Course Chem 345 Lecturer Gellman

Day Friday Date 02/06/2015

Notes Taken By Leslie Rank Total # of Pages 4

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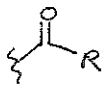
Electrophilic Aromatic Substitution

1) generation of a reactive electrophile
2) nucleophilic attack on the electrophile by the π system
3) removal of proton to regain aromaticity

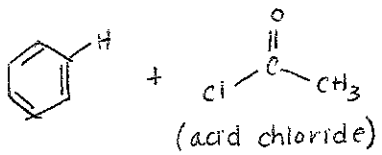
Friedel-Crafts Acylation:

acyl group: 

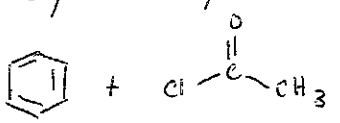
Two distinct steps

not catalytic amount!

example:

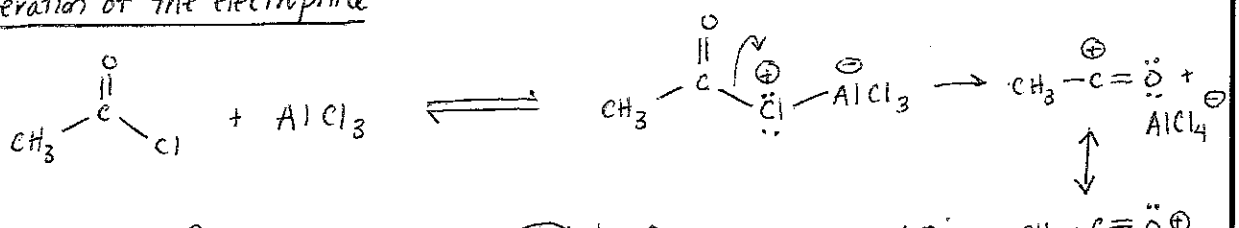


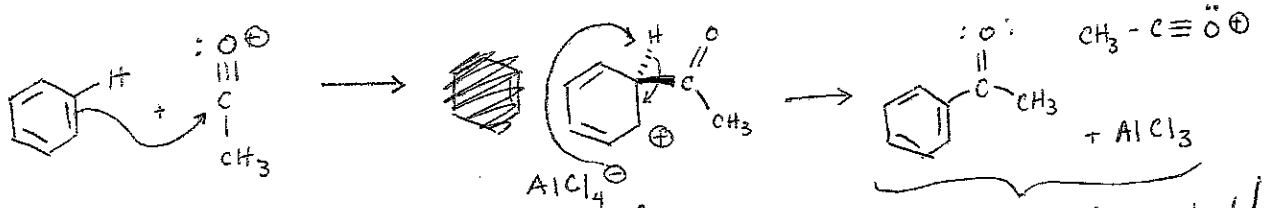
- new C–C bond formed!
- Two seperate steps:



= NONSENSE

Generation of the electrophile





can you draw other resonance structures?

not really the product!

* when the EAS process is completed, the product is a Lewis acid-base complex

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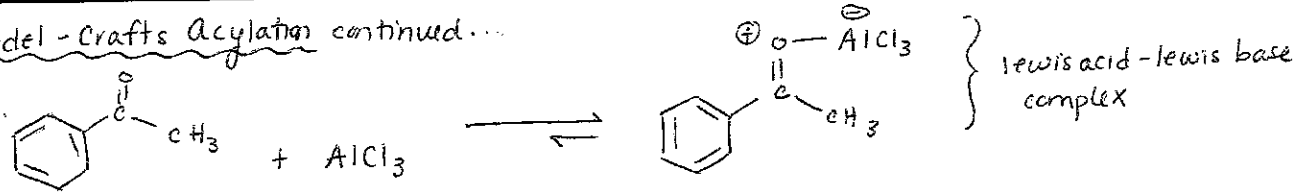
Friedel-Crafts Acylation continued...

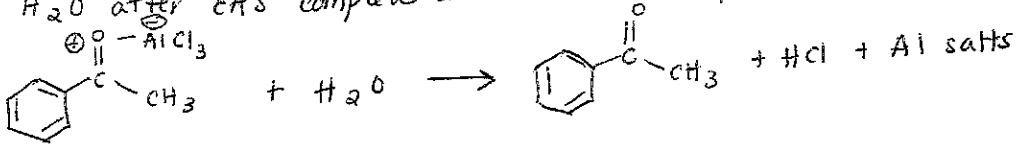


- Recall, ketones are slightly basic!
- product (which has a ketone) forms a lewis acid-lewis base complex

Key Features:

1) need a full molar equivalent of $AlCl_3$ (not catalytic)
   - not catalytic because it forms a lewis acid-lewis base complex with product

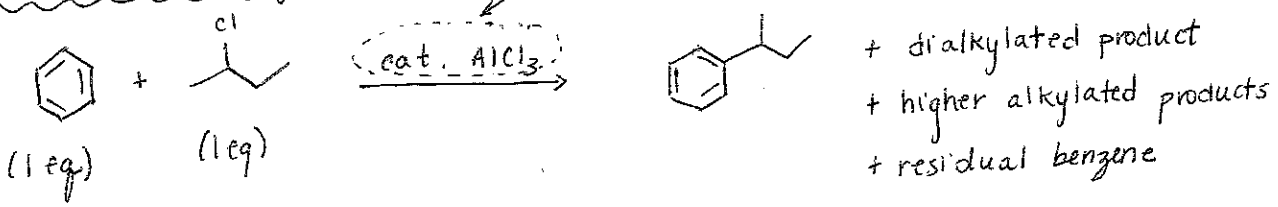
2) Need H_2O after EAS complete = "liberates" the product



* Prof. Gellman notes typo on top of page 761 (structure on left missing an oxygen.

Friedel-Crafts Alkylation

different from Friedel-Crafts Acylation!



- This product is b/c of similar quantities of starting material
- different from previous EAS cases ⇒ multiple products
- synthetic perspective: this rxn is NOT useful be of multiple products

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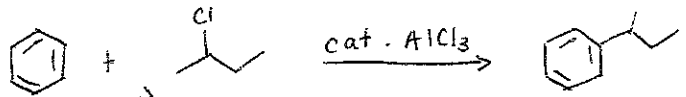
Friedel-Crafts alkylation continued....

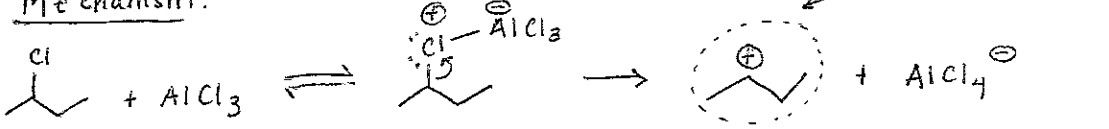
As an organic chemist, what can I do to get only the monoalkylated benzene?



(large molar excess) + lot of residual benzene

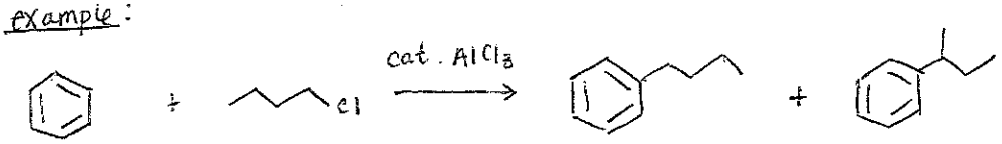
- only reasonable if easy to separate product from excess starting material
- only reasonable if starting material is cheap

Mechanism: carbocation formation



- Note: unlike acylation no H_2O is needed in this rxn!
- Note: carbocations can undergo rearrangements!!!

example:



(excess)

why do we get di- tri- alkylated products? why not in acylation, bromination, nitration?

Q: Why does F.C alkylation tend to give multiple products, while other EAS rxns can be stopped after 1 addition?

A: Depends on whether substituent causes the ring to be more or less reactive than benzene.

"Activating" vs "Deactivating" Substituents

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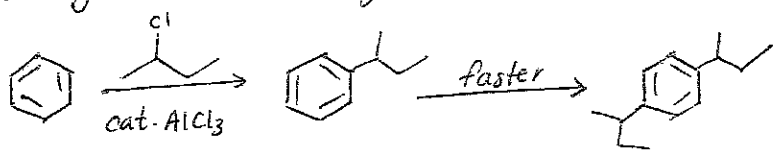
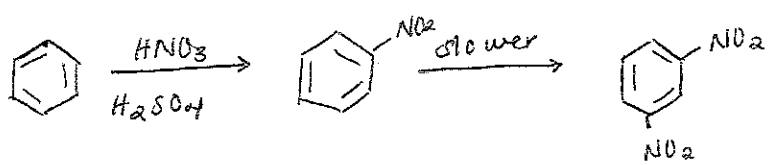
Activating vs Deactivating Substituents



alkyl groups "activating"



Nitro group "deactivating"

* If the 2nd step is slower, it is possible to stop rxn after 1st addition (single addition product < reactive than starting material)

* If the 2nd step is faster, then it is impossible to stop after a single addition (product is more reactive than starting material).