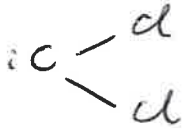
Course Chem 343 Lecturer Gellman
Day Wednesday Date 11/11/2015
Notes Taken By Lu Liu Total # of Pages 5

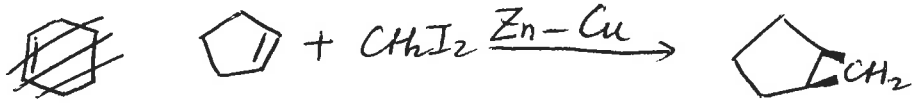
Submit a *Single-sided Copy* to the Undergraduate Office
NO NOT STAPLE - ONLY WRITE NOTES INSIDE THE SQUARE BELOW

Recall: Carbenes.



6e⁻ on carbon: very reactive!

Simmons–Smith reagent: use a metal atom to "tame" a carbene ($:CH_2$)



Reagent:

$I-CH_2-Zn-I$

Interstellar Carbenes:

$H_2C=C=C:$

$H_2C=C=C=C:$

etc.

Prof. R. McMahon @ UW

Alkyl halides as precursor for organometallic species with carbanion-like reactivity.

↓

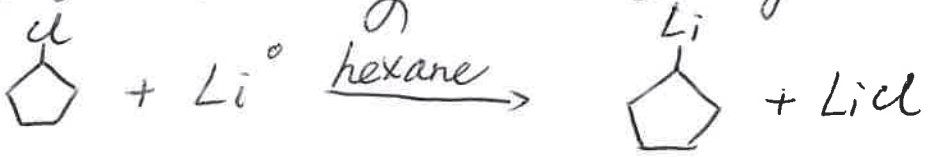
nucleophilic & basic @ C.

Course Chem 343 Lecturer Gellman
Day Wednesday Date 11/11/15
Notes Taken By Jin Liu Total # of Pages 5

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

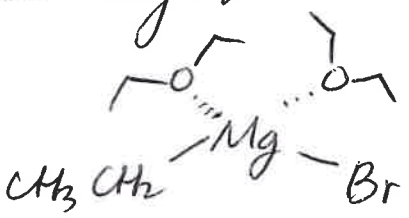
Two families:
Grignard Reagents (Mg)
Organolithium Reagents (Li)

Ex: $CH_3CH_2-Br + Mg^{\circ} \xrightarrow{Et_2O} CH_3CH_2-Mg-Br$



Role of Solvent

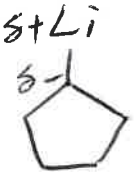
Ethers serve as lewis bases, can stabilize organo-metallic reagent.



← Solvent as lewis base
(Mg = Lewis acid)

e⁻-rich carbene!

$CH_3\overset{\delta-}{C}H_2-\overset{\delta+}{Mg}Br$ sort of like "$CH_3\overset{\ominus}{\ddot{C}}H_2\ \overset{\oplus}{Mg}Br$"



"

"

Explain why the carbon atoms are nucleophilic (stay tuned...) & strongly basic.

Course Chem 343 Lecturer Gellman
Day Wednesday Date 11/11/15
Notes Taken By Ian L. Total # of Pages 5

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

Rapid rxn of RMgX or RLi with even relatively weak acids, eg., H_2O. Use this reactivity for ~~site~~ sitespecific introduction of D. (D = deuterium (H isotope)

Ex. $CH_3CH_2\underset{Cl}{CH}CH_3 \xrightarrow[Et_2O]{Mg} CH_3CH_2\underset{MgCl}{CH}CH_3 \xrightarrow{D_2O} CH_3CH_2\underset{D}{CH}CH_3$

(Ditto for $CH_3CH_2\underset{Li}{CH}CH_3$)

Usually we try to avoid acid-base reactivity of R-Li or RMgX in order to harness nucleophilic reactivity

Chap. 10 — Alcohol (R-OH) & Thiols (R-SH)

Rec. Problems: 1, 3–28, 30, 31, 38a–41, 43-51, 57–59, 66, 68a, b.

Acid-base chemistry

CH_3O-H $pK_a \sim 16$ $\left(H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OH\right)$ $pK_a \sim 19$

Formation of alkoxides

"quantitative deprotonation" (i.e., complete deprotonation)?

Course Chem 343 Lecturer Gellman
Day Wednesday Date 11/11/15
Notes Taken By Ln L. Total # of Pages 5

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

Note: NaOH, KOH inadequate !

$CH_3CH_2\ddot{O}H + K^{\oplus}\,{}^{\ominus}\ddot{O}H \rightleftharpoons CH_3CH_2\ddot{O}:^{\ominus}\,K^{\oplus} + H_2\ddot{O}:$

NOT quantitative – expect substantial quantities of both $EtO^{\ominus}$ & $^{\ominus}OH$.

Need a stronger base for quant. deprotonation.

$\Rightarrow NaH \approx$ "$Na^{\oplus}:H^{\ominus}$" ← strong base !

Hydride.

pKa H–H ? ~37.

Thus:

$CH_3CH_2OH + NaH \longrightarrow CH_3CH_2\ddot{O}:^{\ominus}\,Na^{\oplus} + H_2(\uparrow)$ (quant.)

Thiols, pKa ~ 10.

$\therefore CH_3CH_2O^{\ominus}Na^{\oplus} + \sim\!\!\sim SH \underset{(\leftarrow)}{\longrightarrow} CH_3CH_2OH + \sim\!\!\sim \ddot{S}:^{\ominus}\,Na^{\oplus}$

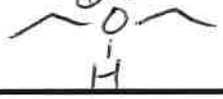
Alcohols as bases (weak)

$CH_3CH_2\ddot{O}H + HCl \rightleftharpoons CH_3CH_2\overset{H}{\overset{|}{\overset{\oplus}{O}}}-H \;\; Cl^{\ominus}$

$\left(H-\overset{H}{\overset{|}{\overset{\oplus}{O}}}-H\right)$

pKa ~ −2.

Ditto for ethers.



pKa ~ −2.

Course Chem 343 Lecturer Gellman

Day Wednesday Date 11/11/15

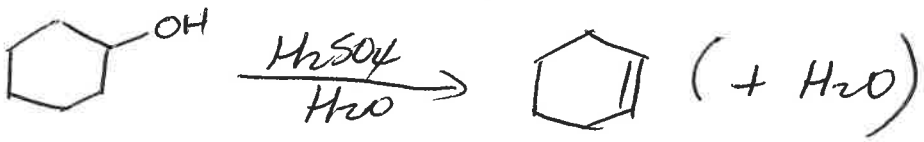
Notes Taken By Ln L Total # of Pages 5

Submit a *Single-sided Copy* to the Undergraduate Office

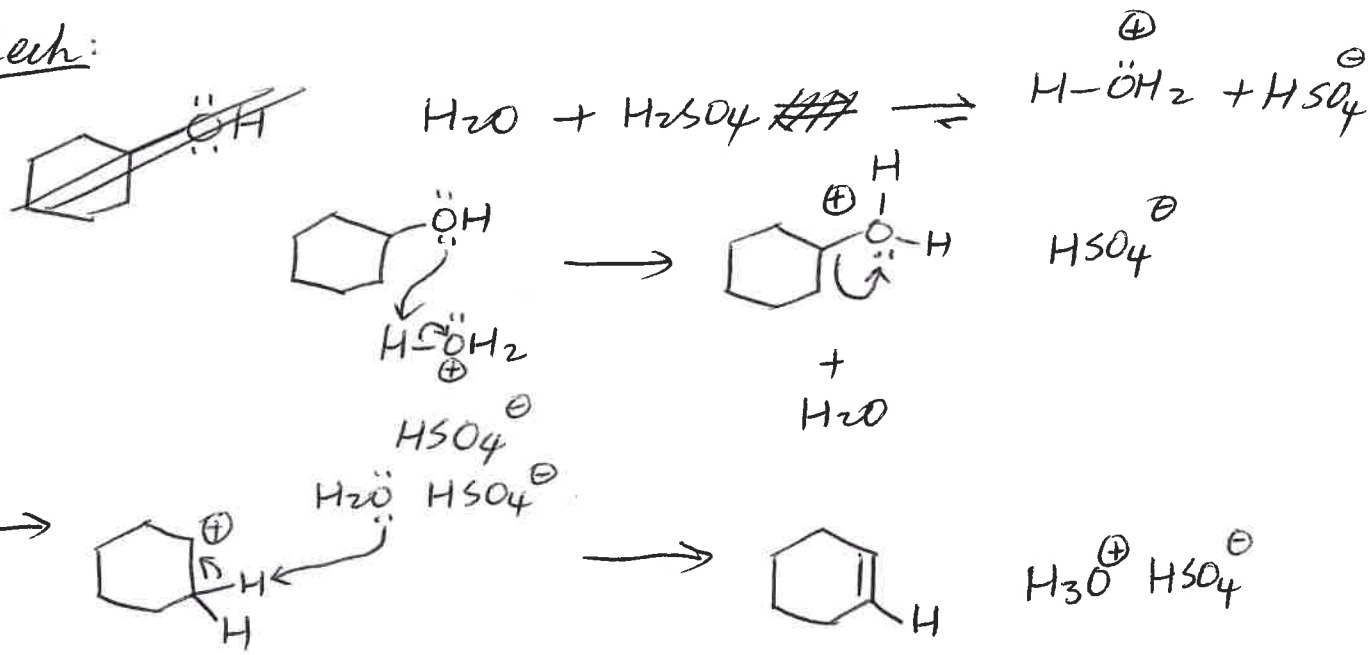
NO NOT STAPLE - ONLY WRITE NOTES INSIDE THE SQUARE BELOW

Acid catalyzed dehydration of alcohols (to form alkene)

Ex.



Mech:



E1