Course 345 Lecturer Gellman (Dr. Barta)

Day Wed Date 2/26

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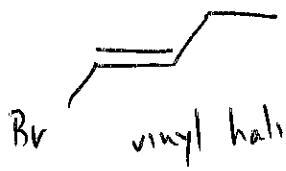
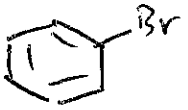
Aryl + vinyl halides



vinyl halide



aryl halide

* Do not participate in S_N2 or $S_N1/E1$ rxns

↑ due to sterics

↑ due to $sp^2 \rightarrow sp$ transition

(unstable intermediates)

Nucleophilic aromatic substitution reactions

Requirements:

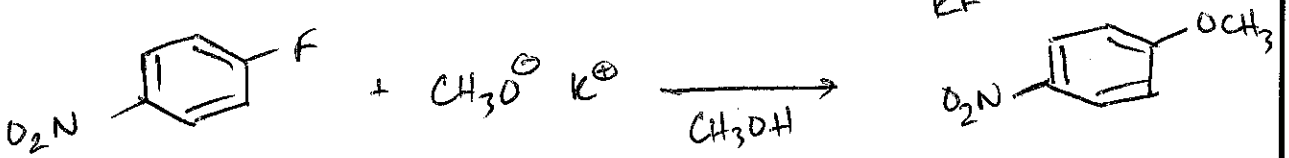
1) Good leaving group

reactivity trend: Ar-F >> Ar-Cl ≈ Ar-Br > Ar-I

opposite trend as compared to S_N2!

2) Strong e^--withdrawing group ortho or para to L.G.

(example: $-NO_2$)



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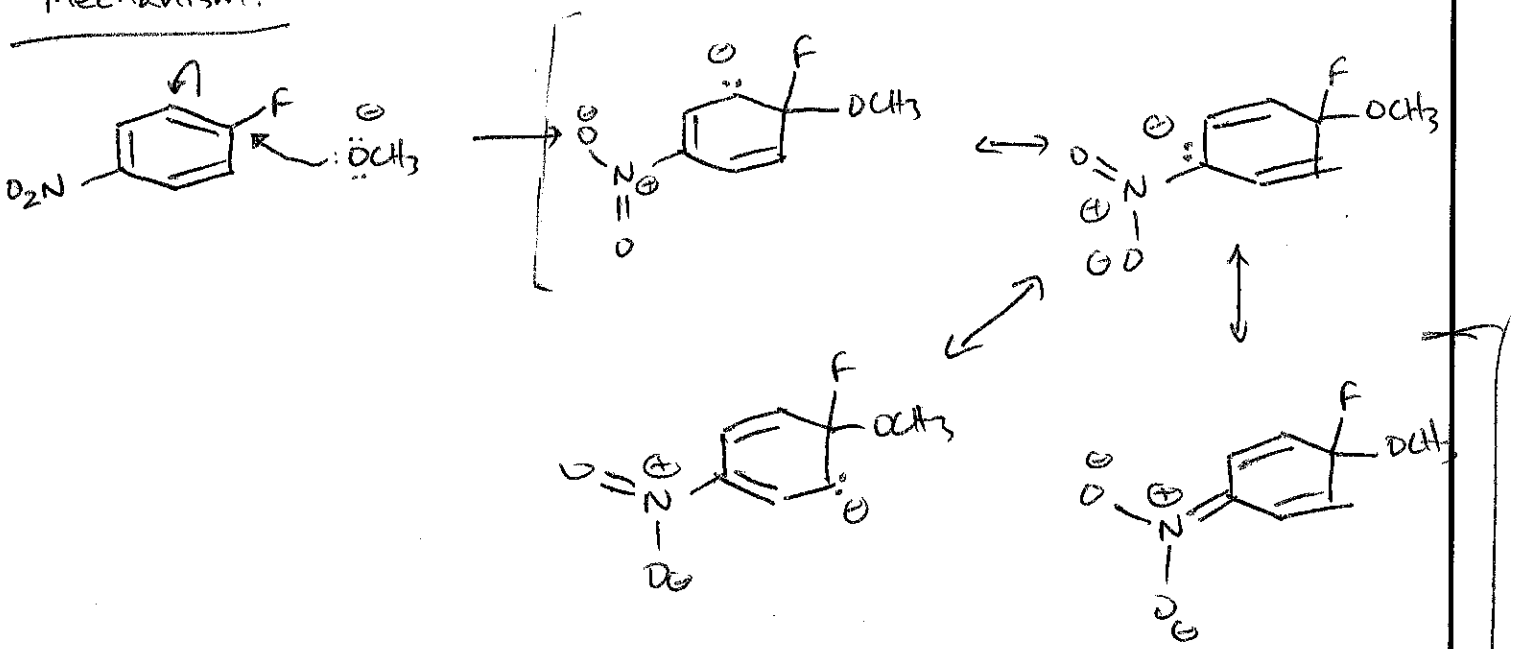
Mechanism:



end of mechanism:

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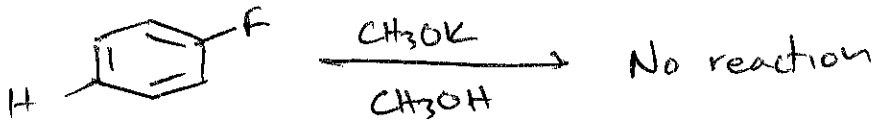
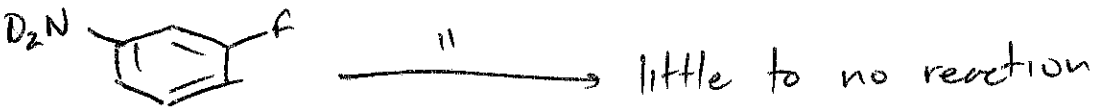
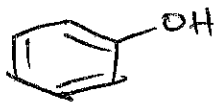
other cases....



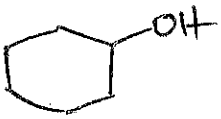


Phenols



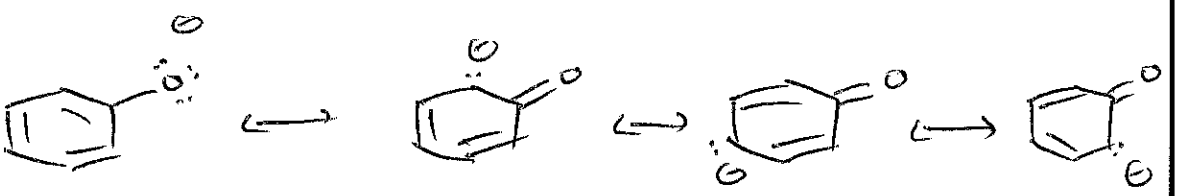
$pK_a \sim 10$ (memorize this)

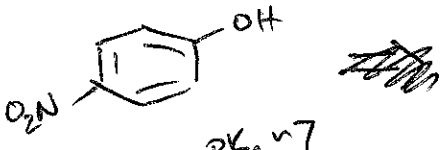
compare to



$pK_a \sim 17$

- resonance stabilization of conjugate base gives phenol its acidity





$pK_a \sim 7$

- Electron-withdrawing groups increase acidity of phenol

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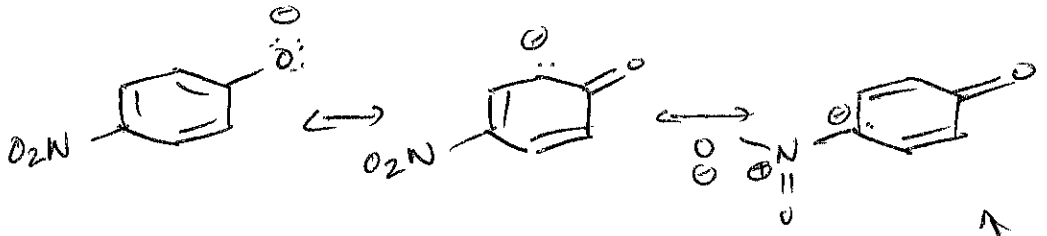
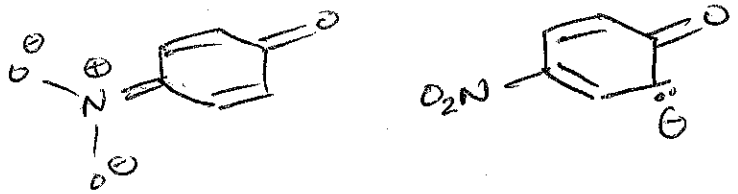
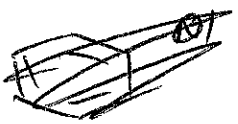
res:

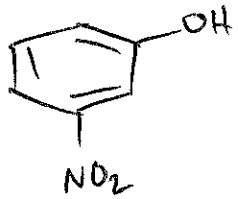


- NO_2 group lowers pK_a the most when in ortho/para position



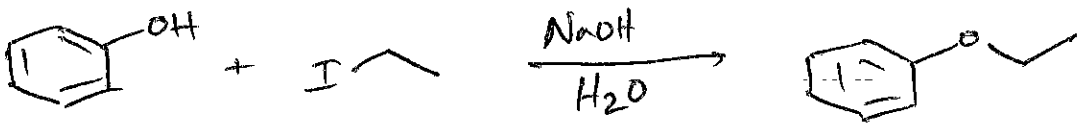
- In meta, it still lowers pK_a due to inductive effects, but not to same extent





$pK_a \sim 8.4$

- phenolates (i.e. phenoxides) are excellent S_N2 nucleophiles



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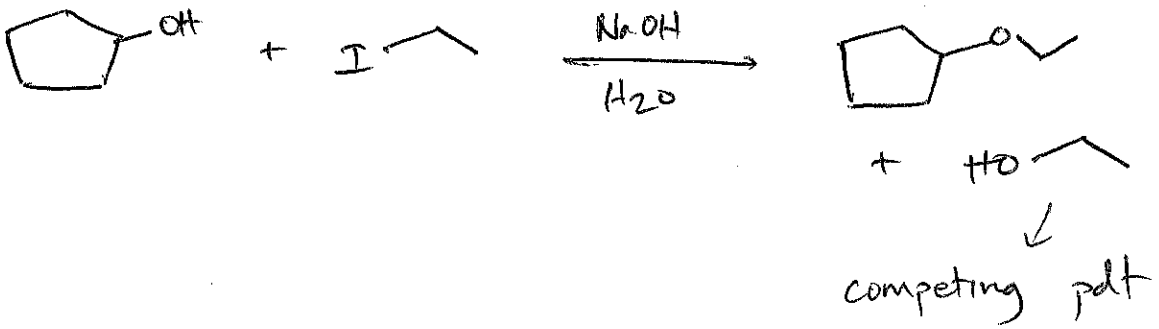
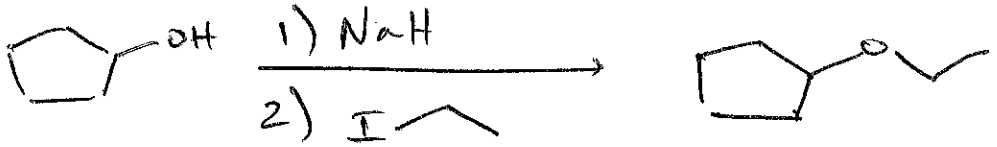
Compare:



competing pdt

Way to actually do this reaction (343):



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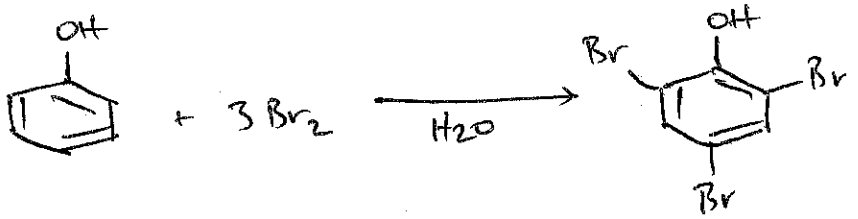
example:



~~don't need FeBr3, due~~

1) No Lewis acid catalyst needed, due to high reactivity of phenol

2) Hard to stop after 1st addition of Br

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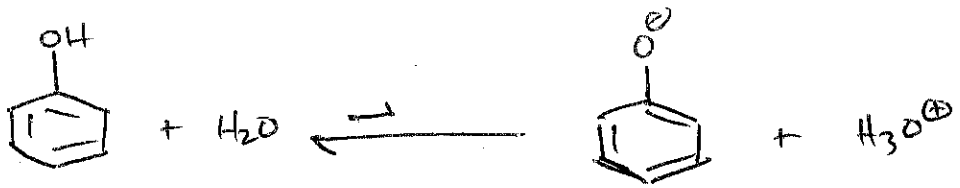
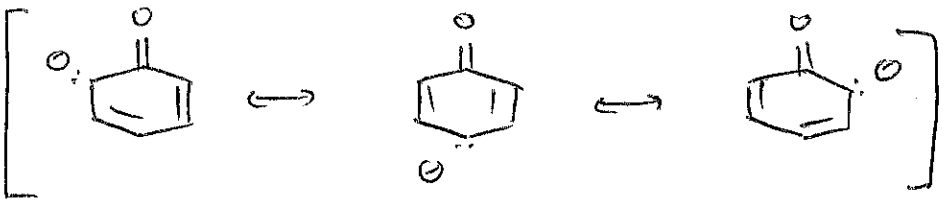
Mech:

strong electrophilic source of Br

Also:



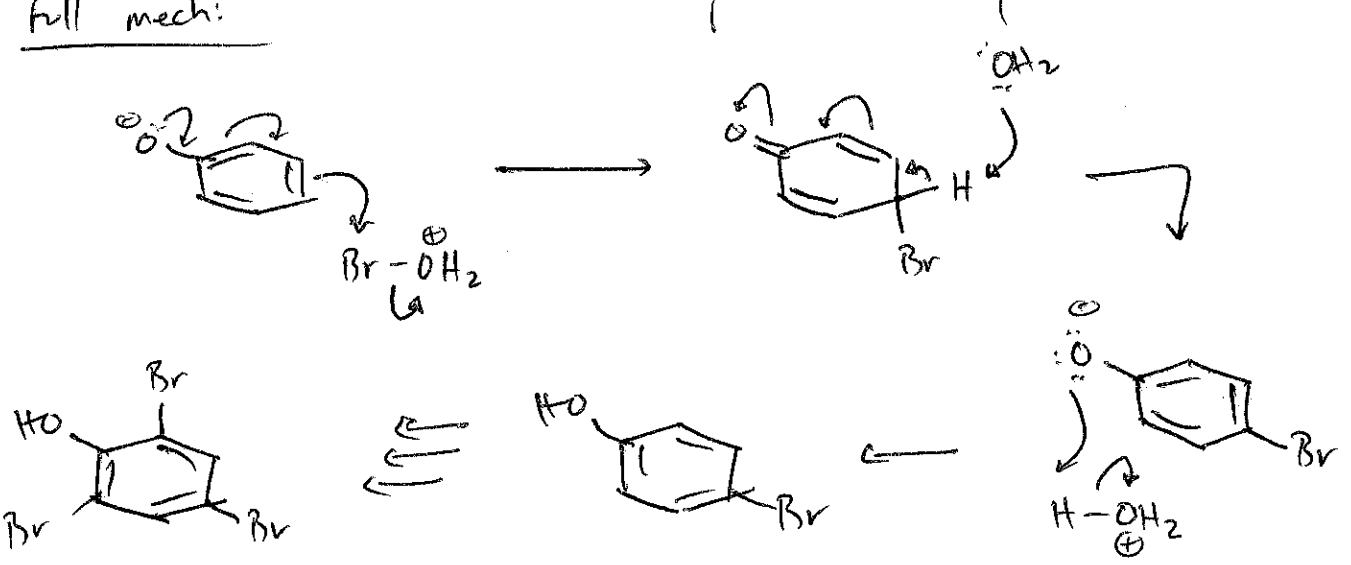
res structures:



enhanced nucleophilicity at o/p position

Full mech:

no charge, stable intermediate



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* 

is more acidic than 

, therefore

subsequent additions of Br occur even faster.

This is why it's hard to stop at one addition.