Do Not Use Pencil *Do Not Staple, Please!*

Course Chem 345 Lecturer Gellman

Day Monday Date 2/29/16

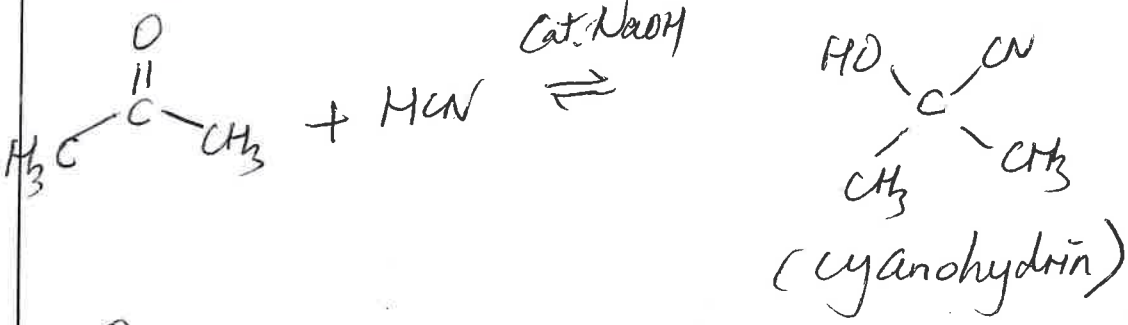
Notes Taken by Lu Liu Page 1 of 6 (Total Pages)

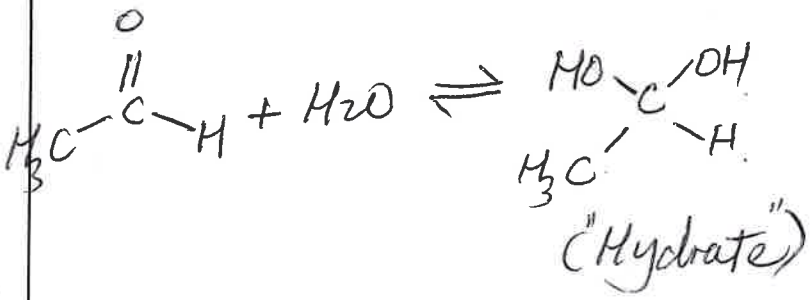
Submit a ***COPY*** of these notes for posting, please.

Office hour TODAY & Next Monday (other than Fridays)

Review Session TODAY (not Wed), B371, 5PM.

Recall: Reversible addn rxns of Aldehydes & Ketones

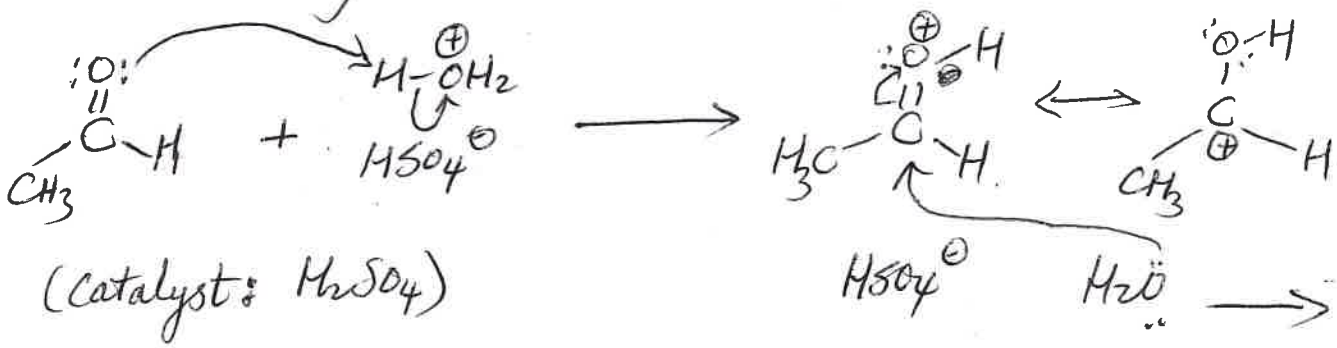




2 mechanisms for hydrate formation:

1) Base-catalyzed (follows cyanohydrin ... you fill in)

2) Acid-catalyzed



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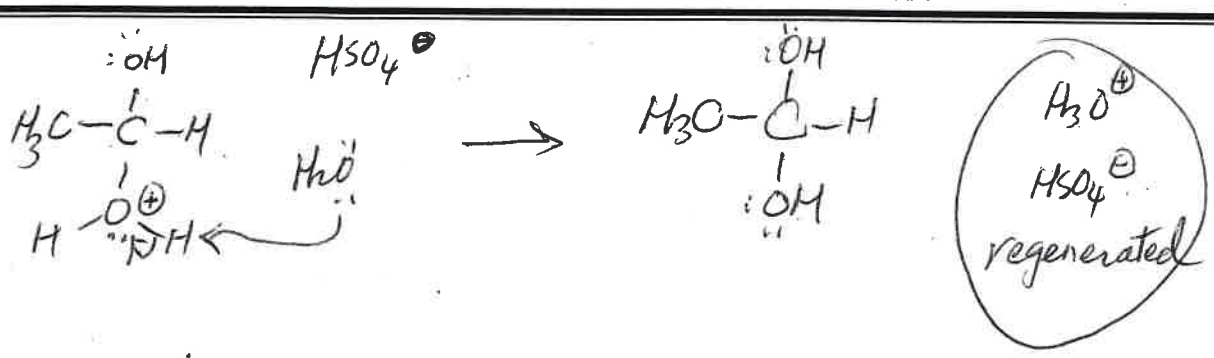
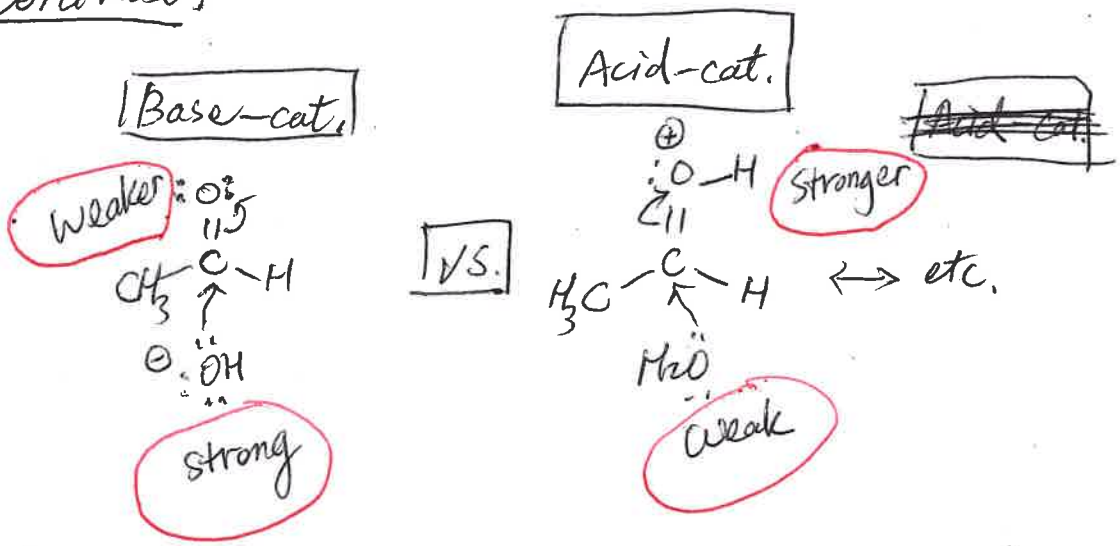


Contrast:

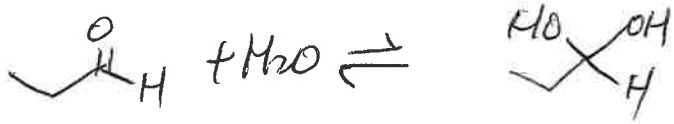


Variations in position of equilibrium (K_{eq}) as a function of A/K structure provides insight on factors that influence A/K reactivity.

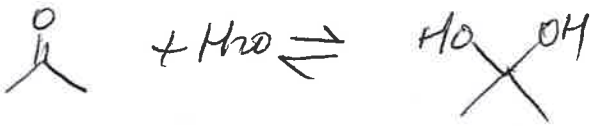
Key observations

1) Aldehydes generally more prone to hydrate formation than analogous ketones.

Ex

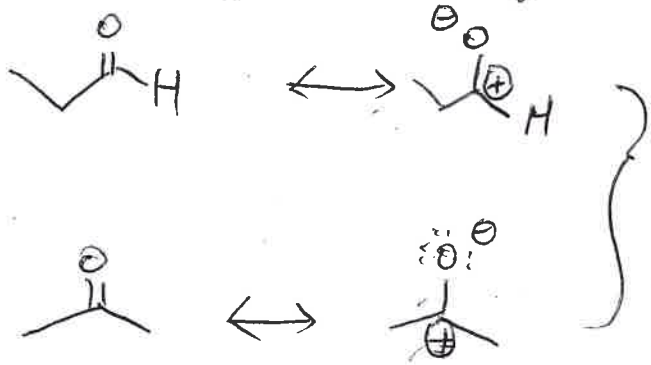


Keq ~4

* 

~0.001

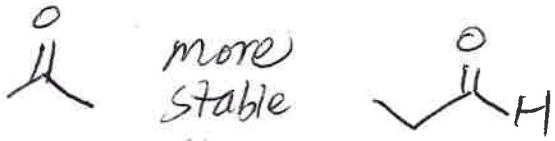
Rationale from "charge-separated structures of A/K...



Recall: $2^\circ C^\oplus$ less stable than $3^\circ C^\oplus$

MINOR

This effect seen in ΔH_f° for aldehyde vs. ketone



more stable than by 7 kcal/mol ($\Delta\Delta H_f^\circ$)

Note: Little or no "$C^\oplus$" nature in hydrate forms (no C=O)

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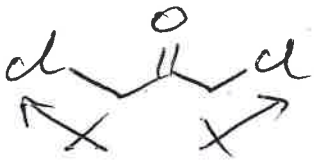
② Electronegative substituents near C=O favor hydrate

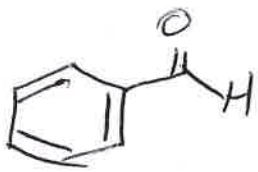
Ex



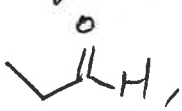
$K_{eq} \sim 10$. (vs. $K_{eq} \sim 0.001$ for )

③ Conjugated π-system disfavors hydrate.

Ex

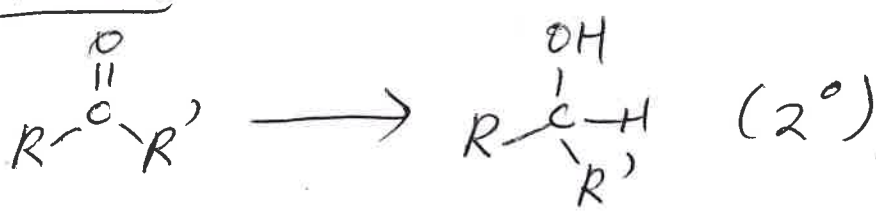


$K_{eq} \sim 0.01$

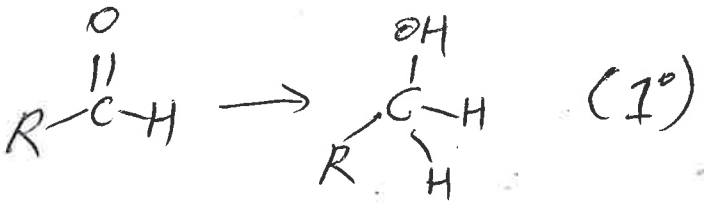
(vs.  , $K_{eq} \sim 1$)

Carbonyl reductions — irreversible addn rxns

General:



(2°)



(1°)

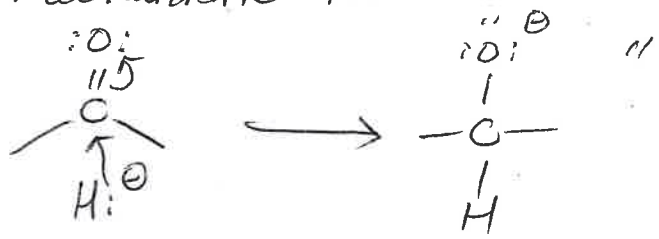
Reagents:

$NaBH_4$ & $LiAlH_4$ — Both sources of "nucleophilic hydride" ("$H:^{\ominus}$")

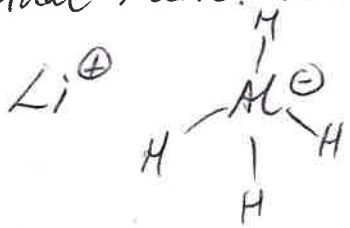
$Li^{\oplus}\ AlH_4^{\ominus}$

$Na^{\oplus}\ BH_4^{\ominus}$

Key mechanistic theme:

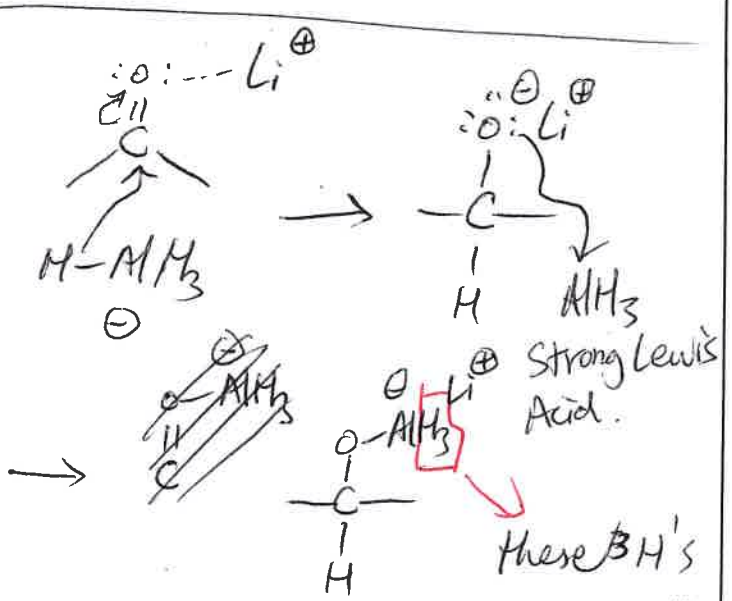


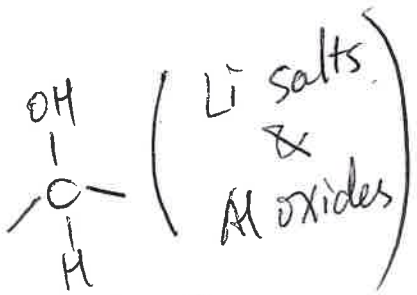
Actual mech. more complex...



Very reactive species.

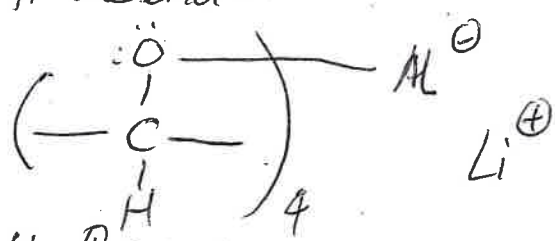
$Li^{\oplus}$ serves as a Lewis acid to activate the carbonyl...

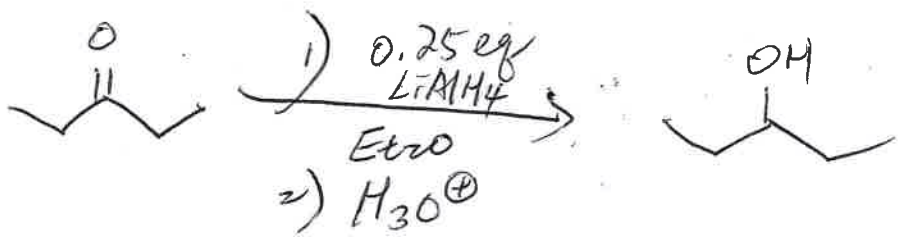




Then add $H_3O^{\oplus}$ (H_2O)

At the end...





Note: Aprotic solvent

Et2O ≡ 

(vs. ~~H2O~~) ~~EtOH~~ → side rxns