Course Chem 345 Lecturer Gellman

Day Wed. Date 2/25/15

Notes Taken By C. Weatherly Total # of Pages 5

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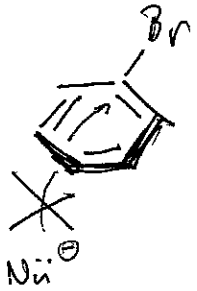
Recall: Aryl & vinyl halides... $C_{(sp^2)}-Cl$ (etc.)
vs. $C_{(sp^3)}-Cl$ (etc.)

No S_N2 reactions



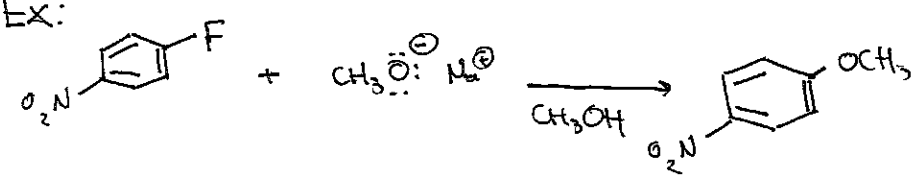
Nucleophile approach blocked by ring (for backside attack)

Alternative substitution mechanism available in some cases—
Nucleophilic Aromatic Substitution (NAS).

Requirements for NAS:

1) Ring must bear a leaving group - usually a halide, including F.
2) Electron-withdrawing groups ortho & para to LG.
(~~usually~~ commonly $-NO_2$)

Ex:



Course Chem 345 Lecturer Gellman

Day Wed. Date 2/25/15

Notes Taken By C. Weatherly Total # of Pages 5

Submit a *Single-sided Copy* to the Undergraduate Office

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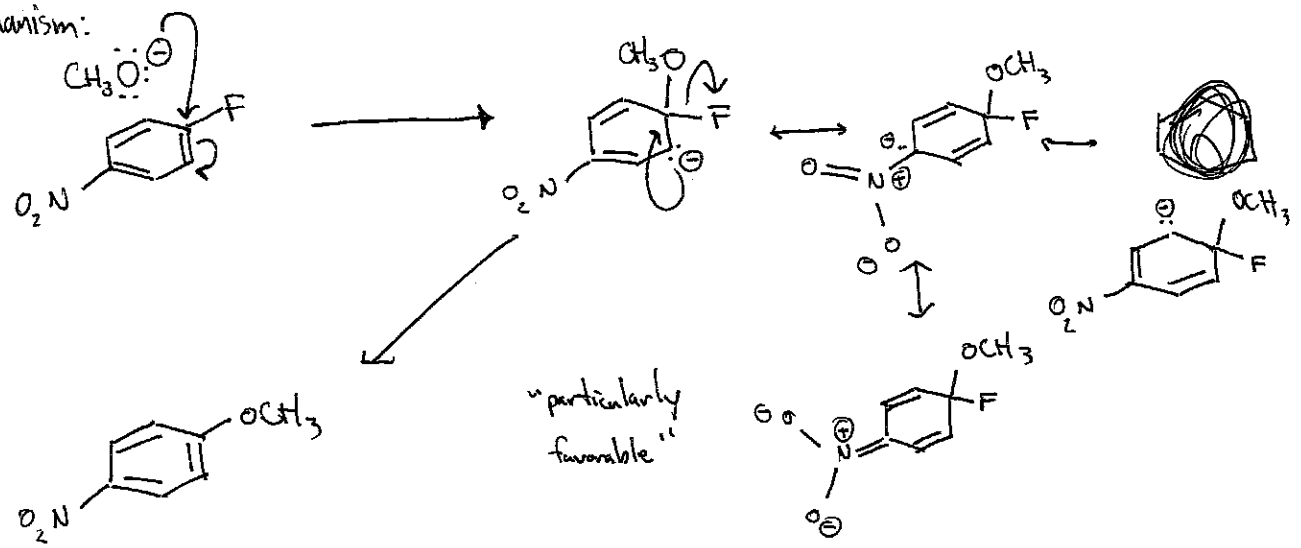
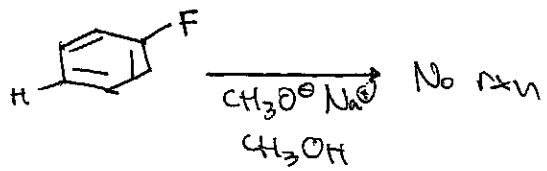
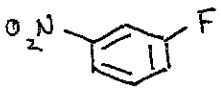
Mechanism:



Note: No EWG ----> no rxn



Also note:

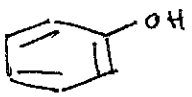


⇒ little or no reaction

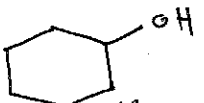
(Draw in hypothetical intermediate; observe that negative charge cannot delocalize onto NO_2.)

[§18.5, 18.6] – skip

Phenols – acidity



$pK_a \sim 10$ vs.



$pK_a \sim 17$

Course Chem 345 Lecturer Gellman
Day Wed Date 2/25/15
Notes Taken By C. Weatherly Total # of Pages 5

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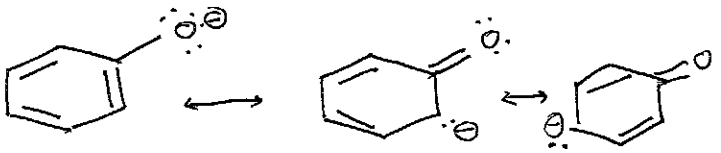
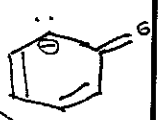
Origin of enhanced acidity of phenol?
→ resonance delocalization of ⊖ in conj. base.

localized charge

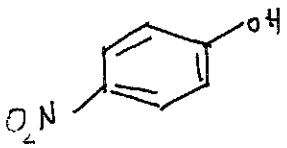
vs.



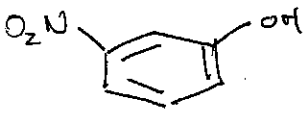


This delocalization of charge enables qualitative predictions of substituent effects on pK_a values.

Ex:



$pK_a \sim 7$ Rationalize lower pK_a relative to phenol via conj. base structure.



$pK_a \sim 8.4$ – lower than phenol's $pK_a \Rightarrow$ e^- withdrawal via inductive effects (σ-bond networks)

"phenoxide" ≡ "phenolate"

→ good nucleophiles; avid participants in S_N2 reactions

Course Chem 345 Lecturer Gellman

Day Wed. Date 2/25/15

Notes Taken By C. Weatherly Total # of Pages 5

Submit a *Single-sided Copy* to the Undergraduate Office

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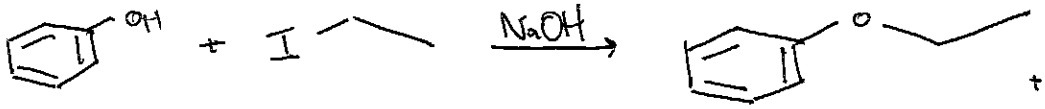
Note: phenols can be quantitatively deprotonated with NaOH.

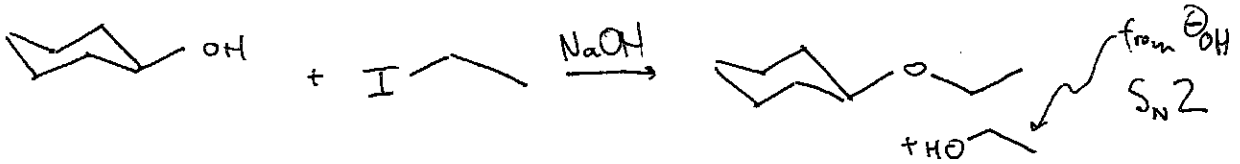
∴ operationally simpler S_N2 rxns relative to simple alcohols.

Thus,



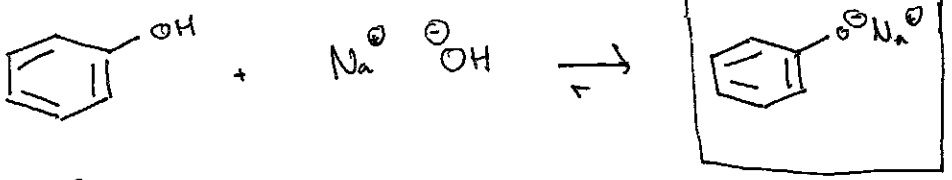
[very efficient]

BUT



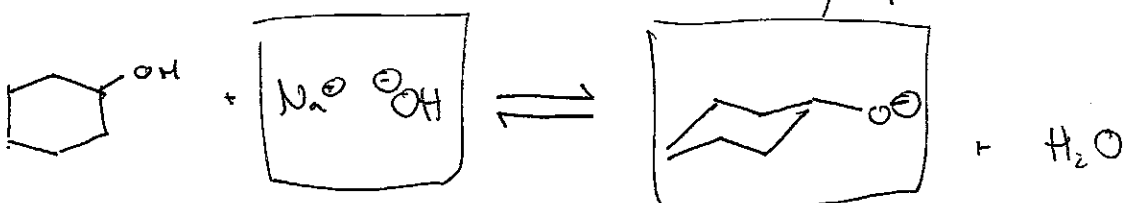
Explanation:

[Not efficient]



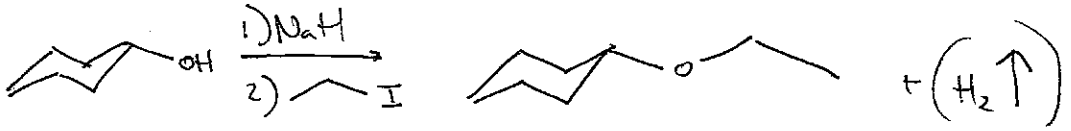
vs.

Only operational $Na^{\oplus}$.



2 operational $Na^{\oplus}$ → pdt mixture

Need stronger base for quant. deprotonation of simple alcohol. (NaH).



Course Chem 345 Lecturer Gellman

Day Wed Date 2/25/15

Notes Taken By C. Weatherly Total # of Pages 5

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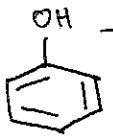
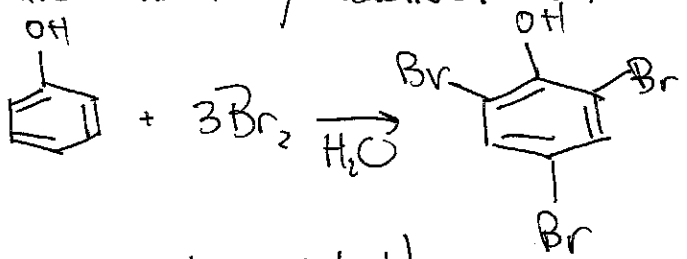
[Skip § 18.8]

Phenols in EAS rxns:

Recall:  OH → Activating for EAS

Phenols are unusually reactive in EAS!



No catalyst!