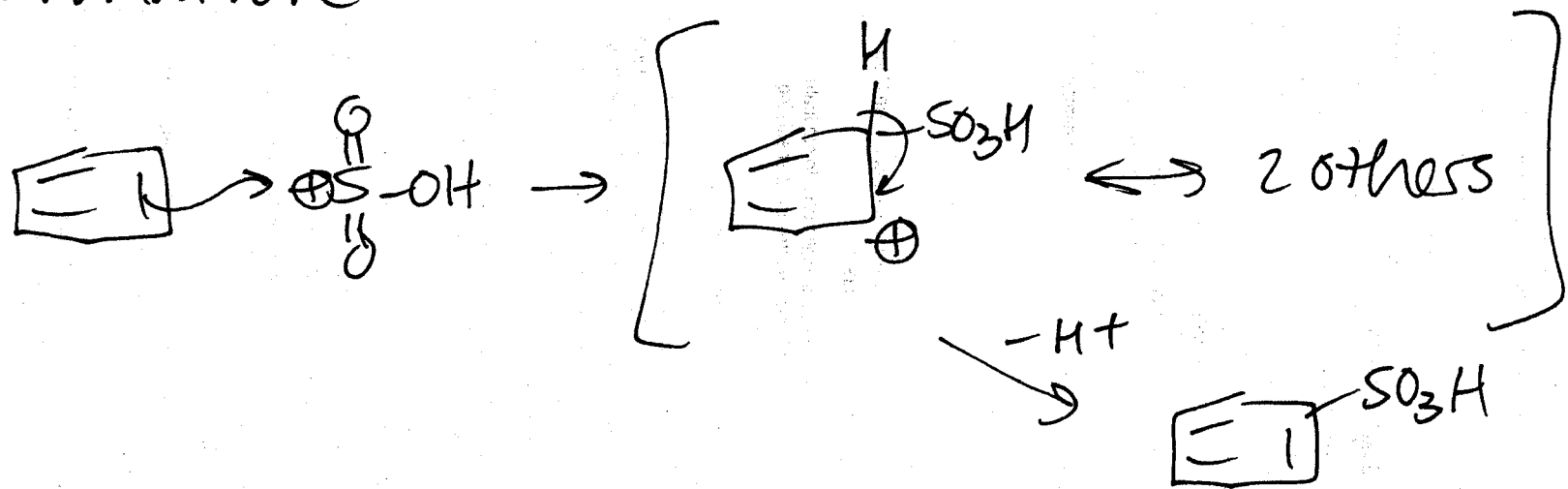
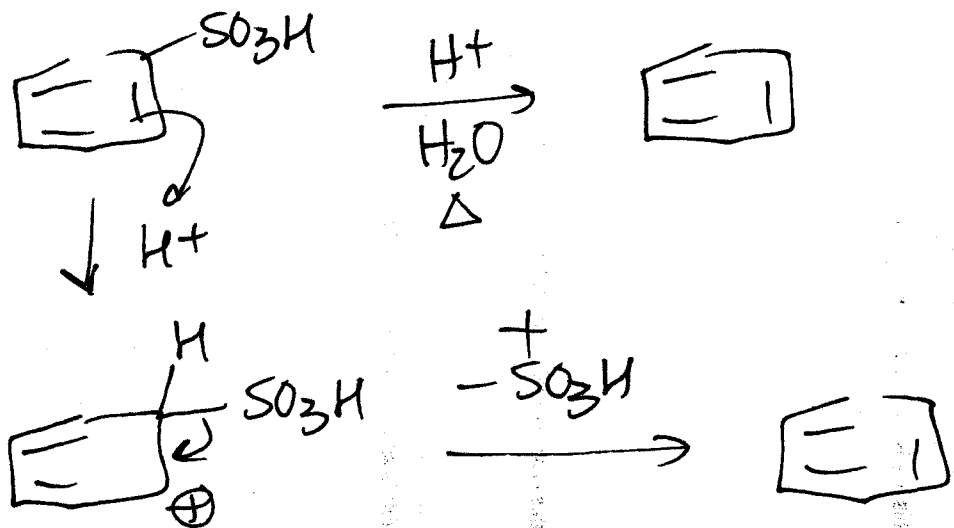


3a Sulfonation

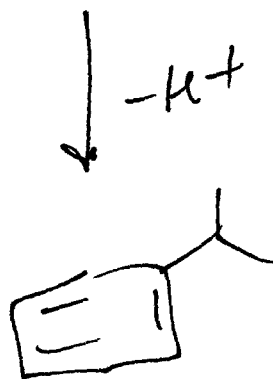
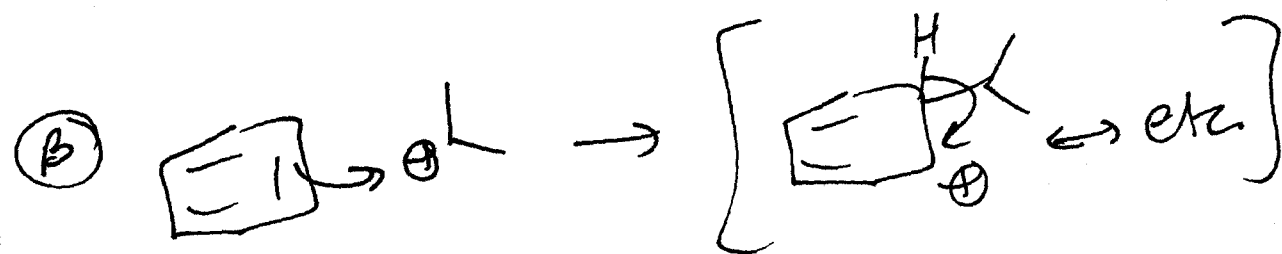
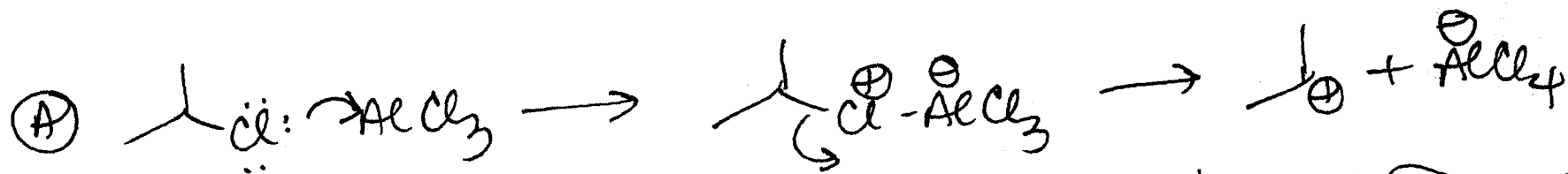
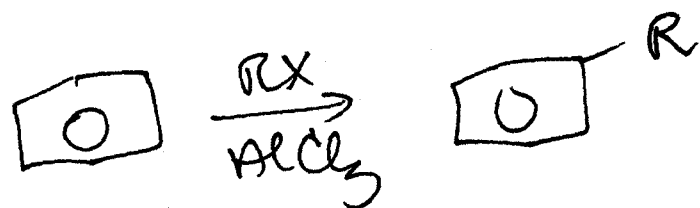


3b. Desulfonation * the only reversible EAS rxn.



* Le Chatelier's Principle
in action

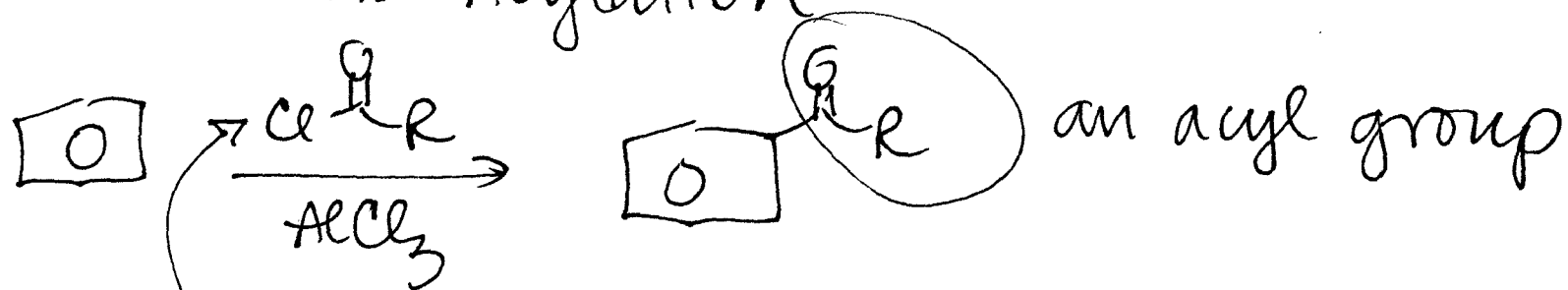
4 a. Friedel-Crafts alkylation



sometimes an ion pair;
sometimes more like the preceding acid-base complex

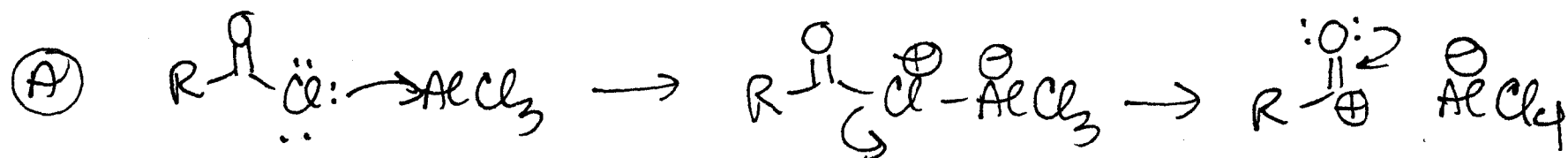
But - always behaves as if it were the carbocation.

4b. Friedel-Crafts Acylation

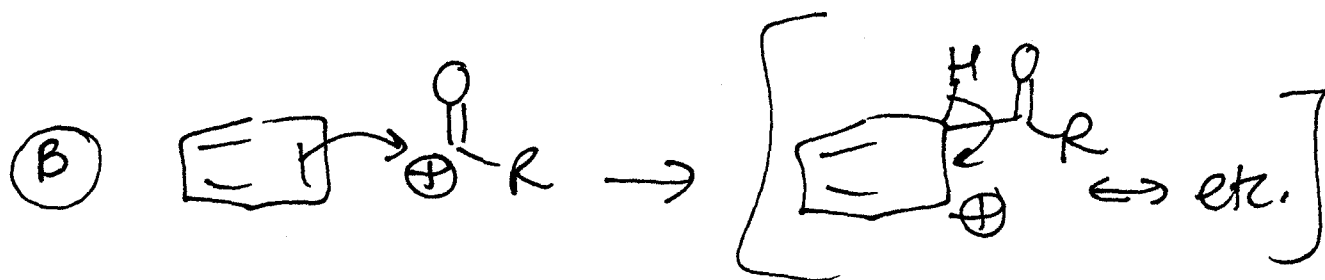


NOT
 R-C(=O)Cl

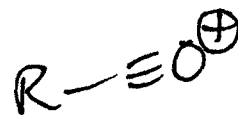
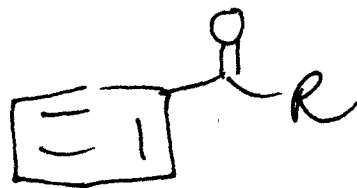
$\text{R-OH} \xrightarrow{\text{SOCl}_2} \text{R-C(=O)Cl}$
 * the Cl is attached to the C=O



an acylium ion



$\downarrow -\text{H}^+$



Issues

1. Electrophile is a cation.
2. Limitations on RX?
3. Reactivity
4. Substituent Effects

F-C Alkylation

Rearrangement is a real problem here!

X must be attached to sp^3 carbon.

Alkylbenzenes are more reactive than benzene. \Rightarrow can see over-rxn.

If there is already a strong e^- withdrawing group on the ring —

NRX.

F-C - Acylation

Acylium ions are stable — no rearr.

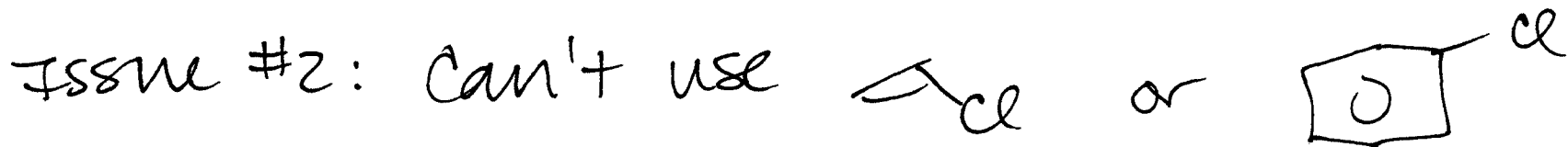
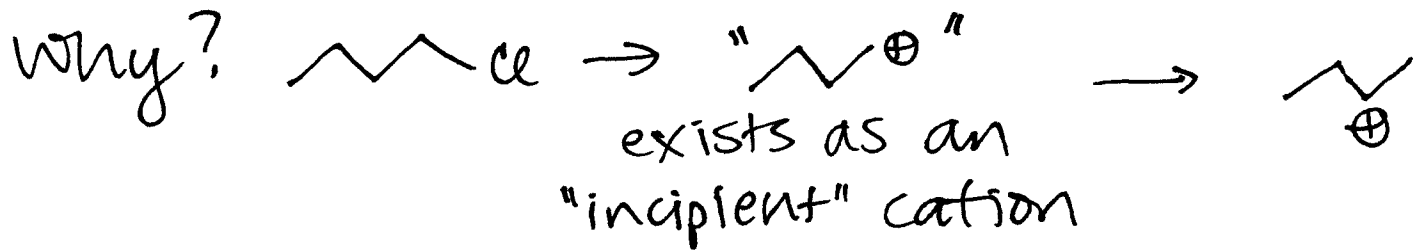
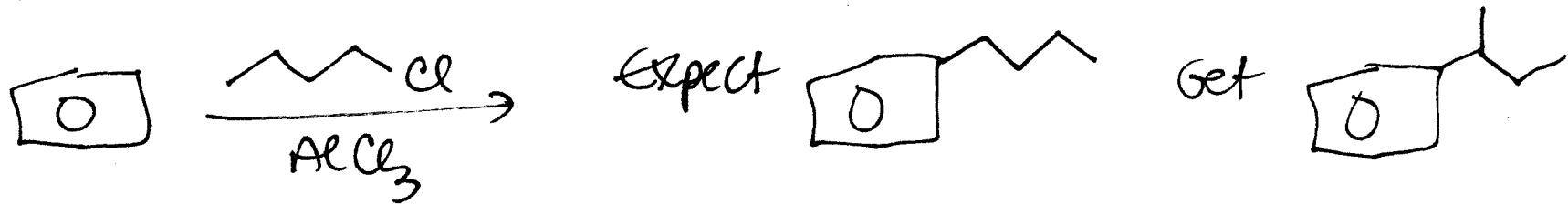
must use $Cl-C(=O)R$
(or $R-C(=O)Cl$)

* $Cl-CH_3$ DOES NOT WORK

Acy benzenes are less reactive than benzene \Rightarrow no over-rxn.

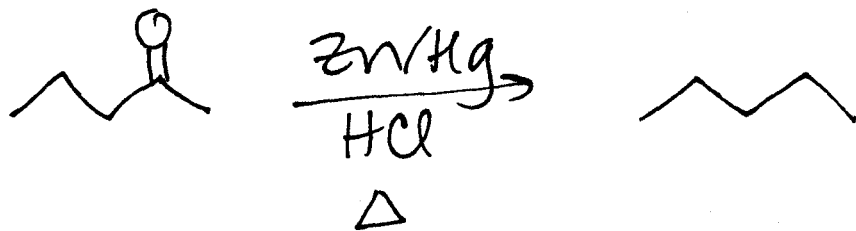
Still a problem.

Example of Issue #1:

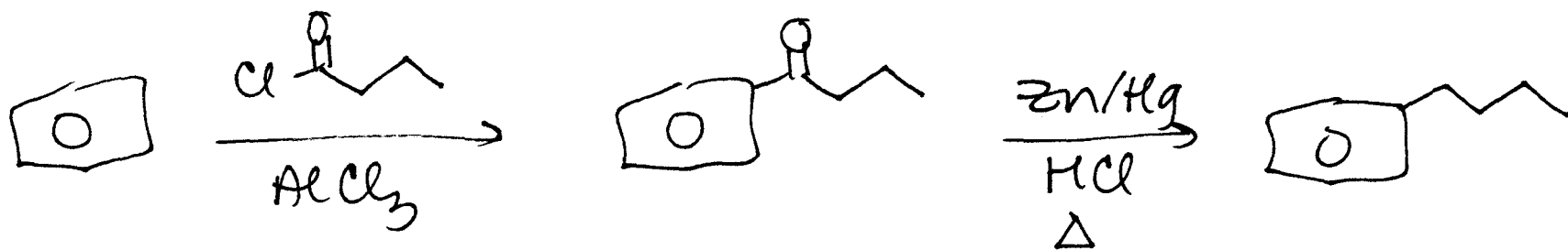
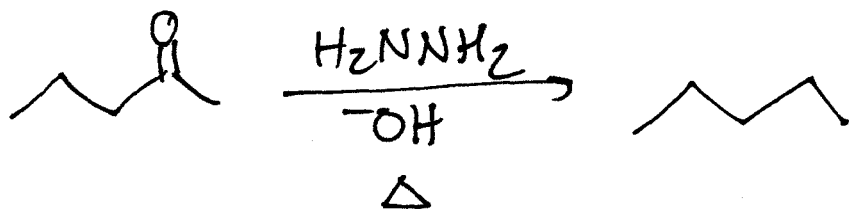


How can we make long chain alkylbenzenes if F-C alkylation leads to branching?

1. Clemmensen Reduction - aldehydes + ketones

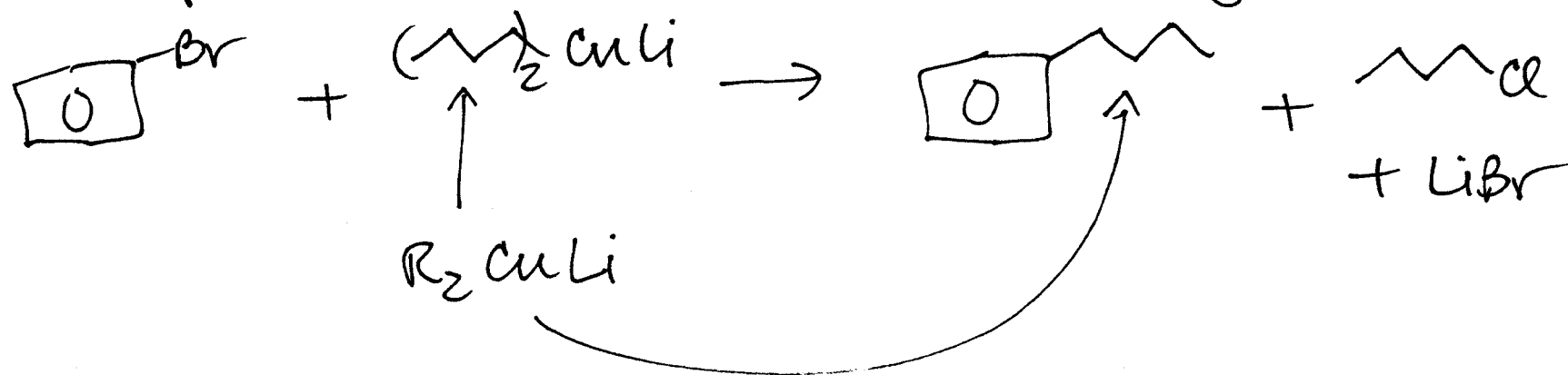


2. Wolff-Kishner Reduction - aldehydes + ketones



Always gives $\text{Ph}(\text{CH}_2)_n\text{R}$

Another option - use a Gilman reagent.



SKIP

{ Gatterman-Koch
Stille
Suzuki

