

Course Chem 343 Lecturer Gellman
Day Monday Date ~~12~~ 11-30-15
Notes Taken By In Liu Total # of Pages 4

Submit a Single-sided Copy to the Undergraduate Office
NO NOT STAPLE - ONLY WRITE NOTES INSIDE THE SQUARE BELOW

Exam #3 on Wednesday (Rooms as before)

Review Section Tomorrow 5pm B371 (chem)

Organometallic Species, Variation in reactivity based on metal

→ in the news

Chap. 14 - Alkynes $R-C\equiv C-R'$

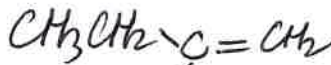
Rec. Problems: 7-27, 29, 31-41, 44-47

Reactions alkynes

① HX addition

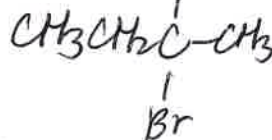
EX: $CH_3CH_2C\equiv CH$

1 equiv.
HBr



(Markovnikov)

2 equiv.
HBr

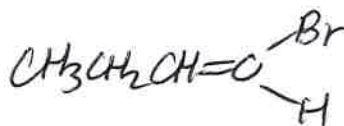


Reversal of selectivity under radical conditions for HBr

EX:



1 equiv. HBr
peroxides



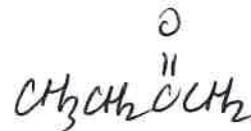
("anti-Markovnikov")

② Hydration (produces Ketones)



$Mg(OAc)_2$

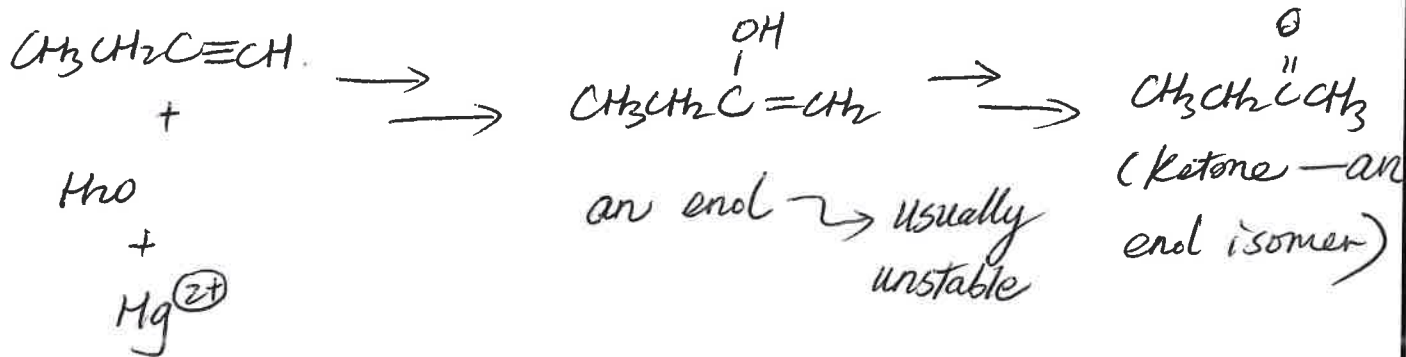
H_2O
 H_2SO_4 (cat.)



(Markovnikov)

Submit a Single-sided Copy to the Undergraduate Office
NO NOT STAPLE - ONLY WRITE NOTES INSIDE THE SQUARE BELOW

See text for mechanism. Key intermediate = "enol".

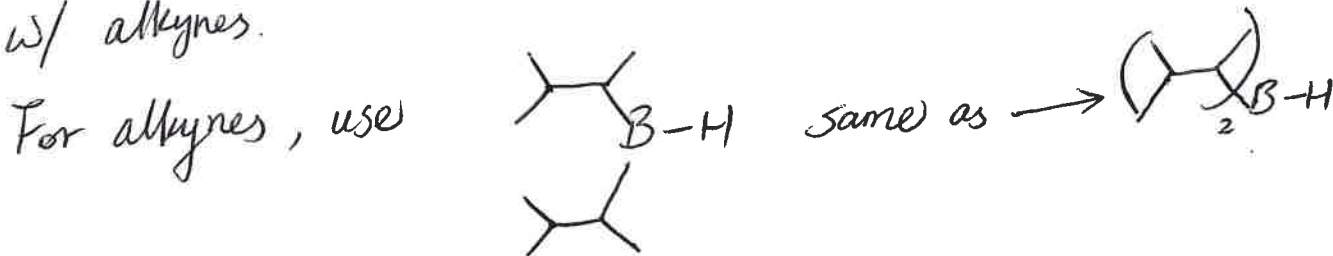


Note: No reduction step (no NaBH_4), in contrast to alkene hydration — see text.

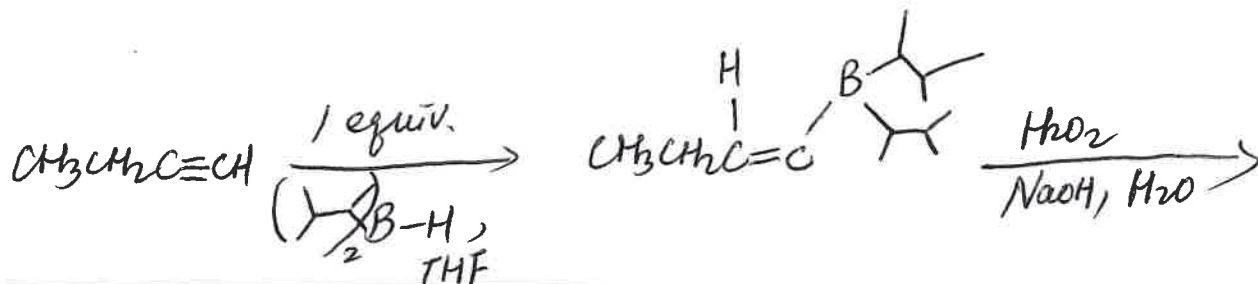
③ Hydroboration/oxidation — anti-Markovnikov product.



Specialized Borane reagent required; BH_3 gives complex products w/ alkynes.

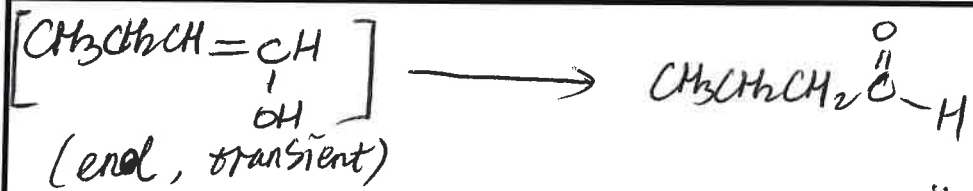


Thus,

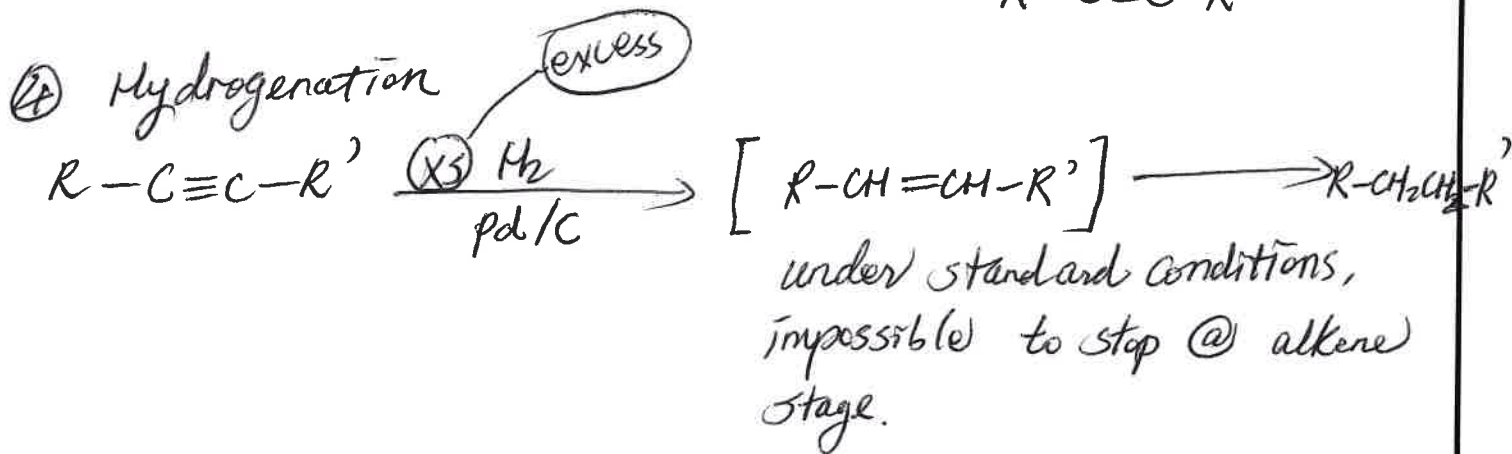


Course Chem 343 Lecturer Gellman
 Day Monday Date 11-30-15
 Notes Taken By LL Total # of Pages 4

Submit a *Single-sided Copy* to the Undergraduate Office
NO NOT STAPLE - ONLY WRITE NOTES INSIDE THE SQUARE BELOW



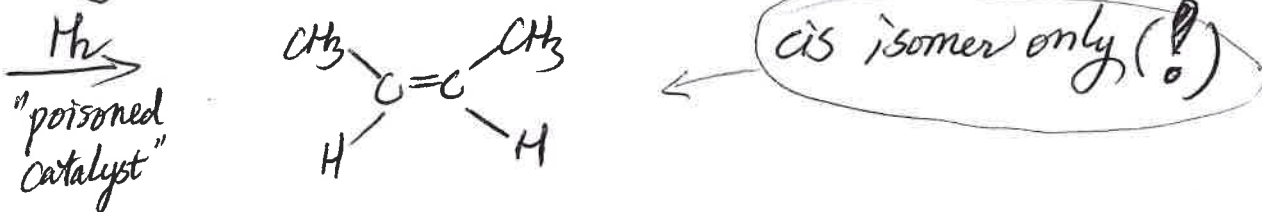
Note: "Markovnikov" vs. "anti-M". ~~para~~ *pertinent only*
 for terminal alkyne. $\text{R}-\text{C}\equiv\text{C}-\text{H}$ (*Internal alkynes - no selectivity possible.*)
 $\text{R}-\text{C}\equiv\text{C}-\text{R}'$



Controlled reduction, alkyne \rightarrow alkene

(i) Selectivity for syn adduct.

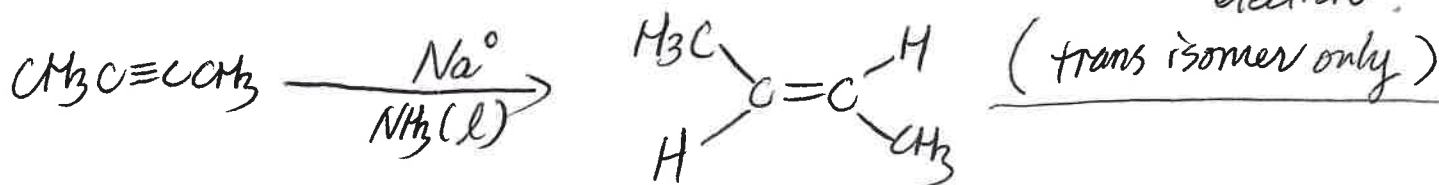
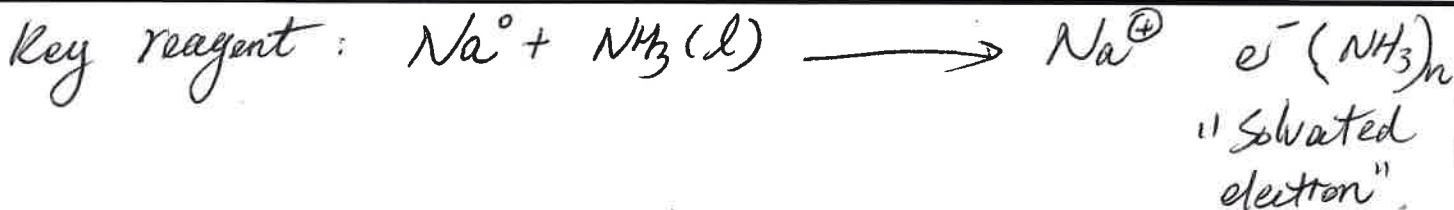
Key concept: "poisoned catalyst". Thus, $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$



(ii) Dissolving metal reduction \rightarrow produces trans alkenes.

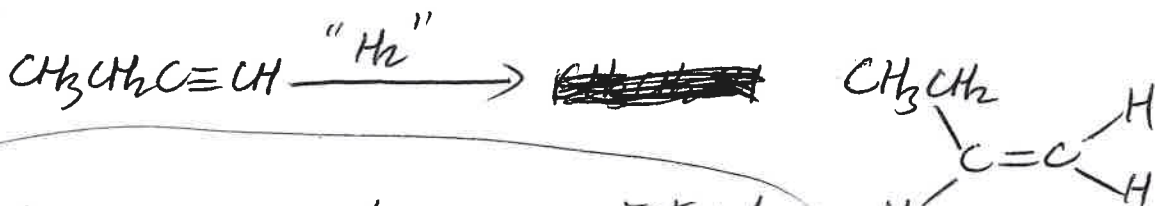
Course Chem 343 Lecturer Gellman
 Day Monday Date 11-30-15
 Notes Taken By LL Total # of Pages 4

Submit a *Single-sided Copy* to the Undergraduate Office
NO NOT STAPLE - ONLY WRITE NOTES INSIDE THE SQUARE BELOW



Note: complementary.

Note:



- Selectivity for cis/trans — internal alkyne related.