

Do Not Use Pencil

Do Not Staple, Please!

Course Chem 345

Lecturer Grellman

Day Wednesday

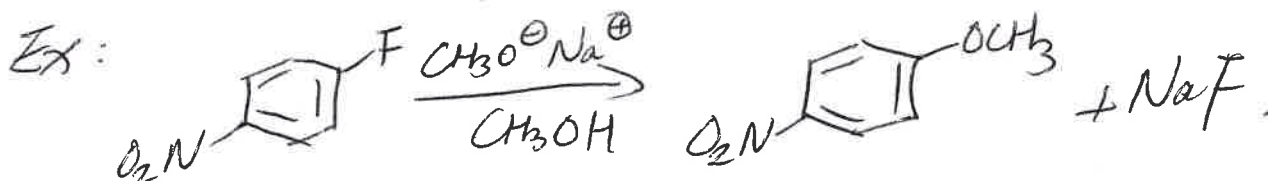
Date 2-24-16

Notes Taken by Lulu

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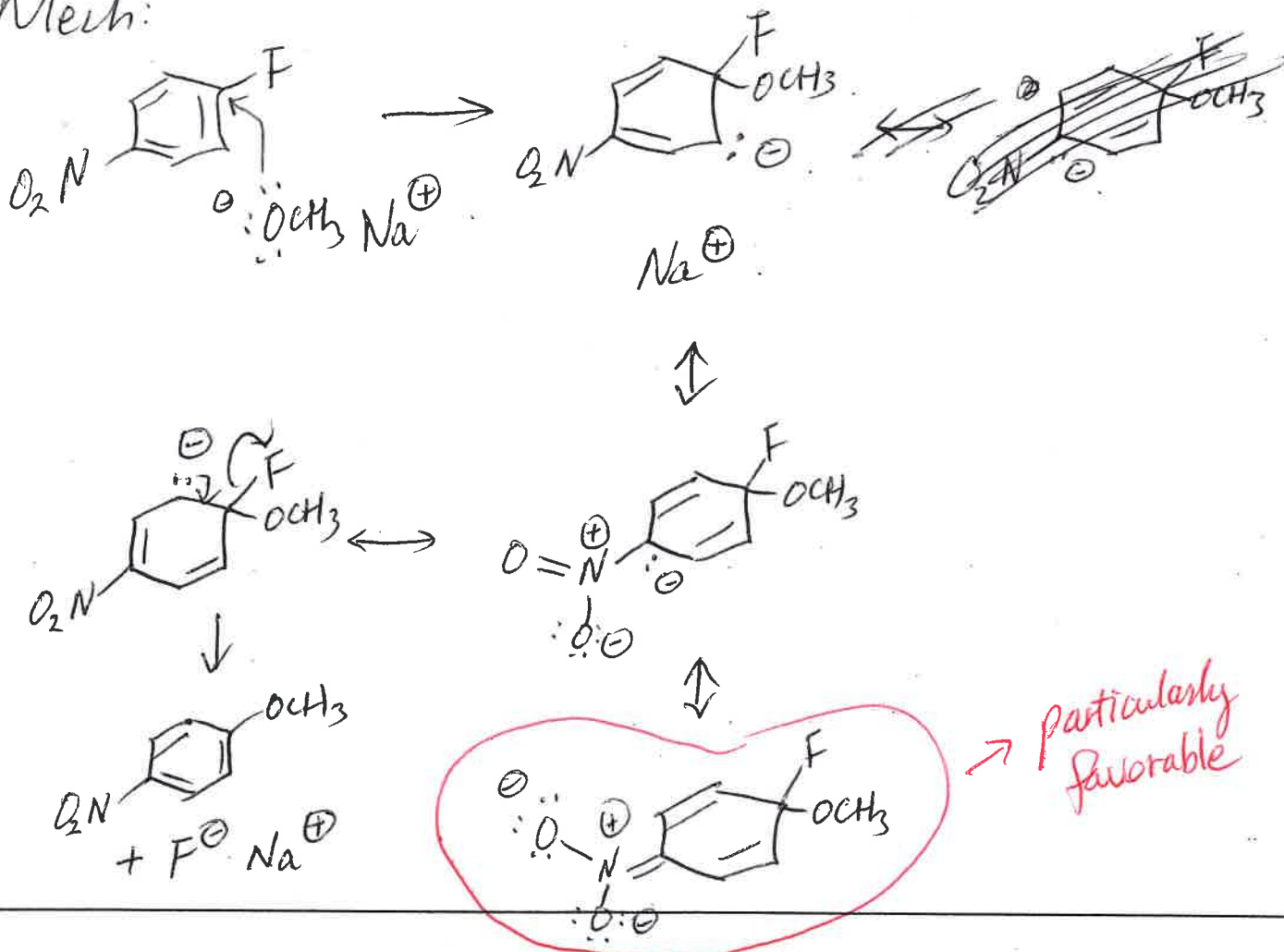
Recall: Nucleophilic Aromatic Substitution (N_AS)



Require:

- Leaving group.
- EWG ortho or para to LG.

Mech:



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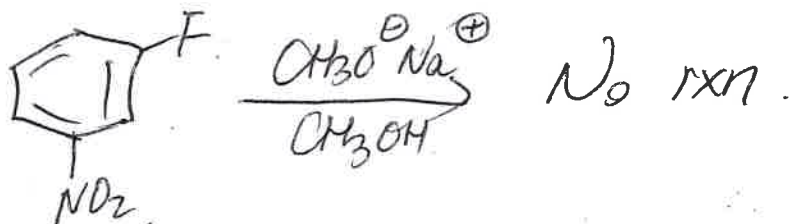
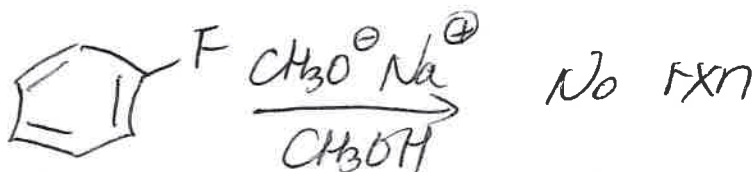
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Importance of EWG illustrated by potential NAs rxns that do not occur.



phenols



vs

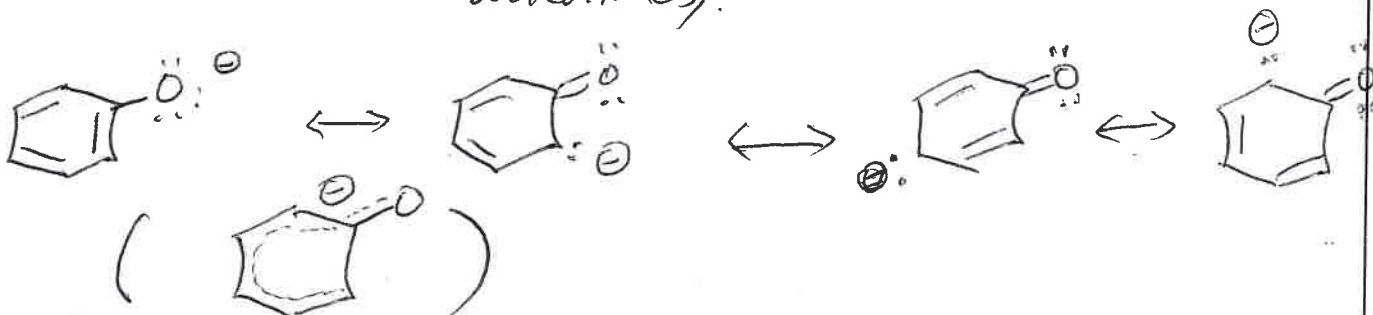


pKa ~ 10.

pKa ~ 16

Conjugate base of phenol. ("phenoxide" or "phenolate") is resonance stabilized

\ominus delocalized (but \ominus localized in saturated alkoxides).



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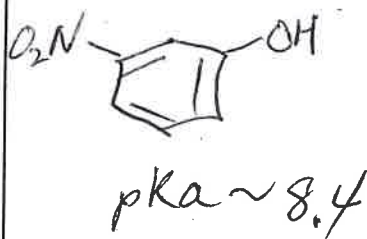
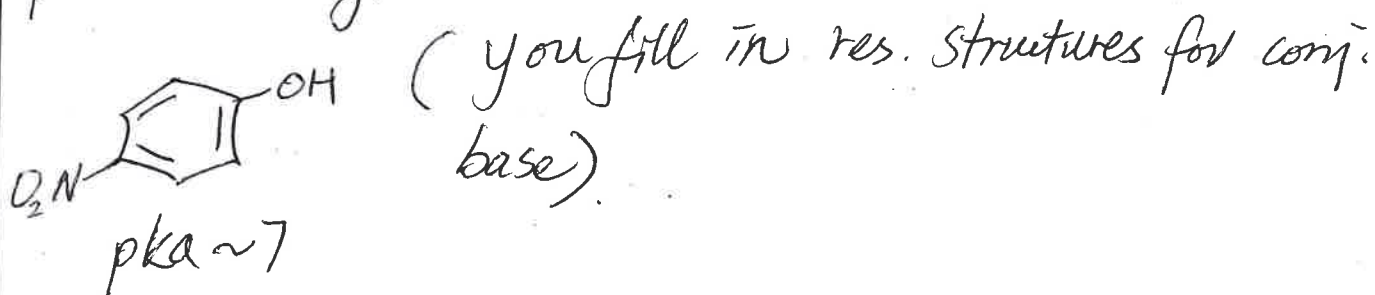
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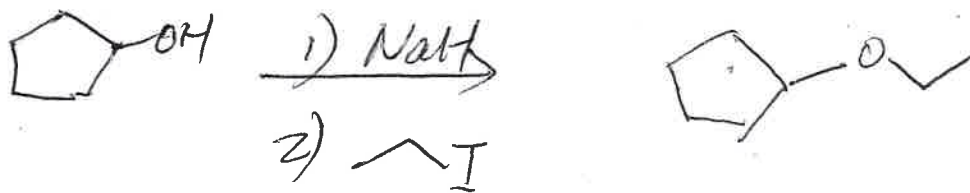
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Qualitatively anticipate substituent effect on phenol acidity.

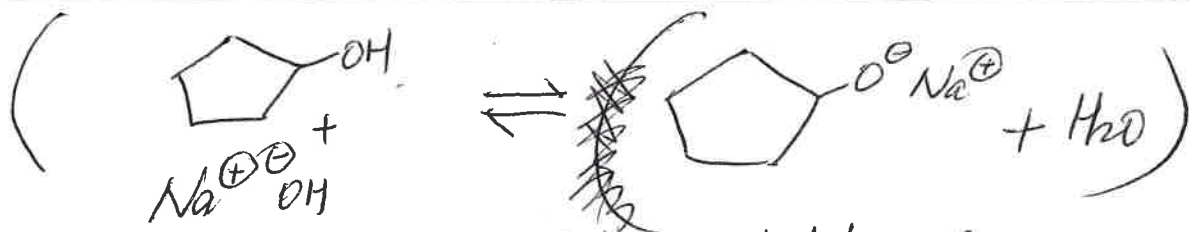


Recall: "RO⁻" as nucleophile, SN2 w/ R'-X
for ether formation: Requires quantitative deprotonation.
Recall further

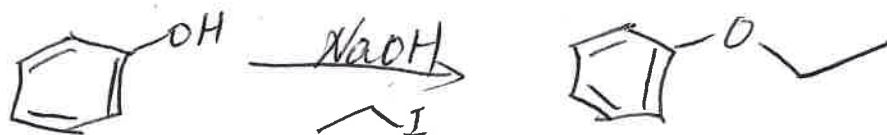


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However, NaOH is ~~not~~ soluble for quant. deprotonation of phenols! Thus,



EAS rxns of phenols \rightarrow very ~~fast~~ facile!
 ("Hard to stop")

EX



Note differences relative to ~~other~~ other (non-phenol) EAS ~~positions~~ rxns:

- 1) No Lewis acid catalyst.
- 2) Hard to stop after 1 Br added (even w/ 1 eq. Br₂)

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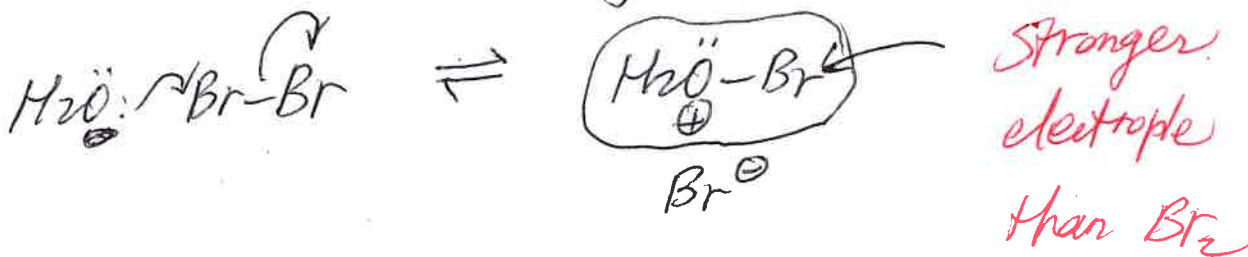
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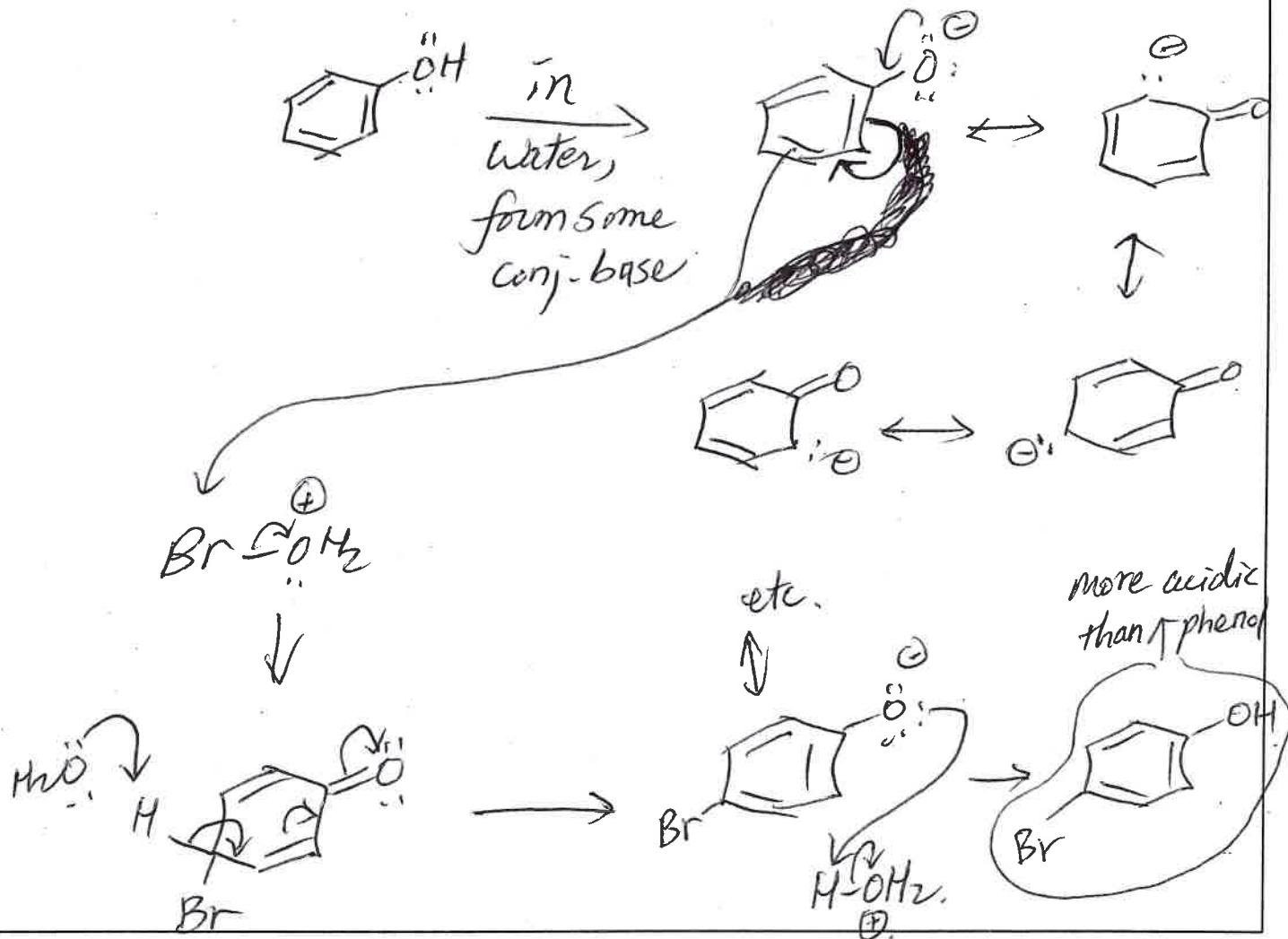
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Rationale:

① Distinctive electrophile from Br₂/H₂O.



Acidity of phenol. C: OH also important



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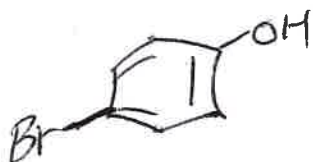
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∴ Greater tendency for OH deprotonation of



rel. to



reacts more rapidly than



Chap 19

Aldehydes & Ketones.