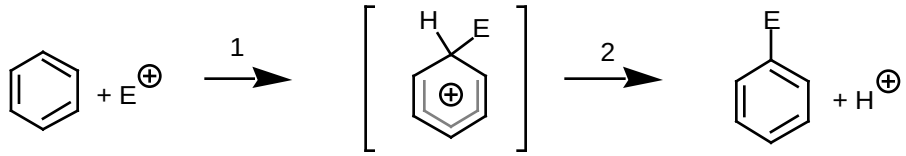
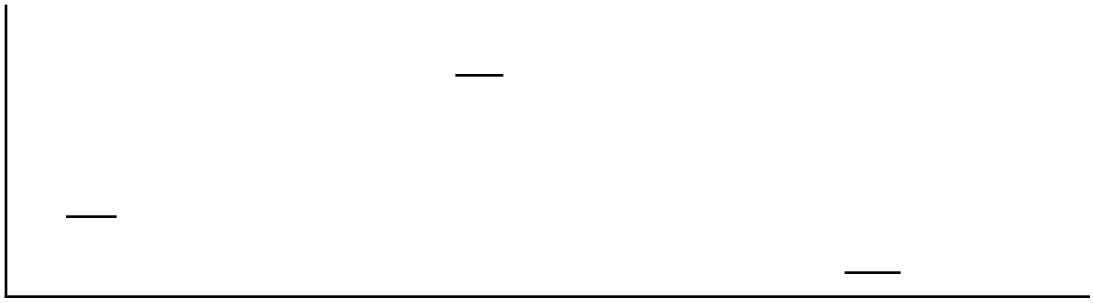
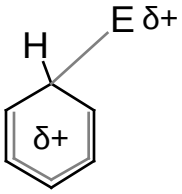
Chemistry 304B, Spring 1999 Lecture Notes 11

Review session Tomorrow: 6:30 pm in rm 120 Frick;
Final reading suggestions specifically for Exam I:
14.1, 14.2, 14.3, 14.4, 14.5, 14.6, 14.7, 14.9, 14.10, 14.11, 14.12,

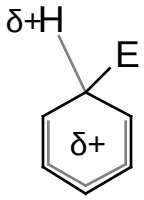
Review:







TS1

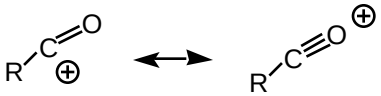


TS2

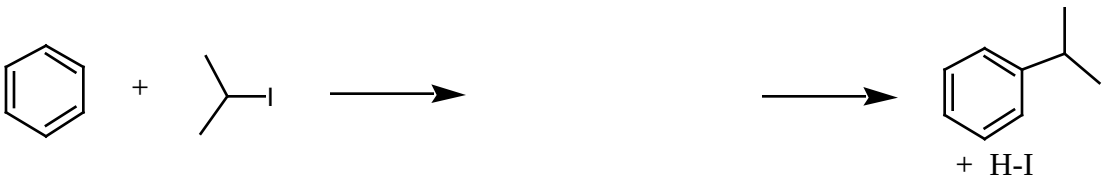
We did: $^{+}NO_2$; $^{+}HSO_3$; Br_2/catalyst; Cl_2/catalyst catalyst: Lewis Acid such as $FeBr_3$, $FeCl_3$

Carbon Electrophiles: Friedel-Crafts Reaction

alkyl cation $R^{\oplus}$ acyl cation



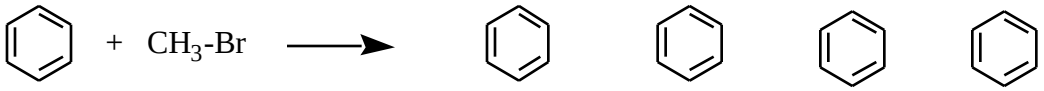
Alkylation:



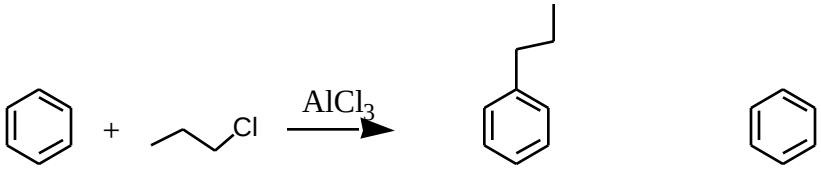
Catalyst?
Benzene is a (weak) nucleophile: S_N1 or S_N2-like?

Problems:

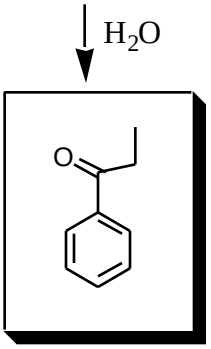
a. Overalkylation. (prob 14.8, text)



b. The usual funny cation stuff:



Acylation:

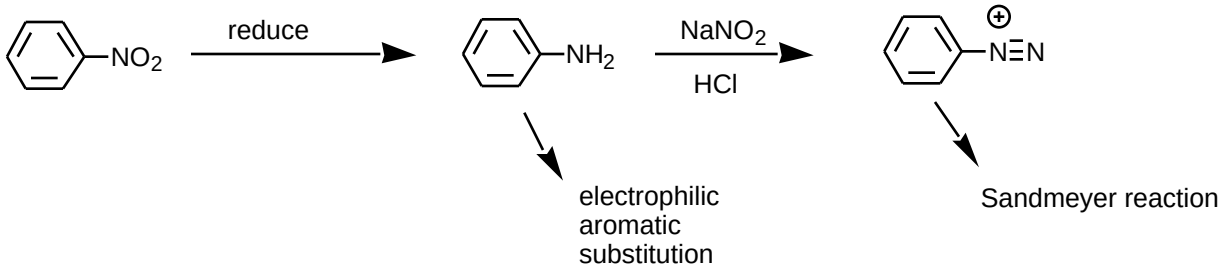


Two interactions with the $AlCl_3$:

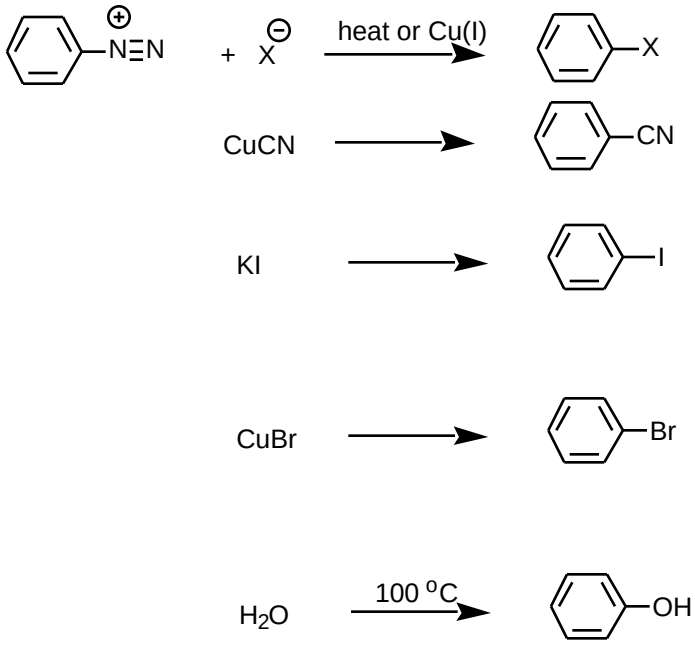
No "over-acylation":

What can we do with the electrophilic sustitution products?

NITROGEN: Nitrobenzene, anilines, and diazobenzenes:

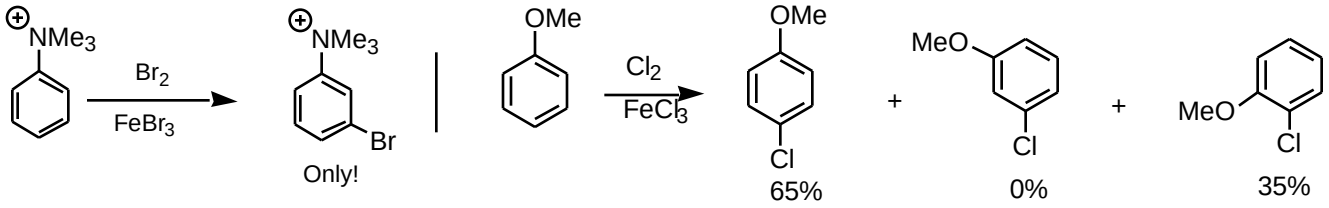


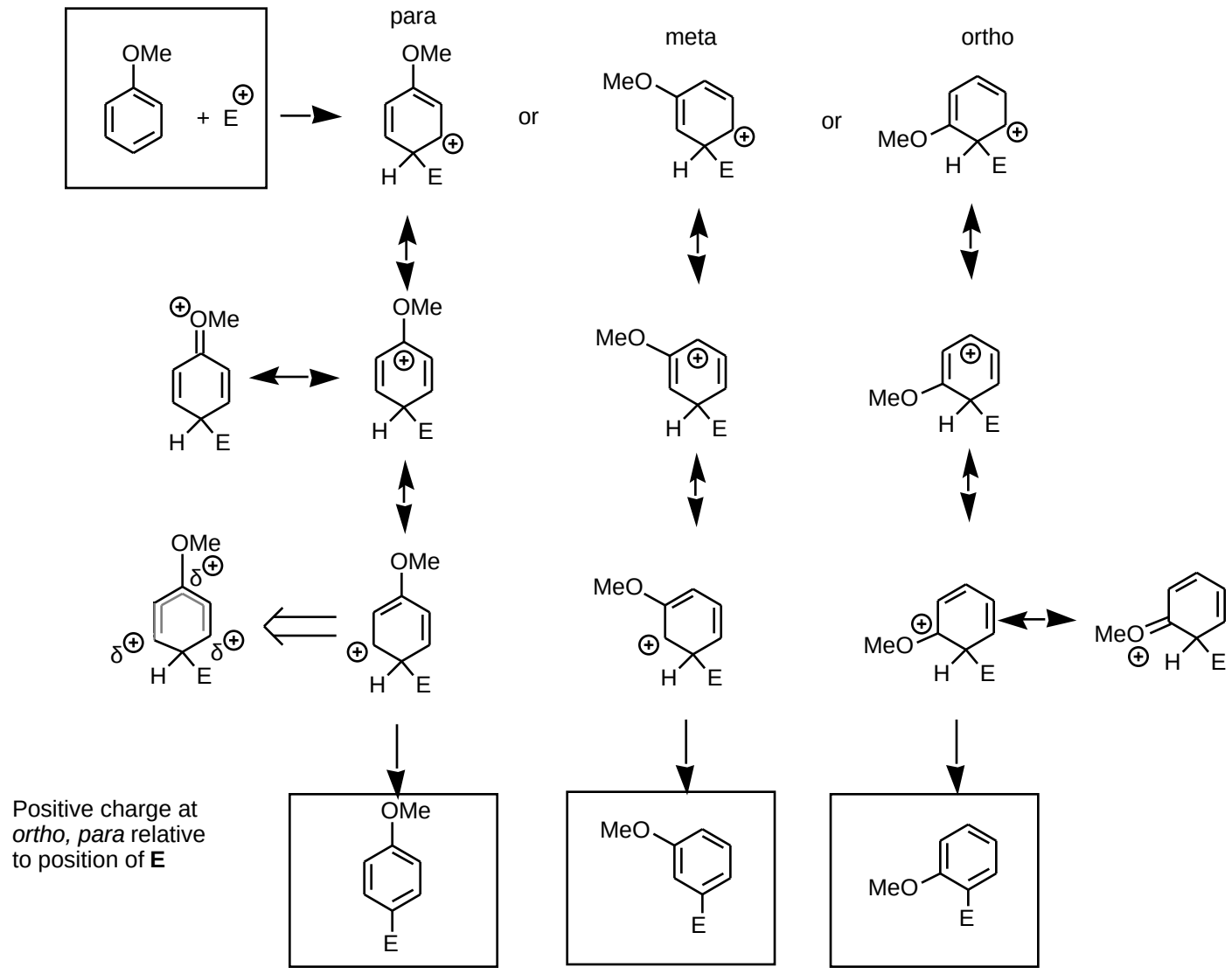
The Sandmeyer Reaction:

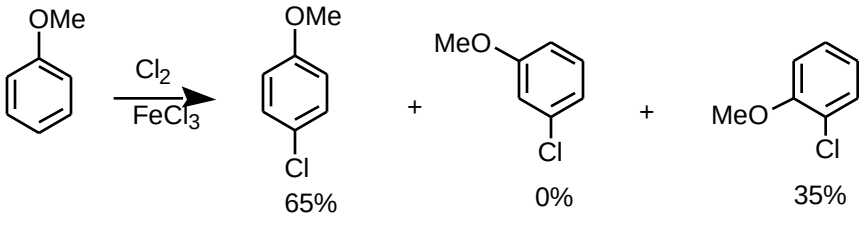


Mechanism: Probably radicals but why not write a Junior Paper on it?

Monosubstituted Benzene: Consider: **MeO vs Me_3N^+**

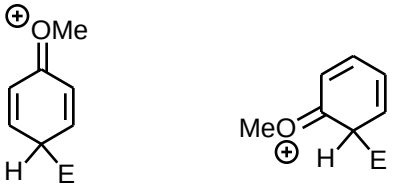






Why para/ortho preferred over meta?

TS leading to para/ortho addition stabilized by direct resonance interaction with -OMe



Why *para* preferred over *ortho*? Statistics would favor *ortho* by 2:1

Two reasons: a. Inductive withdrawing effect of OMe is more effective at *ortho,* disfavoring.

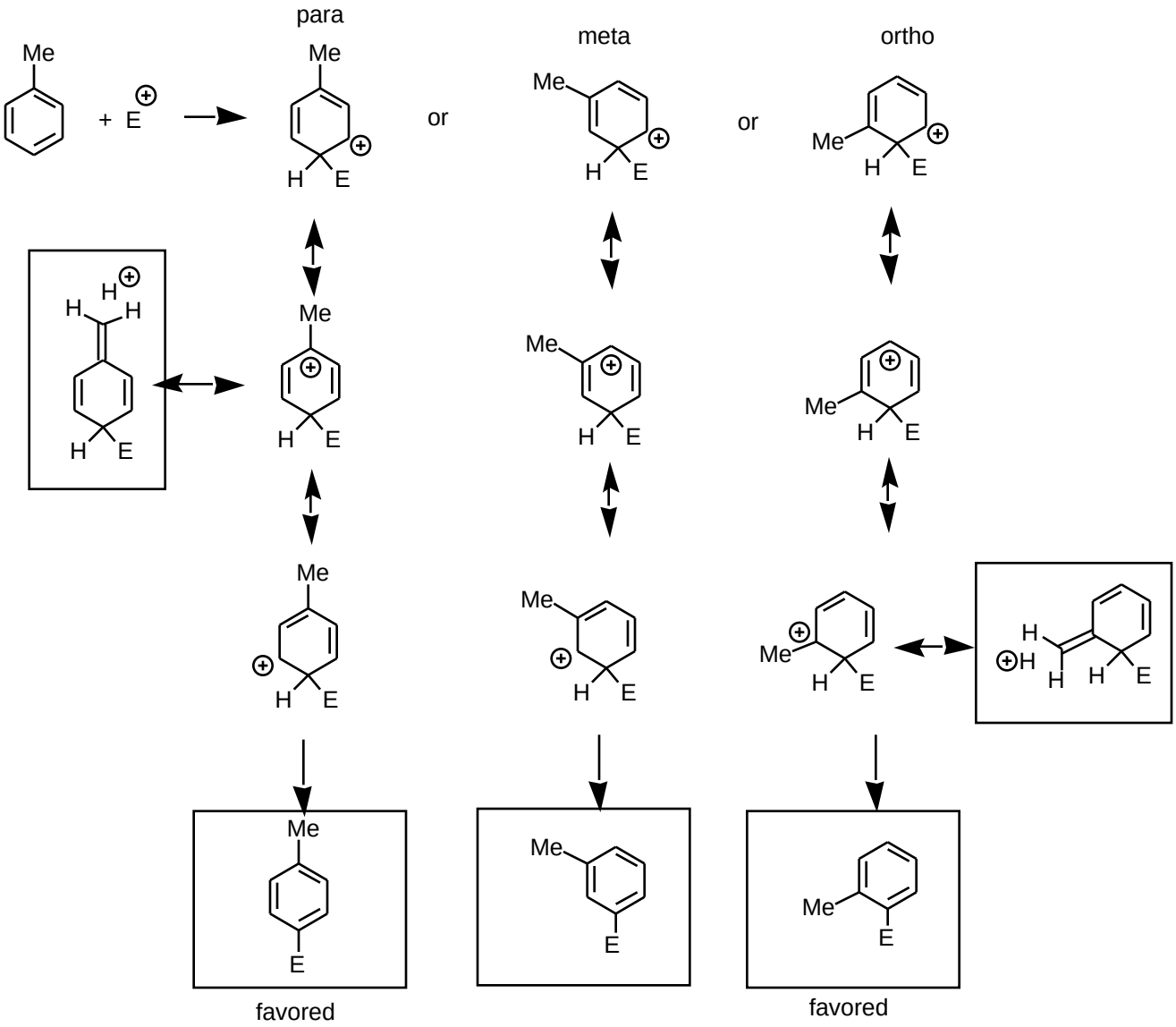
b. The steric effect of OMe is serious at the *ortho* position; disfavoring
absent at *para* (or *meta*)

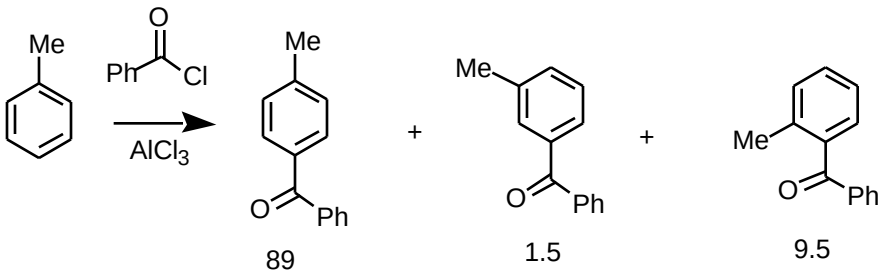
What about rate effects? -OMe gives strong acceleration.
TS energy for *para/ortho* is lowered by resonance interaction of cation with -OMe

Inductive and resonance effects oppose each other in the case of a -OMe substituent--
how to know which dominates?

Do the experiment and memorize the result → resonance dominates for -OMe
Strong rate acceleration, strong o/p director

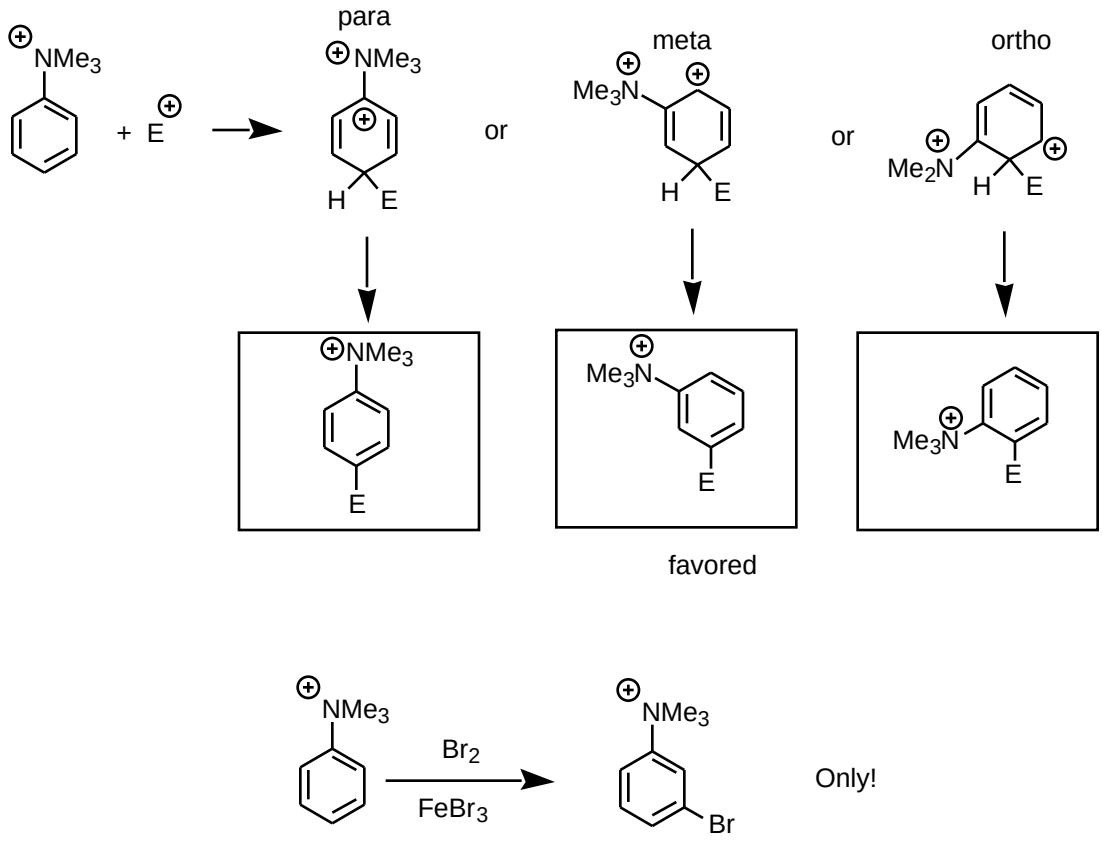
Methyl (toluene):





Note: Me has no inductive effect. Ortho is still <u>disfavored</u> relative to para. Must be a steric effect.

"Extra" resonance structures for *para* and *ortho* substitution.
Accelerate the reaction moderately



$^{+}NMe_3$ is a strong meta director. More precisely, it is a strong inhibitor of substitution o/p
Overall <u>reduction</u> in rate of substitution.

Also:see Table 14.1

$^{+}NMe_3$, $-NO_2$, -CN, SO_2OH, acyl, $-CF_3$ → reduce the rate and prefer META addition
Inductive withdrawing (all)
Resonance withdrawing (some of them)

$-NH_2$, $-NMe_2$, -OH, -alkyl → increase the rate and prefer ORTHO/PARA addition.

Halides: Dominant inductive effect → reduce the rate of addition

BUT: the halide atoms (F > Cl > Br > I) show some resonance donation. Addition at all positions is slowed by the general inductive effect, but additon at ortho/para is selectively increased by resonance donation.

The halides slow the rate of addition of electrophiles BUT show ortho/para selectivity.