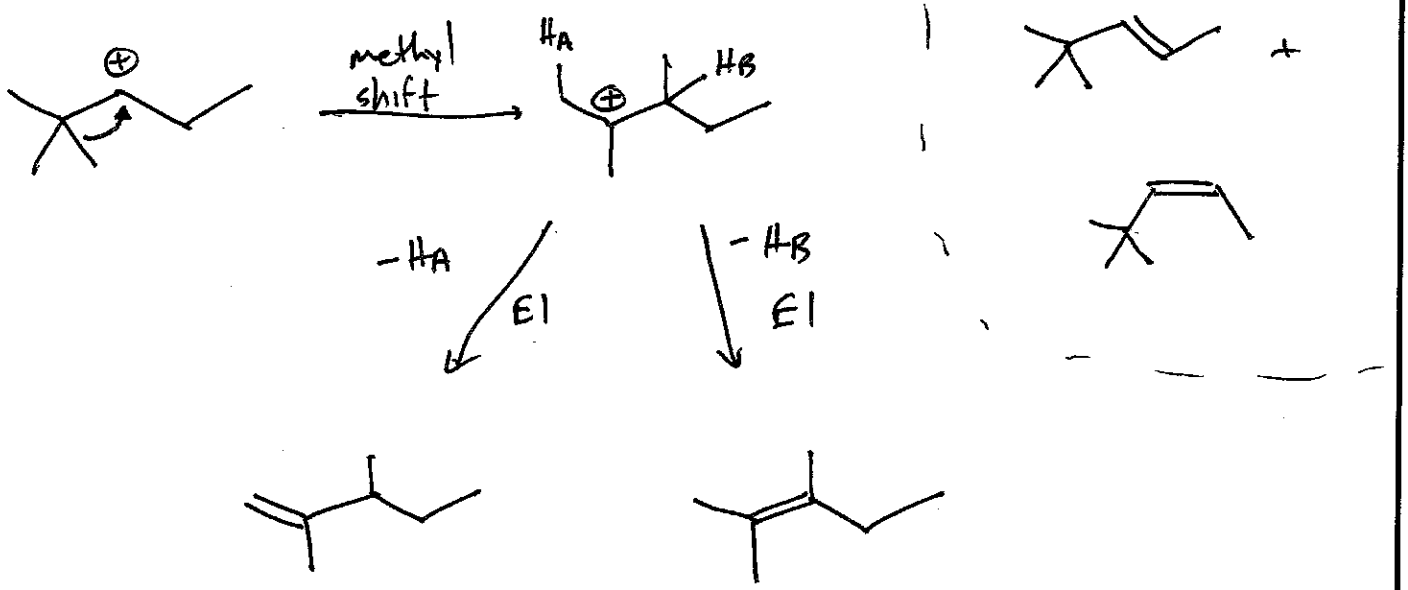
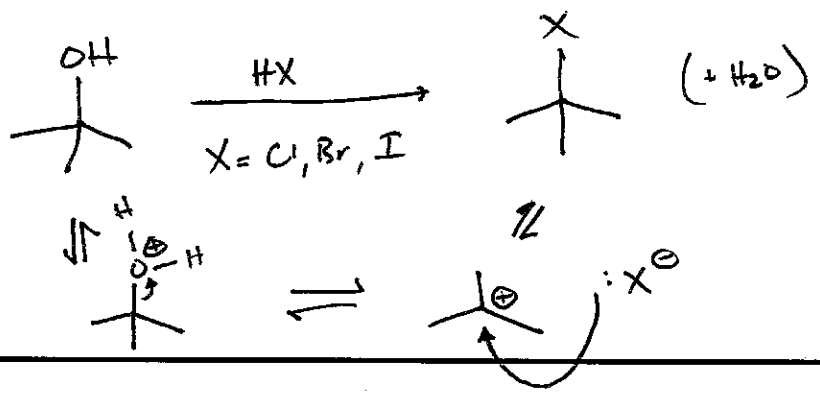
Mechanism:



- Carbocation rearrangement



Conversion of alcohols to alkyl halides:



S_N1 mechanism if we start from 2° or 3° alcohols

Course 343 Lecturer Hackenberger

Day _____ Date 11/11

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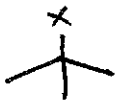
. How to favor formation of  ?

- Run reaction in water

-  is not soluble in H_2O, so it forms a separate layer and does not interact with H_2O to reform the alcohol