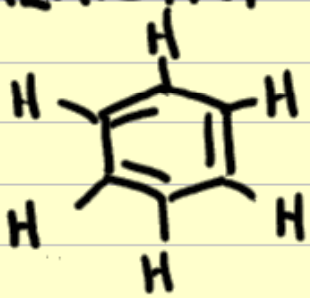
235 Notes

Notebook: jgreen1263's notebook
Created: 11/13/2009 2:45 PM **Updated:** 1/8/2013 11:04 AM

CHEM. 235

AROMATIC COMPOUNDS.

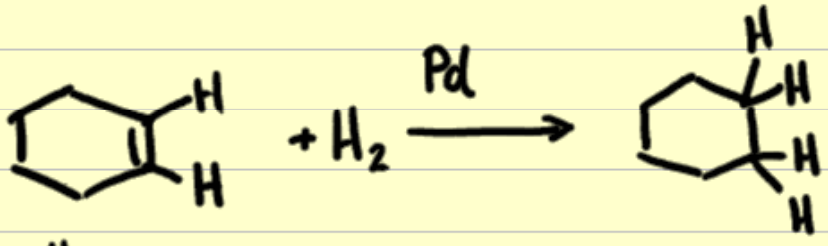
CHEMISTRY OF COMPOUNDS LIKE



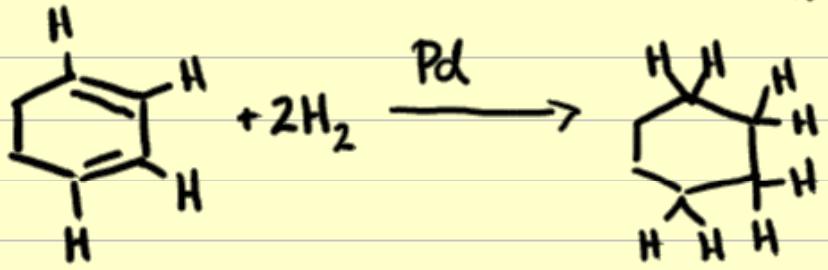
BENZENE

C_6H_6

- SPECIAL CHARACTERISTICS
  - STABILITY

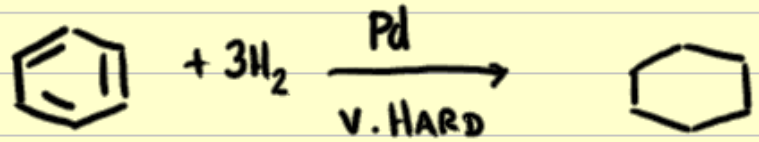


$\Delta H = -120$ kJ/mol



$\Delta H_P = -240$

$\Delta H_A = -231$ kJ/mol



$\Delta H_P = -360$

$\Delta H_A = -208$ kJ/mol

SOMEHOW, BENZENE IS ~ 150 kJ/mol MORE STABLE THAN EXPECTED FROM 3 C=C'S. (~36 kcal/mol)

REALLY MORE LIKE 120 kJ/mol, 28-29 kcal/mol

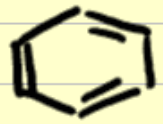
THIS IS THE AROMATIC RESONANCE STABILIZATION OF BENZENE

DEFINITION OF AROMATIC COMPOUND
- A COMPOUND THAT HAS RESONANCE STABILIZATION FAR IN EXCESS OF THAT EXPECTED FOR A STRUCTURE WITH LOCALIZED π- ELECTRONS

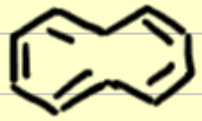
WHAT KINDS OF COMPOUNDS ARE AROMATIC?

HÜCKEL'S RULE:

CONJUGATED CYCLIC POLYENE WITH $(4n+2)$ π- ELECTRONS ($n = 0, 1, 2, 3 \ldots$) HAVE THIS EXTRA STABILIZATION AND ARE CALLED AROMATIC.

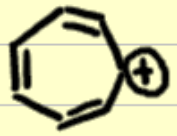


$n=1$
$6\pi e^-$

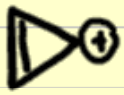


$n=2$
$10\pi e^-$

$n=1$
$6\pi e^-$



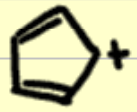
$n=1$
$6\pi e^-$



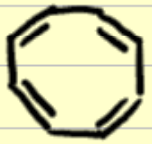
$n=0$
$2\pi e^-$

CONVERSELY, SYSTEMS WITH $4n$ πe^- ARE ESPECIALLY UNSTABLE, CALLED ANTIAROMATIC

$4\pi e^-$
$(n=1)$



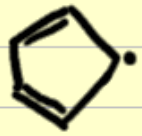
$4\pi e^-$



$8\pi e^-$
$(n=2)$

NOT ISOLABLE

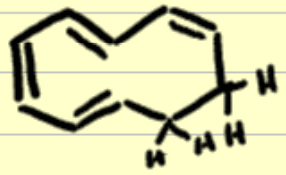
AND THE REST ??



$5\pi e^-$

NON AROMATIC
- NOT ESPECIALLY STABLE OR UNSTABLE
- NOT CONJUGATED CYCLIC POLYENE

$\therefore$ NON AROMATIC.



235 Notes

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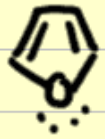
CHEM. 235 - LECTURE 2

AROMATIC $2\pi e^-$ $6\pi e^-$ $10\pi e^-$ $14\pi e^-$...
$(4n+2)$

ANTIAROMATIC $4\pi e^-$ $8\pi e^-$ $12\pi e^-$....
$(4n)$

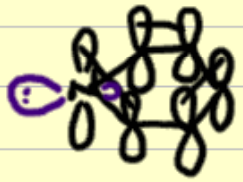
NON AROMATIC = NEITHER.

X = O, S, N-R



ISOELECTRONIC WITH

$6\pi e^-$
∴ AROMATIC



LONE PAIR ORTHOGONAL TO THE π SYSTEM NOT OVERLAPPING WITH IT.

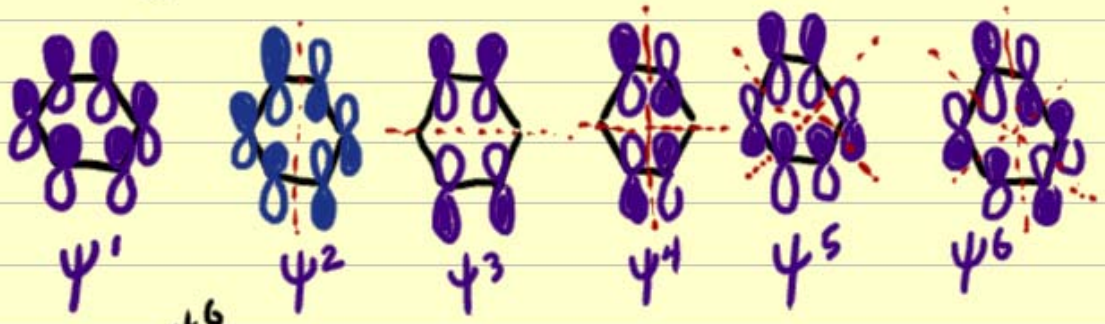
6π - AROMATIC

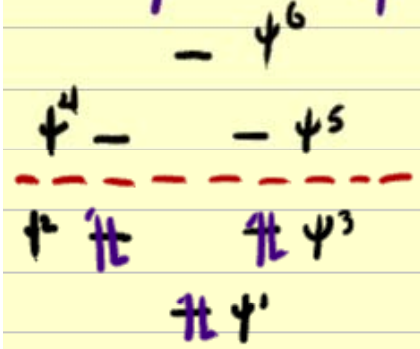
Hückel MO Description

Forget σ Bonds

π Orbitals are Combinations of p Atomic Orbitals

6 p orbitals Combine to Give 6 π Orbitals



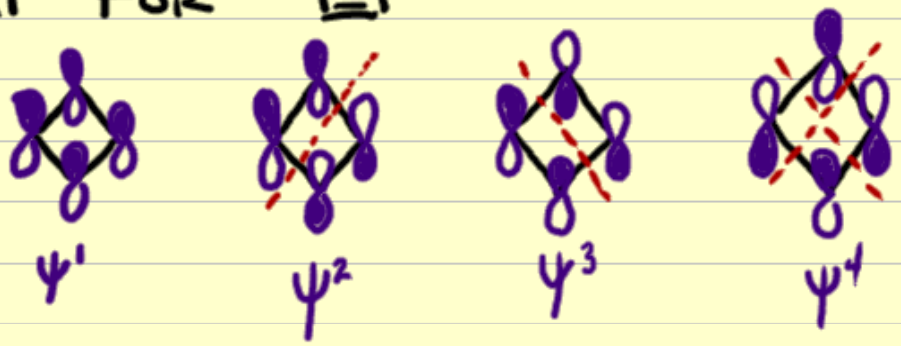


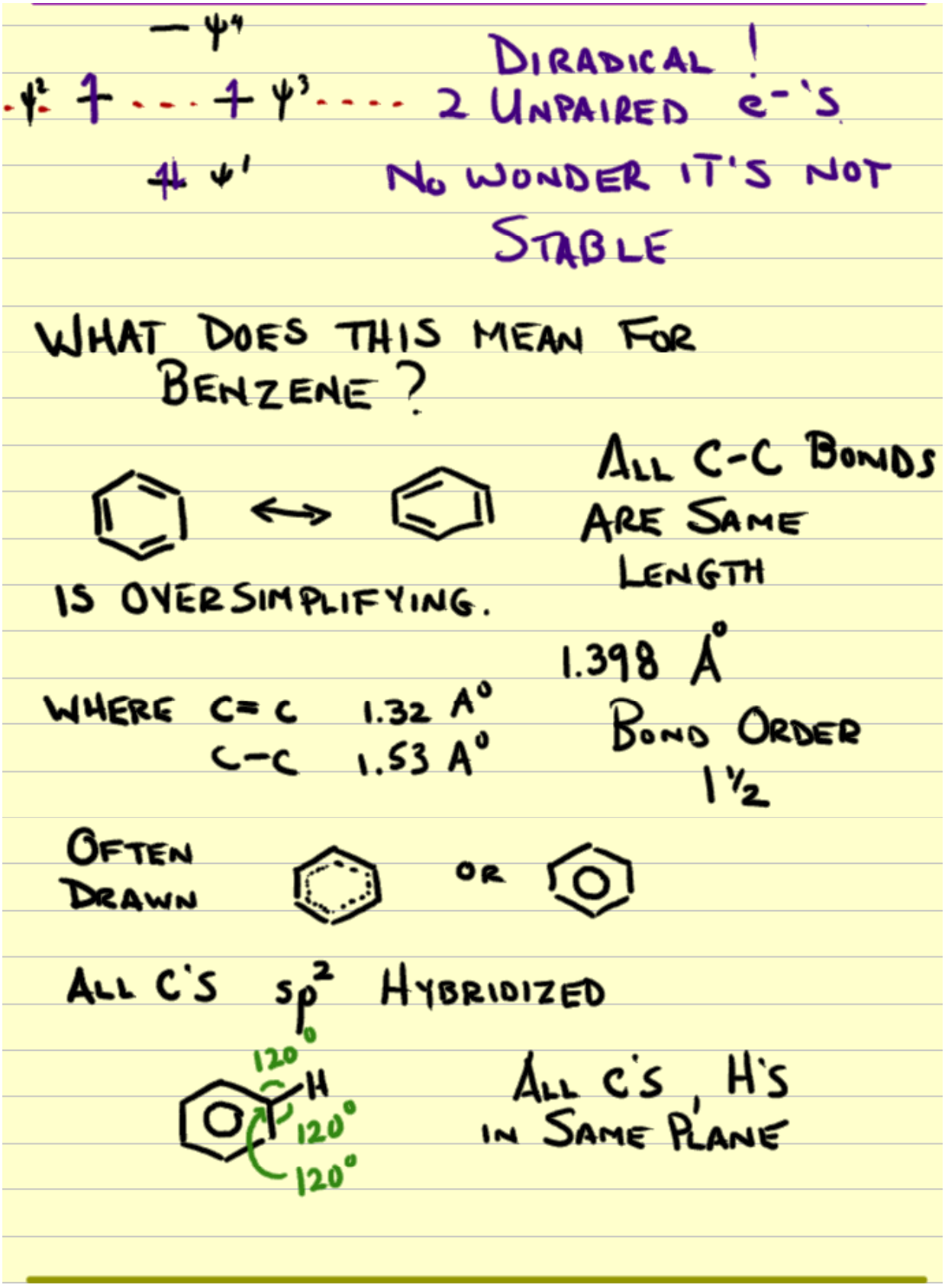
All Bonding Orbitals

All Energetic Stabilizing.

All e⁻s Paired.

But For 




ψ^4
ψ^2 ψ^3
ψ^1
DIRADICAL !
2 UNPAIRED e⁻'S
NO WONDER IT'S NOT STABLE
WHAT DOES THIS MEAN FOR BENZENE ?
ALL C-C BONDS ARE SAME LENGTH
1.398 Å
IS OVERSIMPLIFYING.
WHERE C=C 1.32 A°
C-C 1.53 A°
BOND ORDER 1½
OFTEN DRAWN
OR
ALL C'S sp^2 HYBRIDIZED
120°
120°
120°
H
ALL C'S, H'S IN SAME PLANE

NOMENCLATURE

- TRIVIAL NAMES ABOUND.

TOLUENE

DISUBSTITUTED CASES

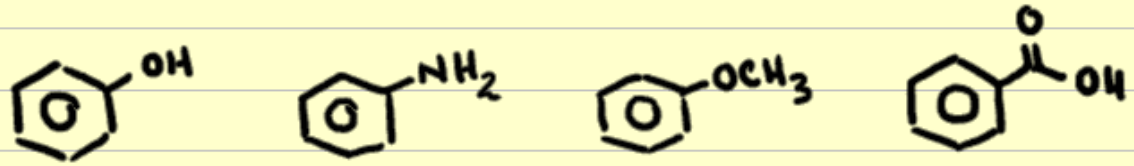
1,2- ≡ ORTHO o-

1,3- ≡ META m-

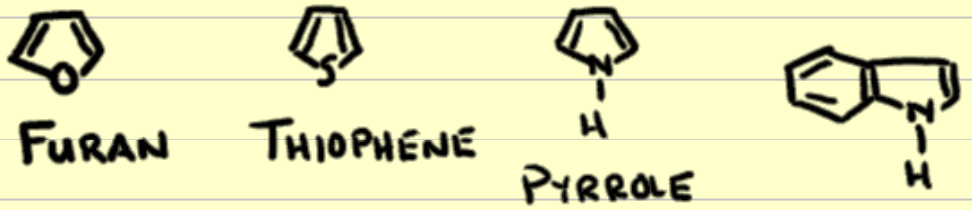
1,4- ≡ PARA p-

TRISUBSTITUTED CASES

- USE NUMBERS



PHENOL ANILINE ANISOLE BENZOIC ACID

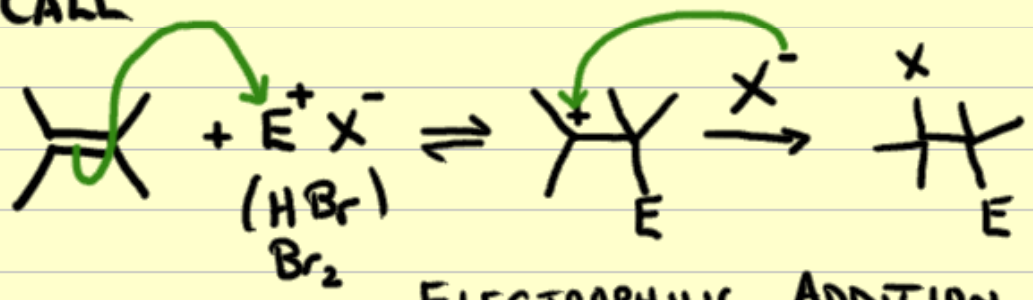


FURAN THIOPHENE PYRROLE INDOLE

Reactions of Benzenes

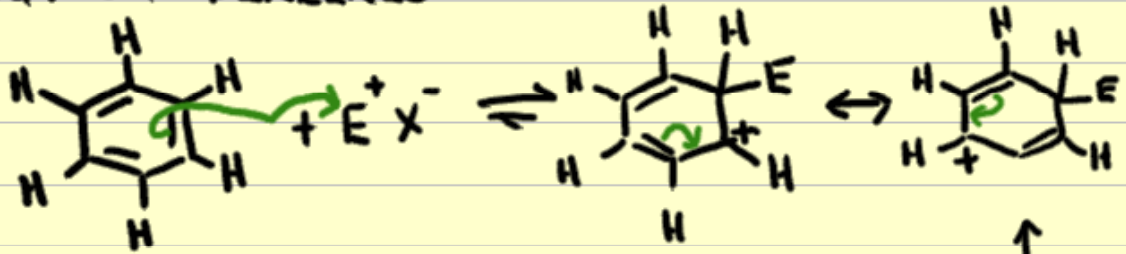
1) Electrophilic Aromatic Substitution

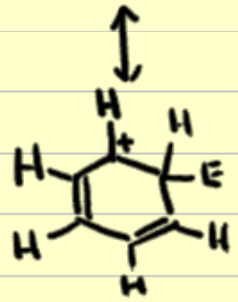
Recall



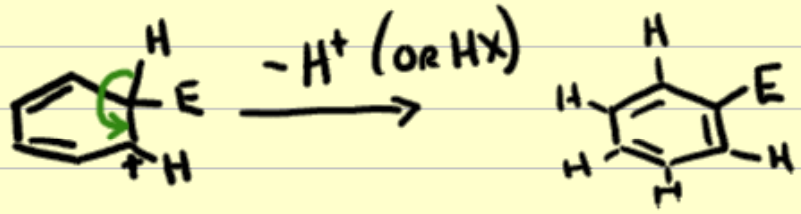
Electrophilic Addition

But on Benzenes





- Lost Aromatic Stabilization (120 kJ/mol)
- Can get it back by losing H^+

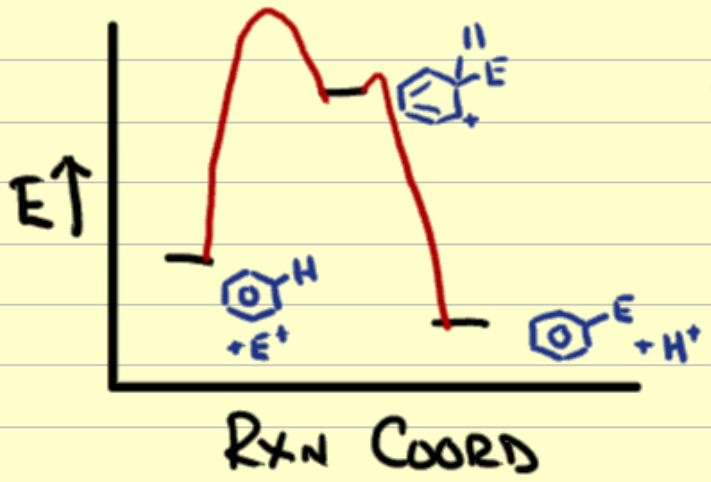


- DIFFERENCE IS THAT THIS IS A SUBSTITUTION. (NOT AN ADDITION)

2 STEPS

- 1ST STEP DESTROYS AROMATICITY (~120 kJ/mol) - SLOW, RATE DETERMINING STEP

- 2ND STEP - LOSS OF H^+ TO REGAIN AROMATICITY - EASY, FAST



SE2 REACTION

SUBSTITUTION ELECTROPHILIC BIMOLECULAR

235 Notes

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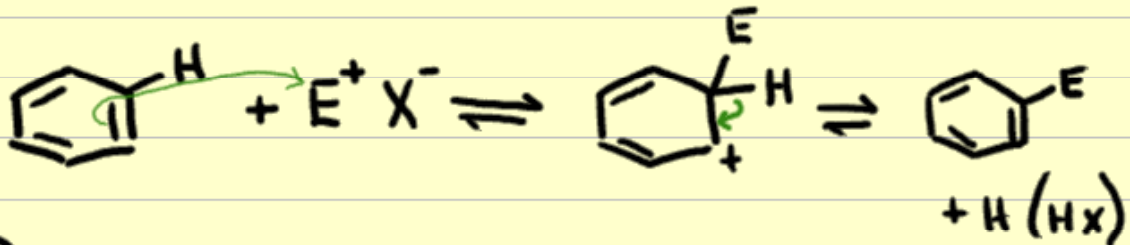
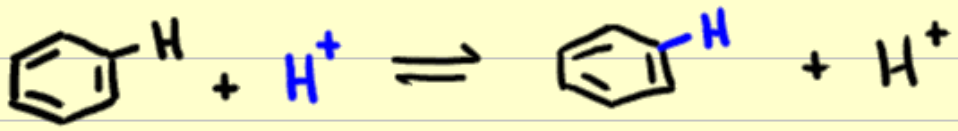
CHEM. 235 - LECTURE 3

REVIEW



REACTIONS - WHAT'S E^+?

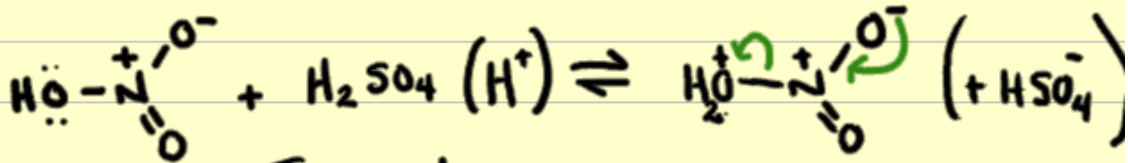
1) PROTONATION $E^+ = H^+$



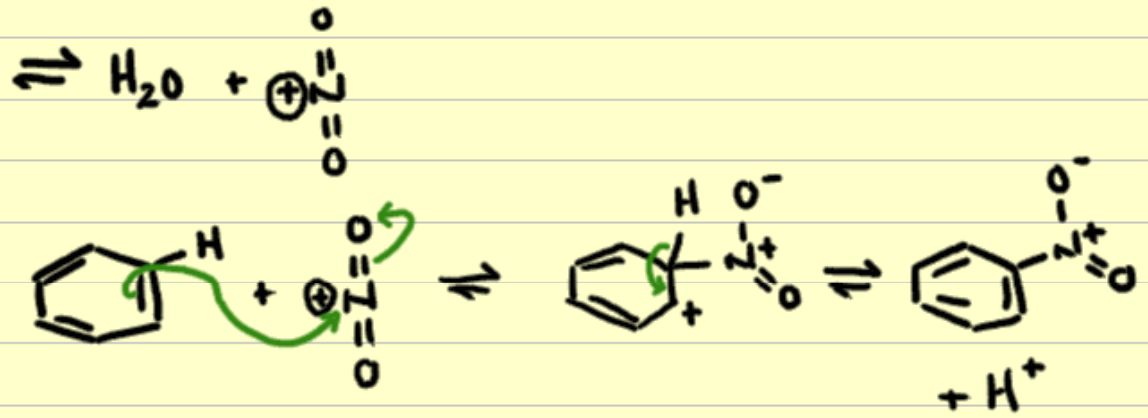
INVISIBLE IN MOST CASES

- UNLESS USING D^+ (DEUTERIUM ISOTOPE OF H^+)

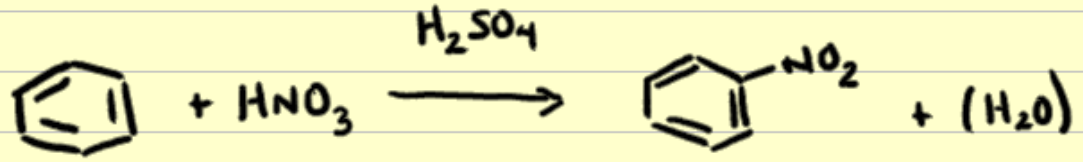
2) NITRATION $E^+ = {}^{+}NO_2$



STRONG ACID

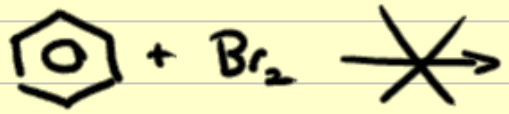


OVERALL



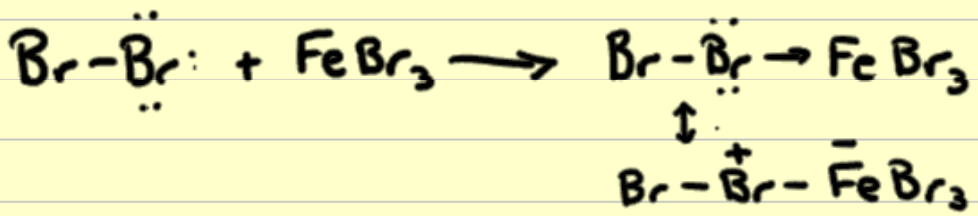
THE BEST WAY OF MAKING AN ARENE C-N BONDED COMPOUND.

3) HALOGENATION ($E^+ = Br^+$ OR Cl^+)

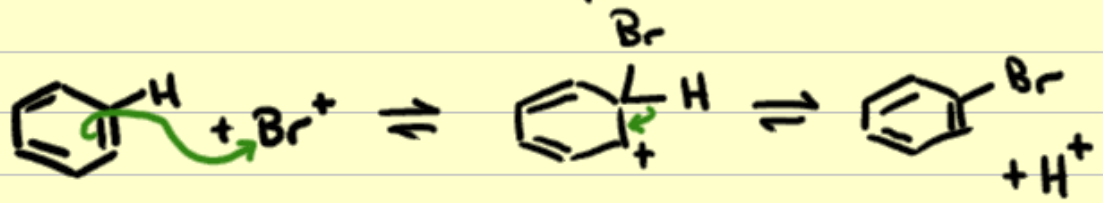


- NEEDS HELP FROM A LEWIS ACID.

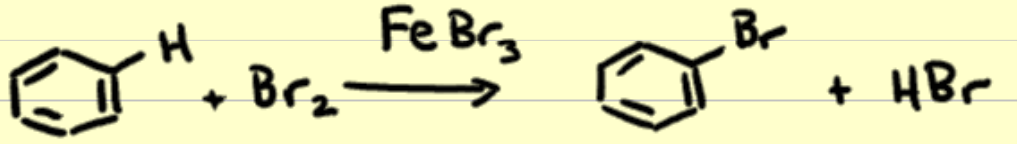
$FeBr_3$ (FOR Br^+) OR $FeCl_3$ (FOR Cl^+)

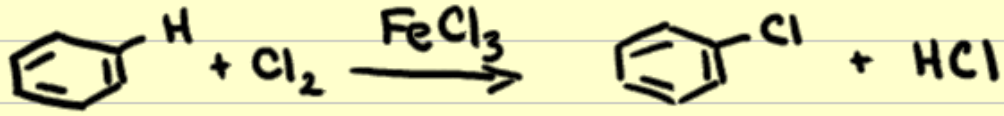


WRITE AS Br^+ $FeBr_4^-$

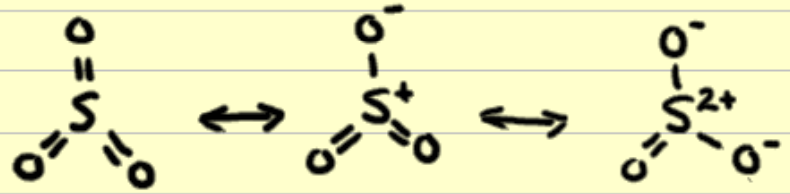


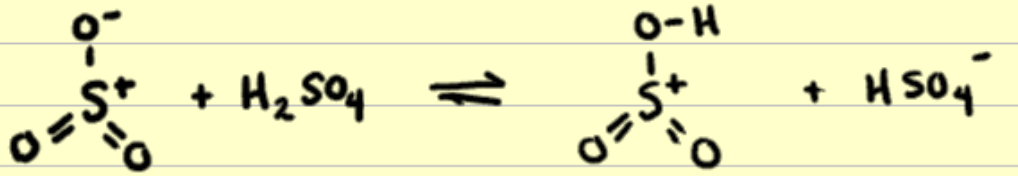
OVERALL

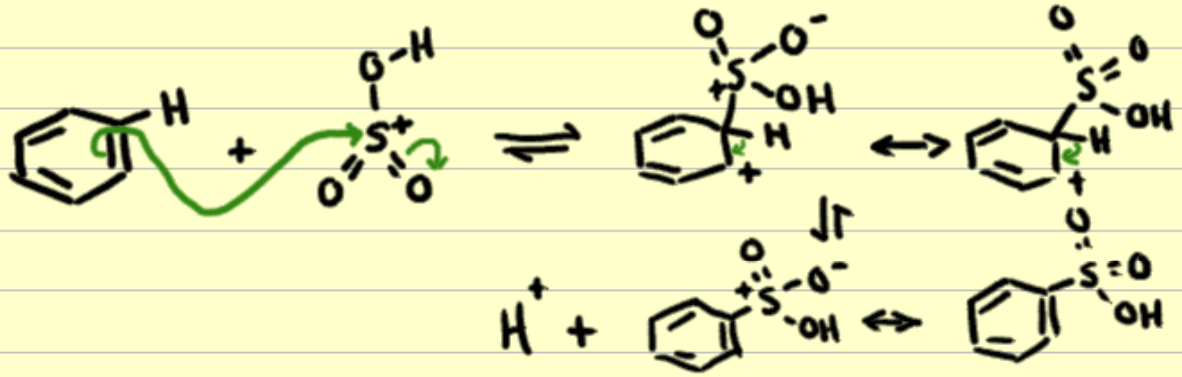




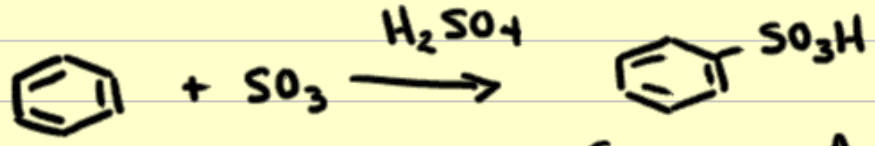
4) SULFONATION ($E^+ = {}^{\cdot\cdot}SO_3{}^{\cdot\cdot}$)







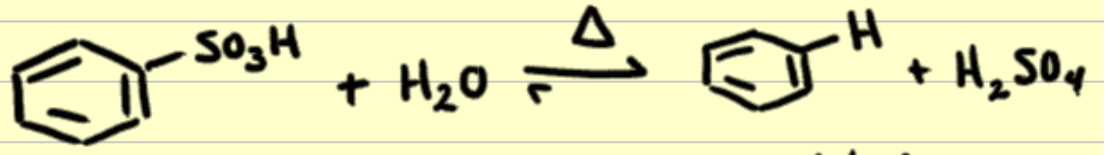
OVERALL.



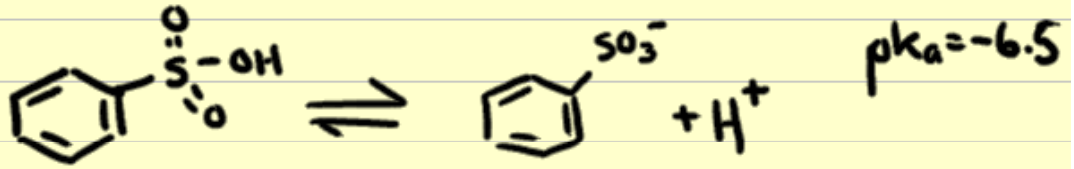
SULFONIC ACID.

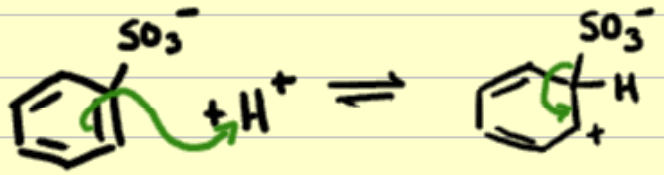
SPECIAL FEATURE OF SULFONATION

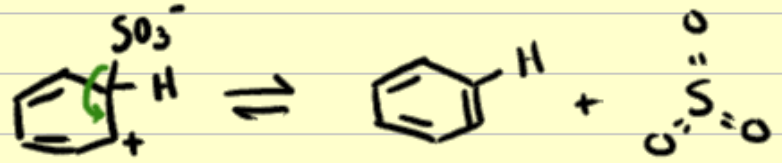
- IT CAN BE REVERSED.



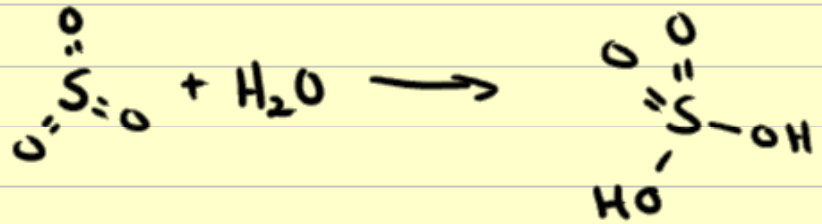
WHY? SULFONIC ACIDS ARE V. ACIDIC





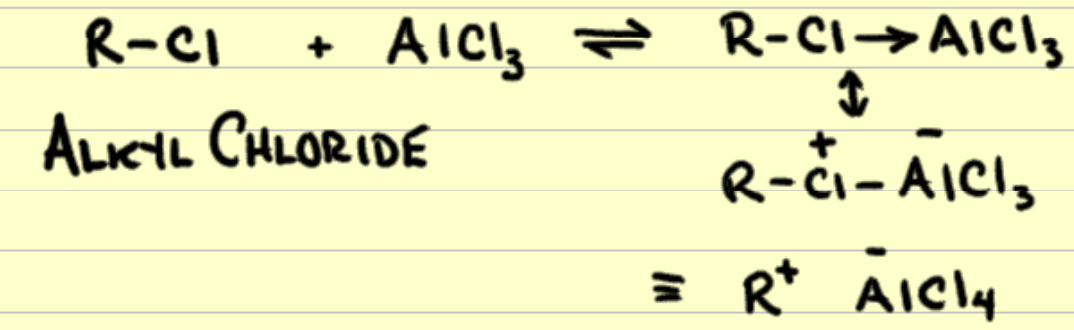


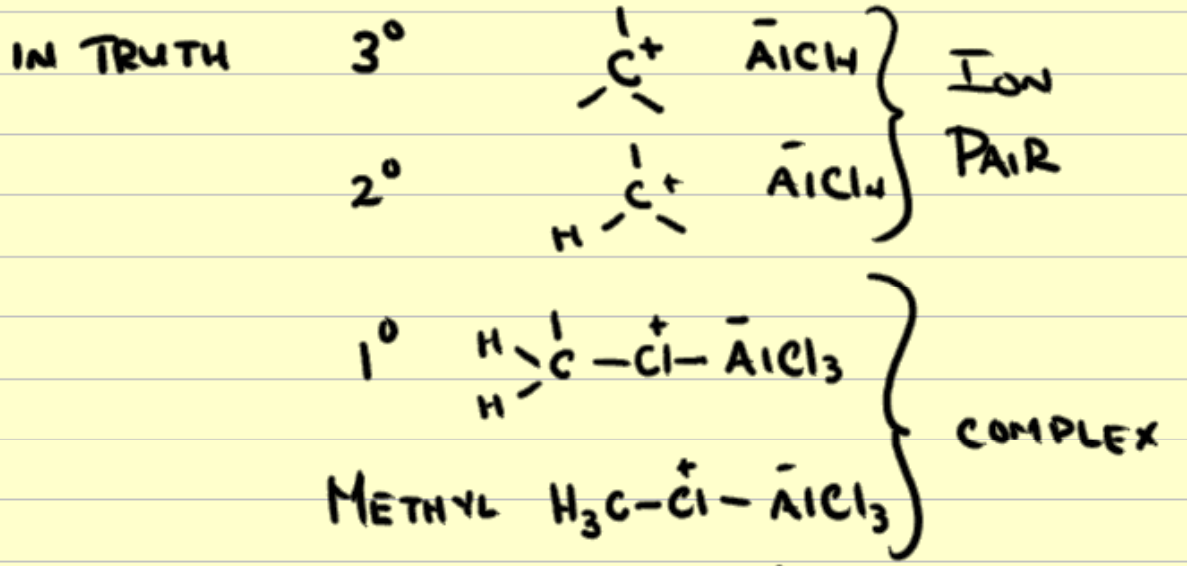
SO_3 IS DESTROYED IN WATER

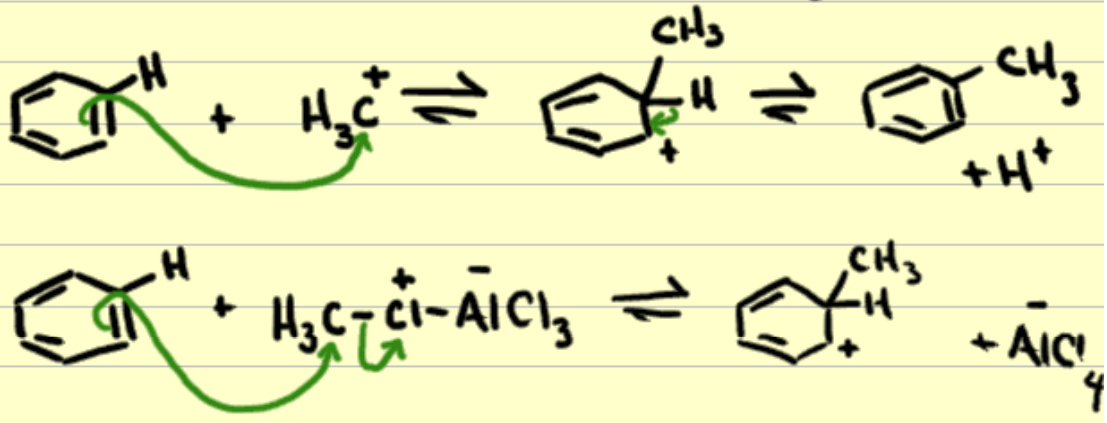


5) Friedel-Crafts Alkylation

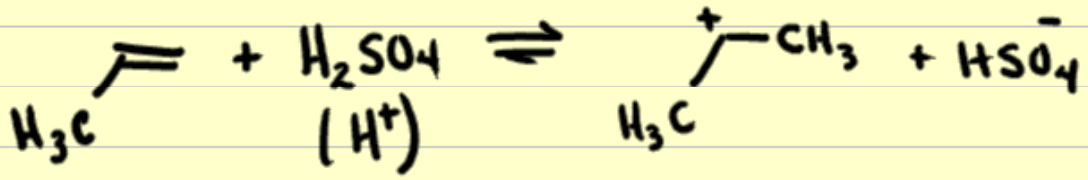
($E^+ = R_3C^+$)



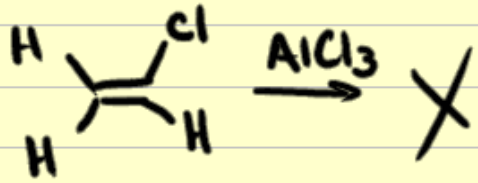




NOT THE ONLY WAY TO GENERATE R^+

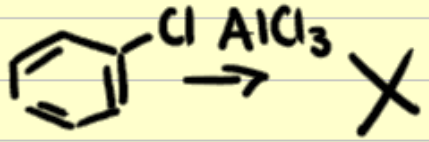


NOT EVERY C^+ CAN BE GOTTEN THIS WAY.



VINYL CATIONS

-NO

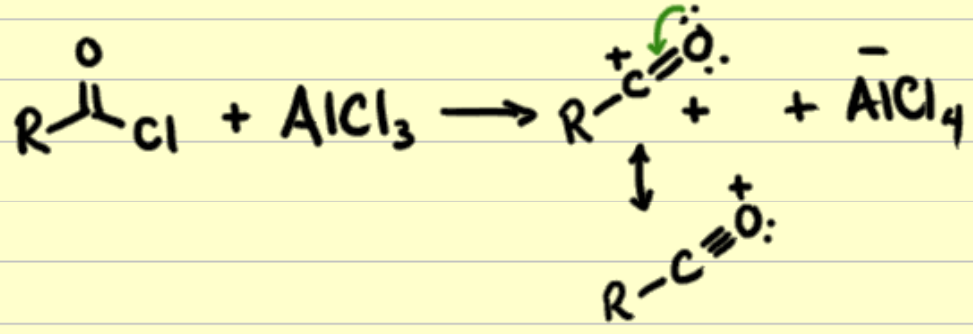


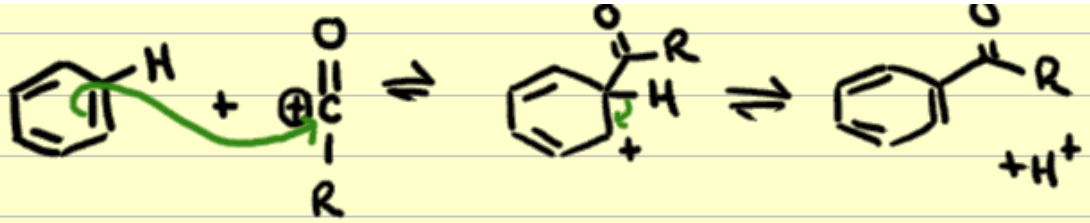
ARYL CATION

-NO

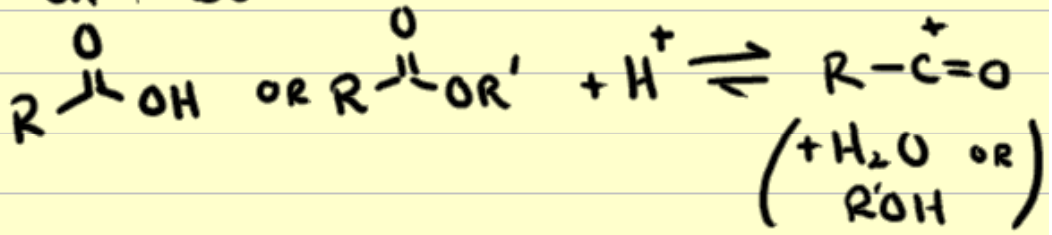
6) FRIEDEL CRAFTS ACYLATION

$E^+ = R-\overset{\oplus}{C}=O$ ACYLIUM ION

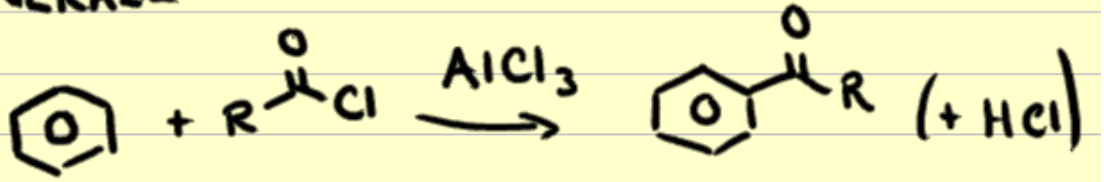


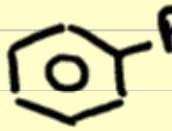


ALSO CAN DO

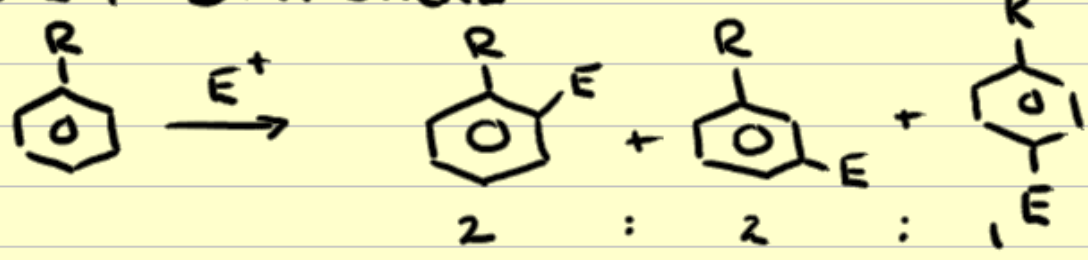


OVERALL



NEXT QUESTION - WHAT HAPPENS WITH  ??

PURELY STATISTICAL

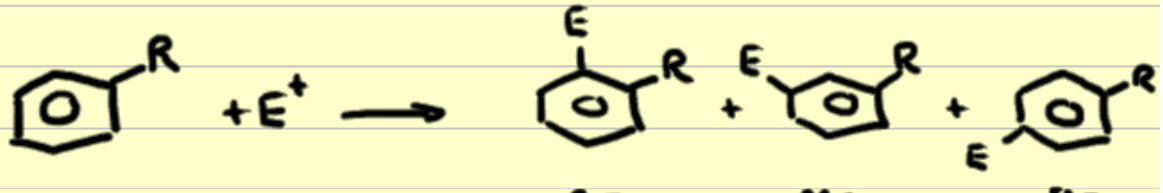


NEVER GET THIS.

235 Notes

Notebook: jgreen1263's notebook
Created: 11/13/2009 2:45 PM **Updated:** 1/17/2013 11:20 AM

CHEM. 235 - LECTURE 4

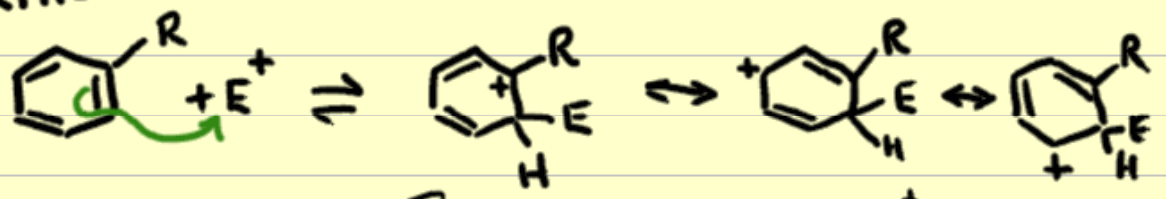


STATISTICAL RATIO 2 : 2 : 1

- NEVER GET IT EXACTLY

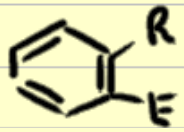
1) IF R IS DONATING e⁻ DENSITY INTO THE RING
+I (INDUCTIVE) OR +M (RESONANCE)

ORTHO

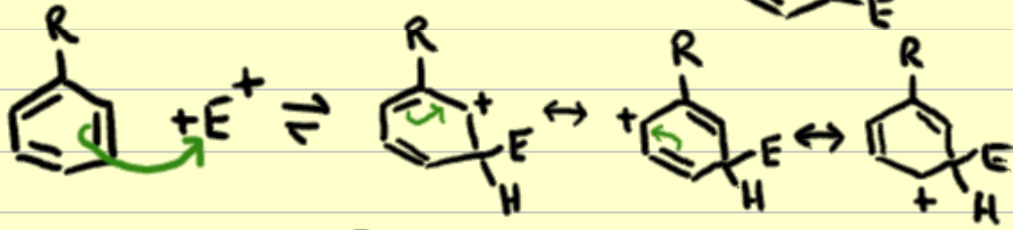


STABILIZING (i.e. GOOD)

-H+

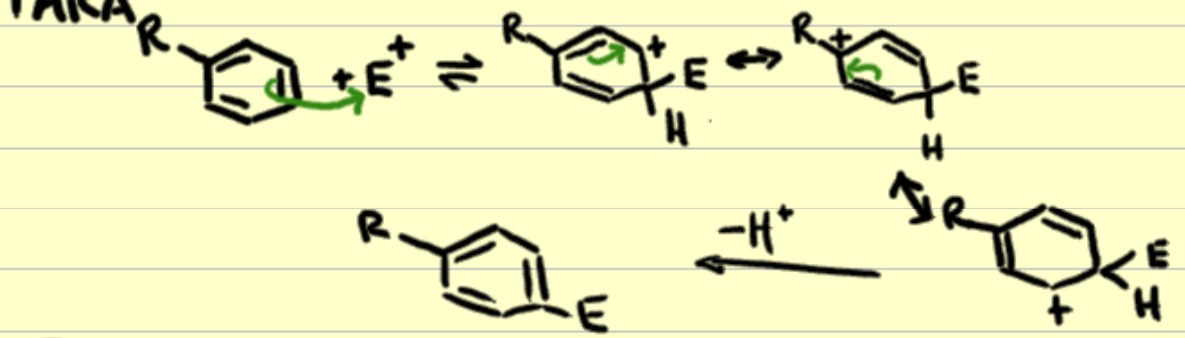


META



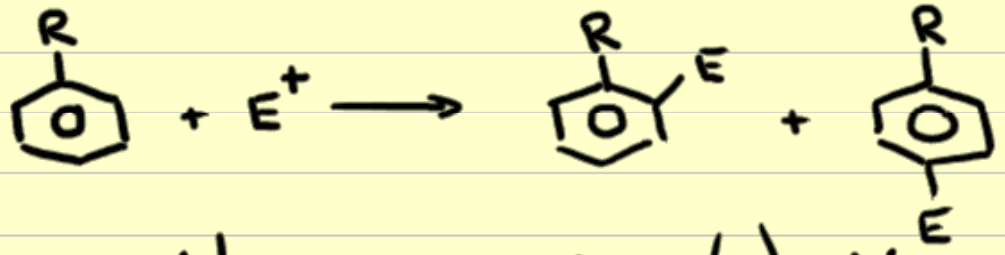
- NONE OF THESE IS BAD, BUT NOT AS GOOD AS ORTHO (OR PARA) ∴ VERY LITTLE

PARA



FAVOURED, MUCH LIKE THE ORTHO
+ CHARGE GETS ON C BEARING THE EDG. (R)

SO EDG'S (WHETHER +I OR +M)
GIVE ORTHO- & PARA- PRODUCTS



NORMALLY MINOR (o-) MAJOR (p-)

AND FASTER THAN BENZENE

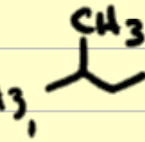
WHAT ARE THESE GROUPS?

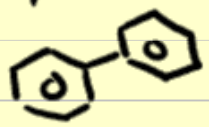
STRONG +$\ddot{N}(R)(R)$ (INCLUDES $-NH_2$)

$-\ddot{O}H$

MEDIUM $-\ddot{O}R$ $(-OCH_3)$

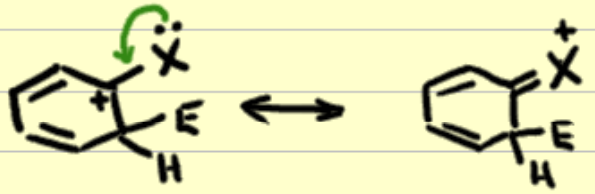
$-\ddot{N}(H)-C(=O)-CH_3$ (AMIDES)

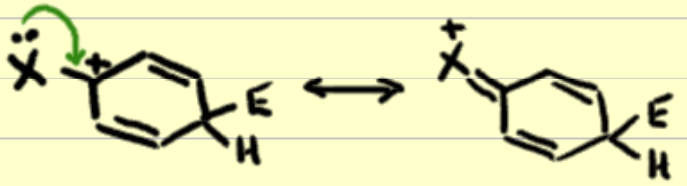
WEAK - ALKYL $(-CH_3,$  $)$

- PHENYL ()

$-\ddot{O}-C(=O)-R$ (O LINKED ESTER)

SO ACTUALLY A 4TH RESONANCE FORM

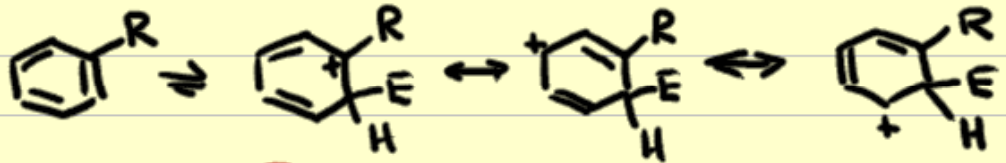




AND ELECTRON WITHDRAWING GROUPS

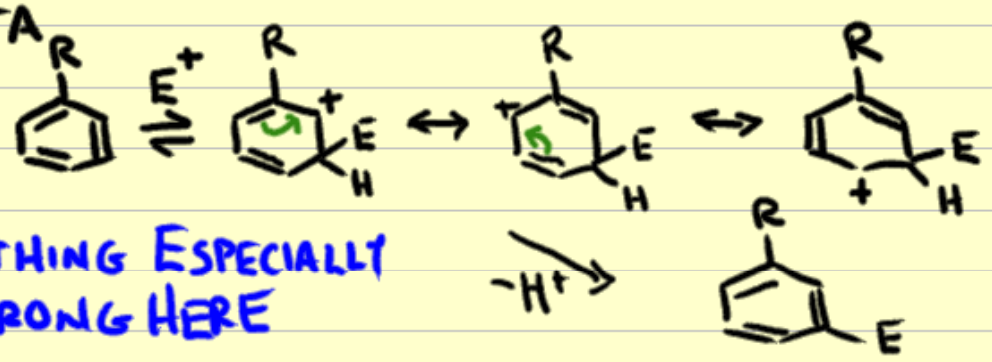
$-I$ OR $-M$

ORTHO



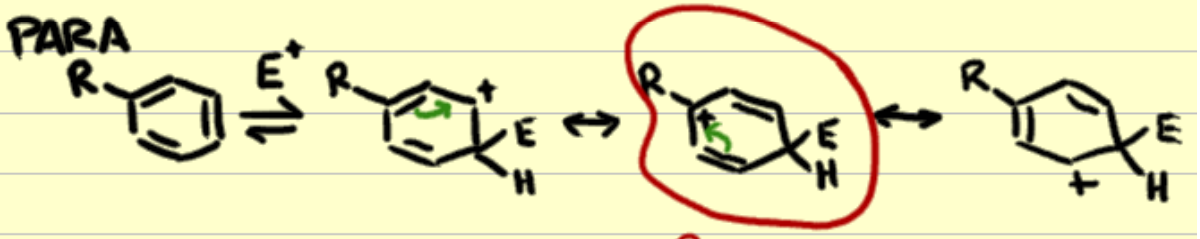
BAD.

META

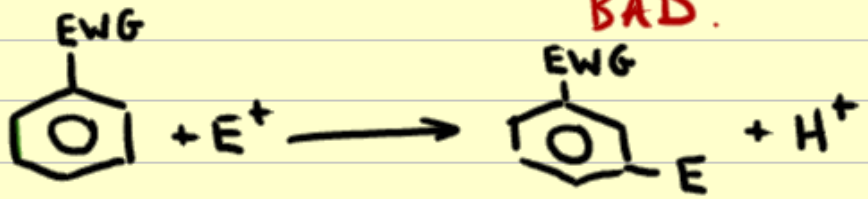


NOTHING ESPECIALLY WRONG HERE

PARA



BAD.



IF THE RXNS GO.

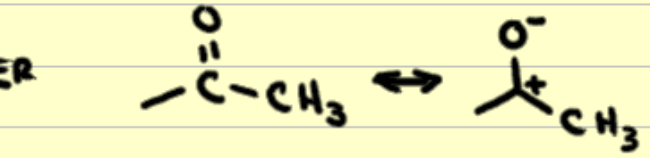
WHAT ARE THE EWG'S ?

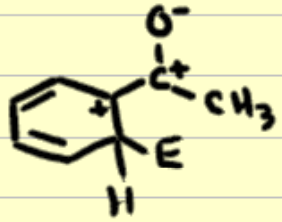
STRONG $-NO_2$ $\left(-\overset{+}{N}\overset{-O^-}{=O}\right)$

$-\overset{+}{N}R_3$ $(-\overset{+}{N}H_3)$

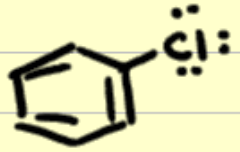
MEDIUM $-CF_3$, $-C\equiv N$, $-\overset{O}{\overset{\|}{C}}-OR$, $-SO_3R$

$-\overset{O}{\overset{\|}{C}}-R$ (INCLUD. $-\overset{O}{\overset{\|}{C}}-H$)

IF WE CONSIDER 

 BAD NEWS.

HOW ABOUT THE HALOGENS?

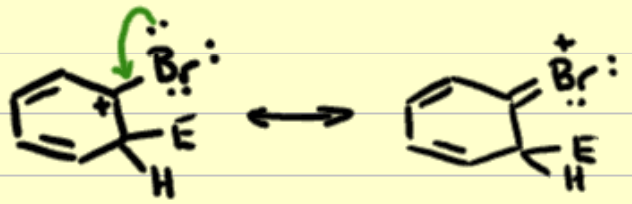


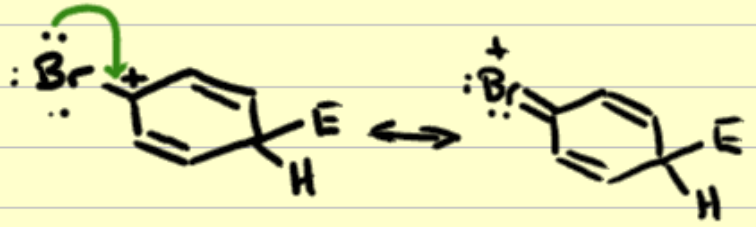
-I GROUPS (EWG)

+M GROUPS (EDG)

- RESULT - DEACTIVATING (SLIGHTLY)

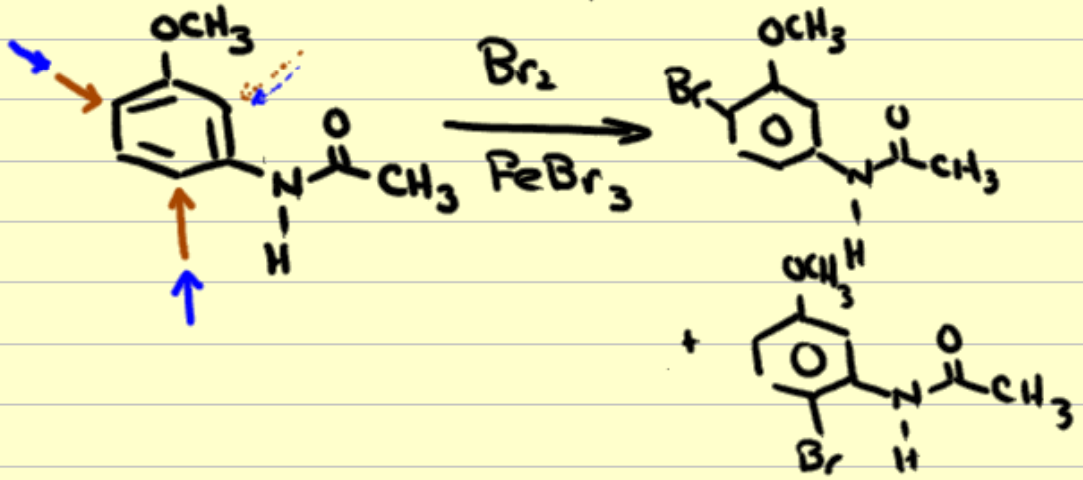
- BUT ORTHO- PARA- DIRECTING.





Disubstituted Cases - What Happens?

1) If both groups direct to the same position, it's easy



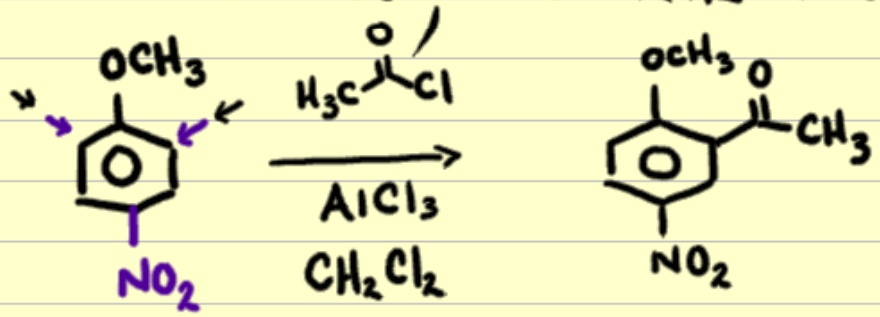
235 Notes

Notebook: jgreen1263's notebook
Created: 11/13/2009 2:45 PM **Updated:** 1/22/2013 11:47 AM

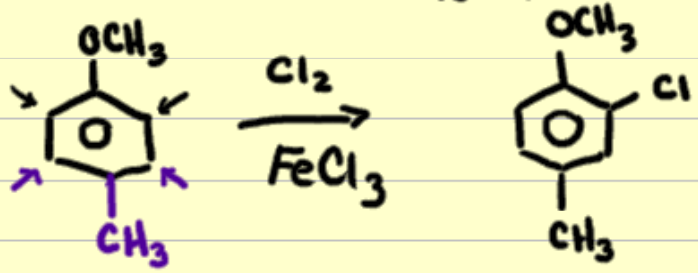
CHEM. 235 - LECTURE 5

CONT'D - DISUBSTITUTED CASES

1) IF TWO EXISTING GROUPS AGREE ON WHERE SUBSTITUTION SHOULD
   - SIMPLE. GOES WHERE EXPECTED

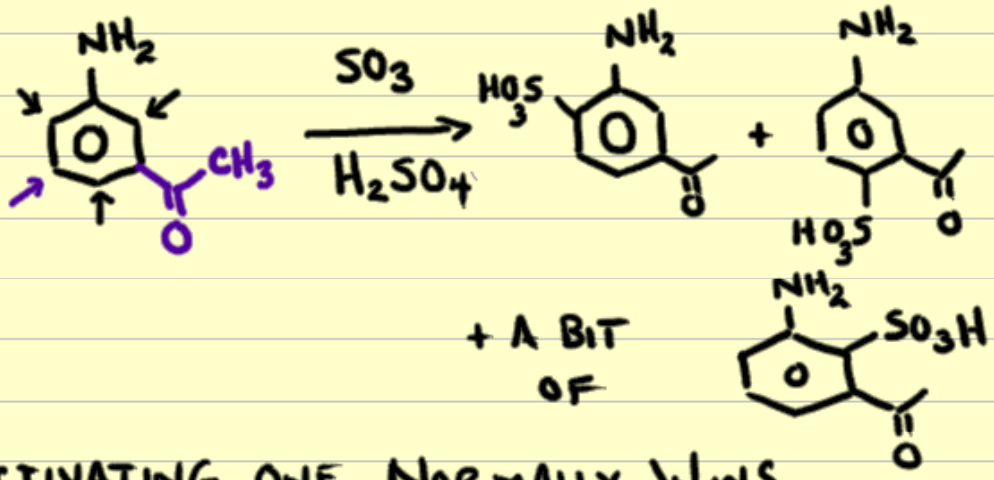


2) IF THEY DON'T AGREE



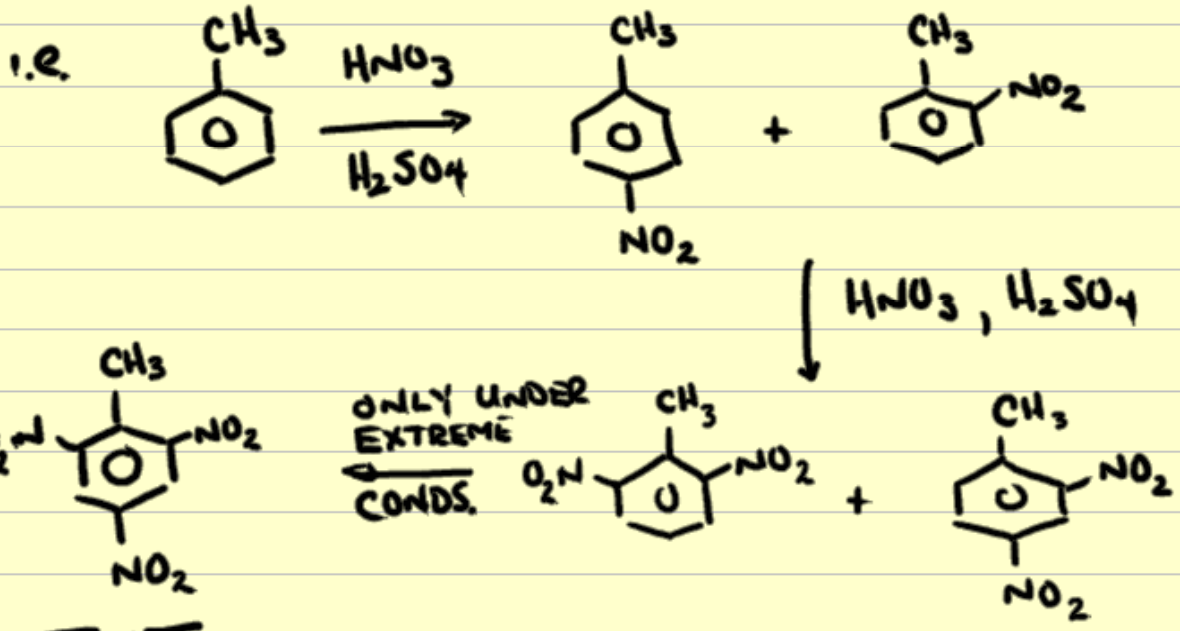
- IF TWO ACTIVATING GROUPS, THE MORE STRONGLY ACTIVATING ONE 'WINS.

3) IF ONE IS ACTIVATING, ONE IS DEACTIVATING

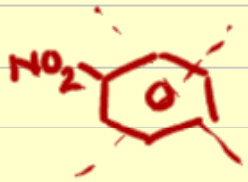


- ACTIVATING ONE NORMALLY WINS

NOTE: IF TWO EWG (DEACTIVATING GROUPS) RXN NORMALLY WON'T GO.



TNT



Side Chain Functionalization

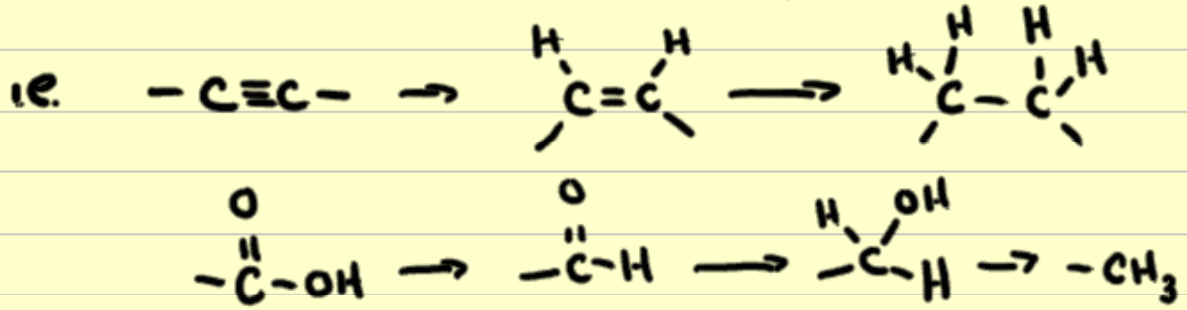
- Simplest ones Oxidation or Reduction Rxns.

Oxidation

- Addition of 'O' Atoms or Loss of H Atoms

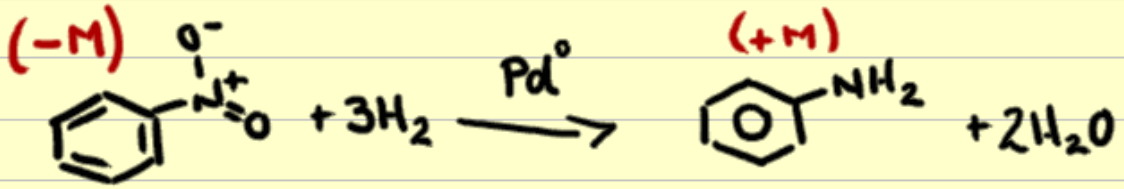
Reduction

- Addition of H Atoms or Loss of 'O' Atoms.



1) Reduction of $-NO_2$ Group

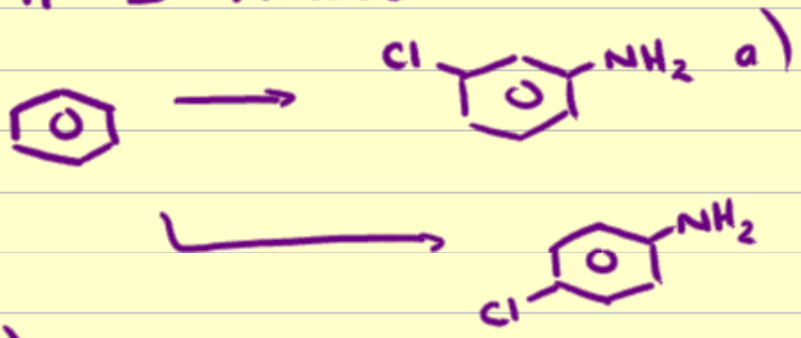
- Under Catalytic Hydrogenation Conditions, $-NO_2$ is Reduced to An $-NH_2$



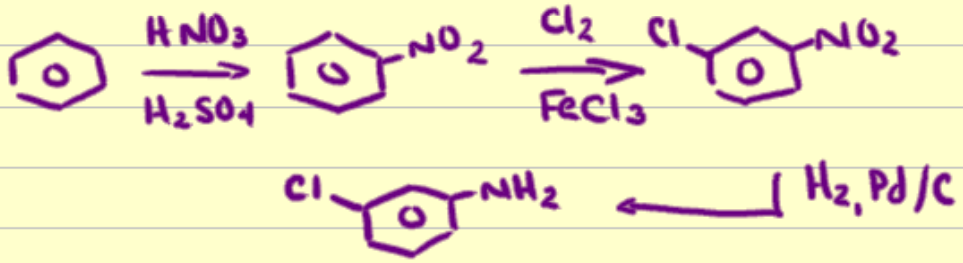
- MOST EASILY REDUCED GROUP IN ORGANIC CHEMISTRY (BY Pd, H_2)

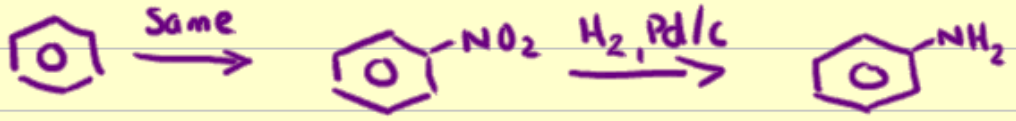
- NOTE: WE'VE CONVERTED A STRONG EWG TO A STRONG (EDG)

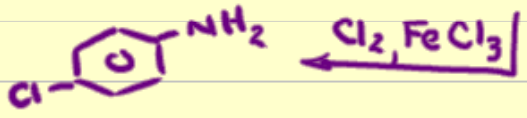
I.E. IF I ASKED



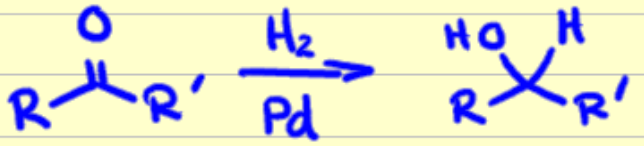
FOR a)



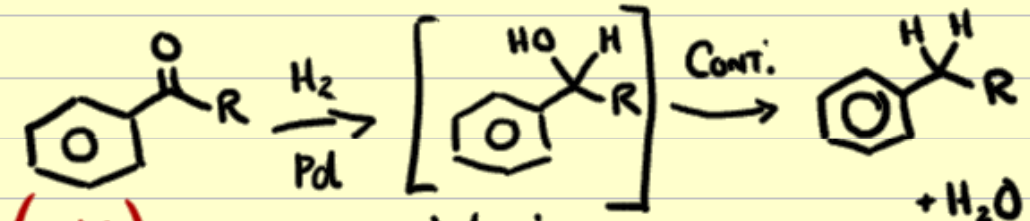
b) 

(+SOME ORTHO) 

2) Reduction of Ketone / Aldehyde

RECALL 

BUT.



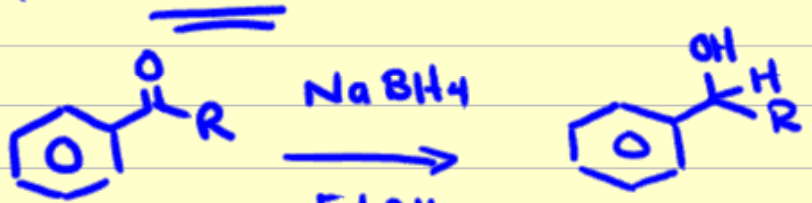
(-M)

Won't Stop

+I (weak)

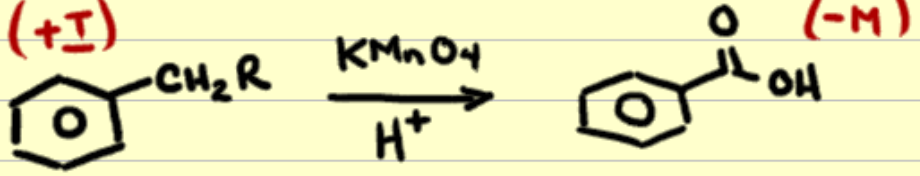
- Combined Hydrogenation / Hydrogenolysis

IF YOU WANT THE ALCOHOL



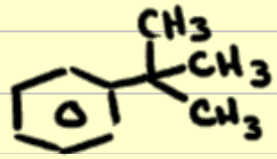
Rxn Stops Here

3) Oxidation of Alkyl Side Chain

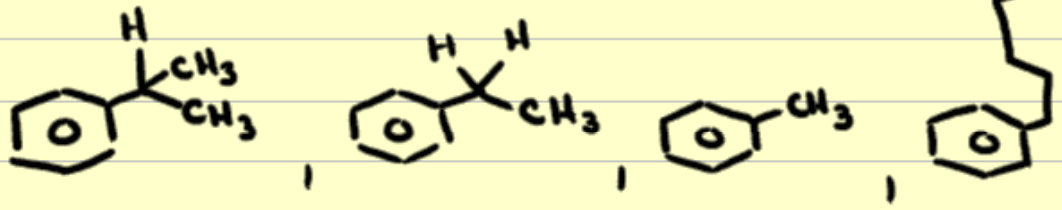


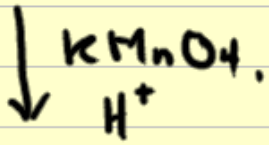
(Some Texts will use $Na_2Cr_2O_7, H^+$)

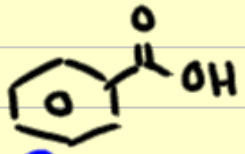
NEED 1 (OR MORE) BENZYLIC H FOR THIS TO OCCUR



WON'T REACT.

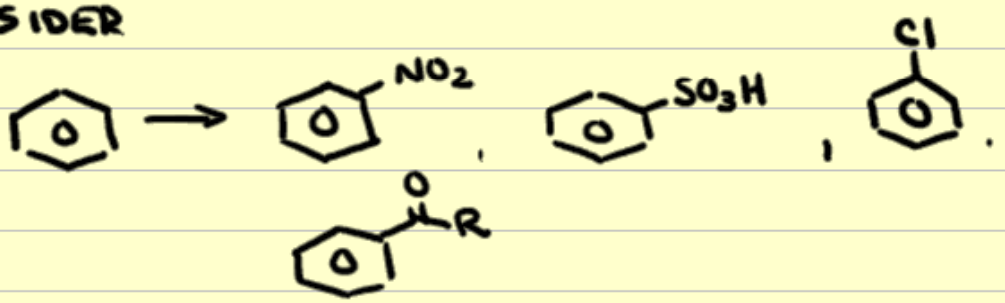






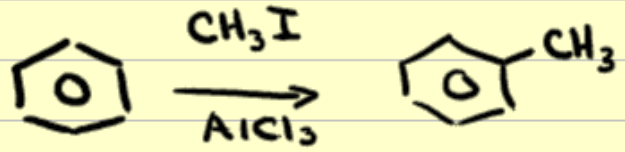
THE FRIEDEL-CRAFTS ALKYLATION PROBLEM

CONSIDER

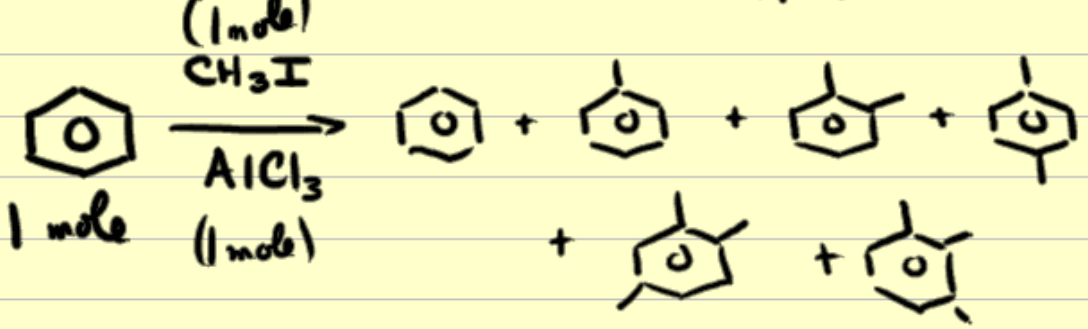


IN EACH OF THESE CASES, THE PRODUCT IS DE-ACTIVATED RELATIVE TO THE STARTING MATERIAL

- EASY TO PUT EACH E^+ IN ONCE AND HAVE THE RXN STOP THERE

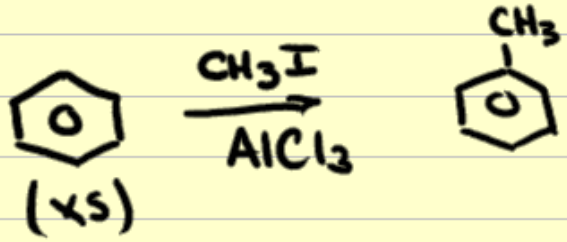
BUT 

PRODUCT IS MORE REACTIVE TO THE RXN CONDS. THAN THE STARTING MATERIAL



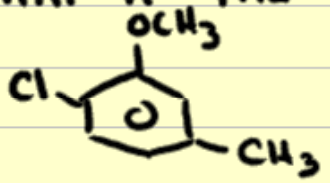
POLYALKYLATION

SOLUTION - IN MANY CASES, THE BENZENE IS CHEAP, SO WE CAN USE IN EXCESS



GOOD YIELD

BUT WHAT IF THE STARTING MATERIAL IS



NOT CHEAP

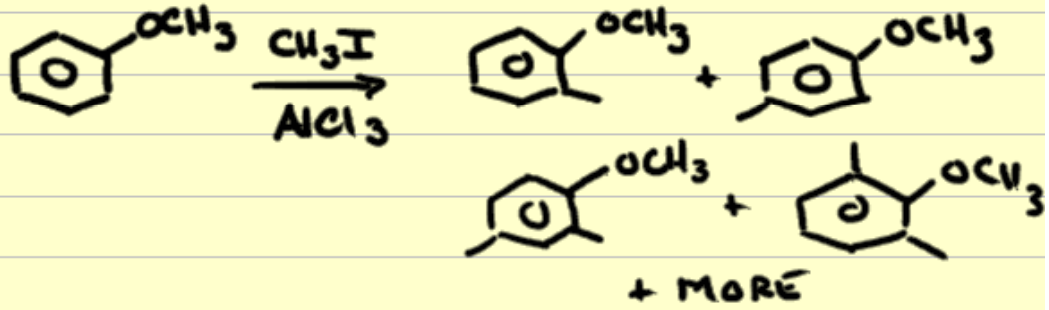
235 Notes

Notebook: jgreen1263's notebook
Created: 11/13/2009 2:45 PM **Updated:** 1/24/2013 11:18 AM

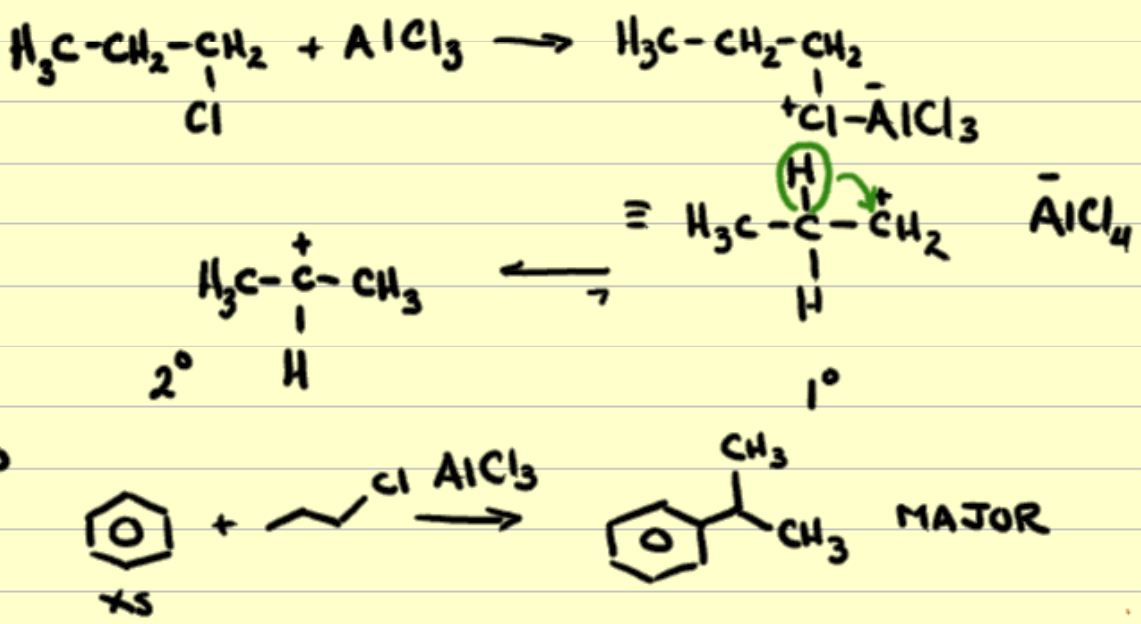
CHEM. 235 - LECTURE 6

F.C. ALKYLATION ISSUES

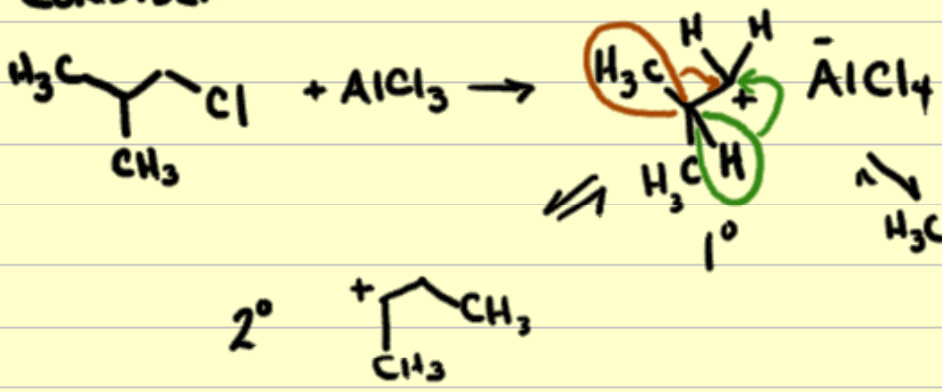
1) POLYALKYLATION



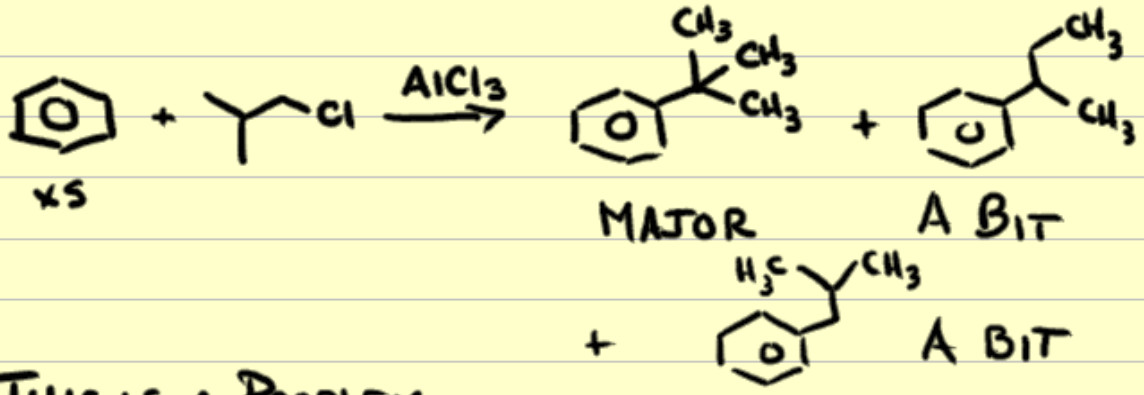
2) CARBOCATION REARRANGEMENTS



CONSIDER



2°

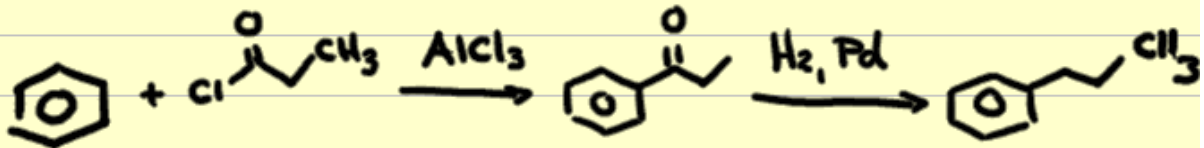


MAJOR A BIT

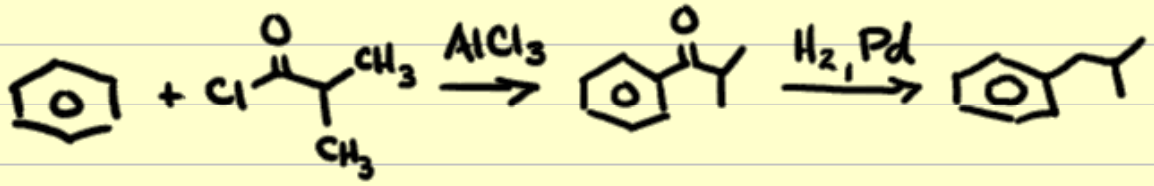
A BIT

THIS IS A PROBLEM.

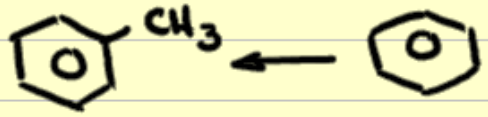
SOLUTION - FRIEDEL CRAFTS ACYLATION, AND THEN REDUCTION



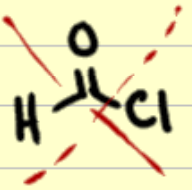
MONOACYLATION ONLY



- THIS IS BETTER APPROACH
  - EXCEPT FOR



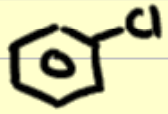
WE WOULD WANT



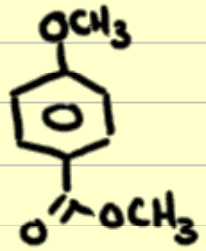
NOT A STABLE COMPOUND.

ONE OTHER ISSUE WITH FRIEDEL-CRAFTS ALKYLATION AND ACYLATION

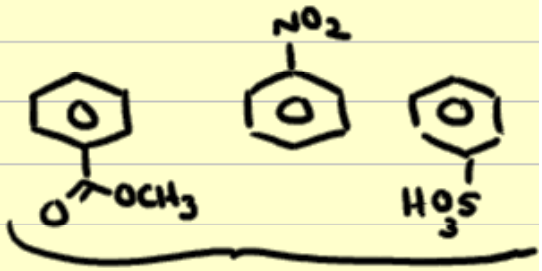
- RXNS DON'T GO IN MEDIUM TO STRONGLY DEACTIVATED SYSTEMS



OK

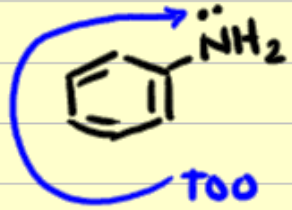


OK



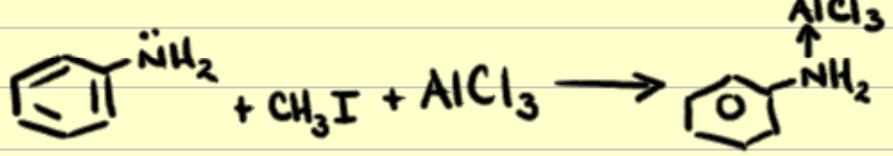
TOO DEACTIVATED.

NOTE

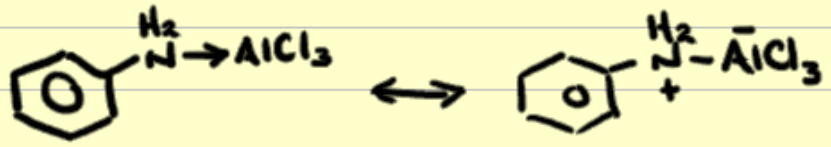


ALSO WON'T GO. (!)

TOO BASIC / NUCLEOPHILIC

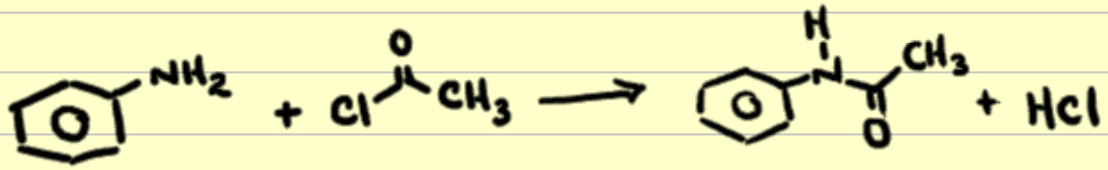


COMPLEX

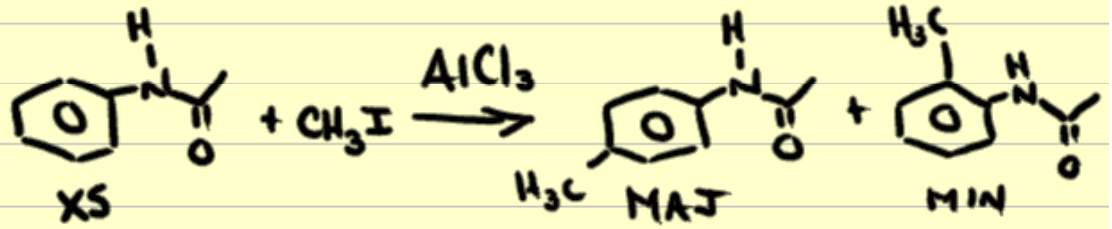


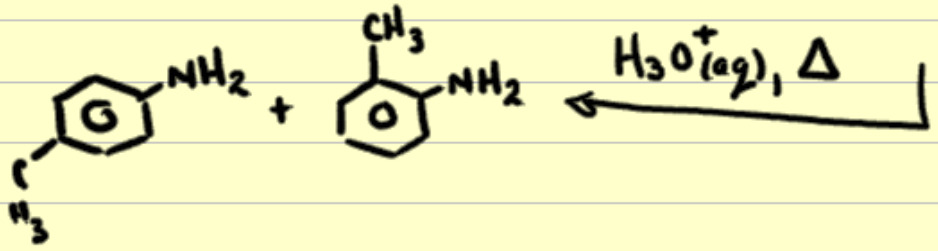
NOW DEACTIVATED

SOLUTION - VIA AMIDE



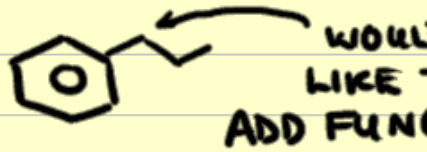
- $\ddot{N}$ IS PARTIALLY TIED UP IN CARBONYL
- STILL ACTIVATING (NOW MODERATE)
- NOT NEARLY AS LEWIS BASE



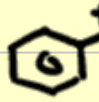


SIDE CHAIN FUNCTIONALIZATION, CONT'D.

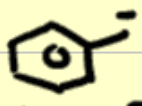
4) RADICAL BENZYLIC BROMINATION



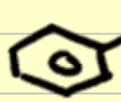
WOULD LIKE TO ADD FUNCTIONAL GROUPS.



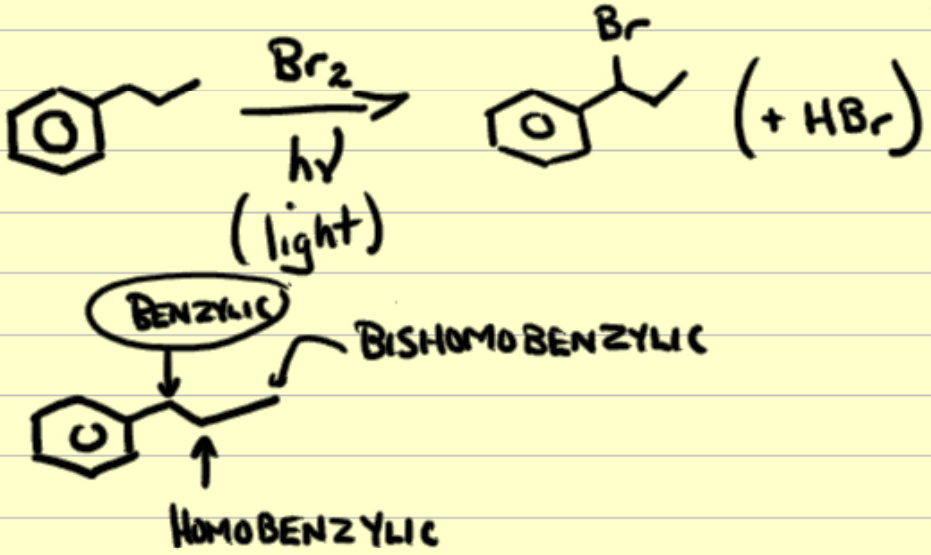
SEEN



WILL SEE HAVE SEEN



FREE RADICAL ??

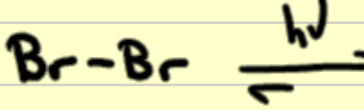


MECHANISM- RADICAL CHAIN MECHANISM

i) INITIATION ii) PROPAGATION

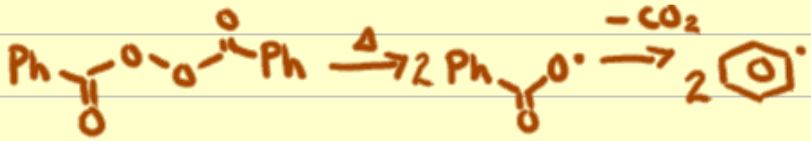
iii) TERMINATION

i) INITIATION - HOW THE 1ST RADICAL IS GENERATED

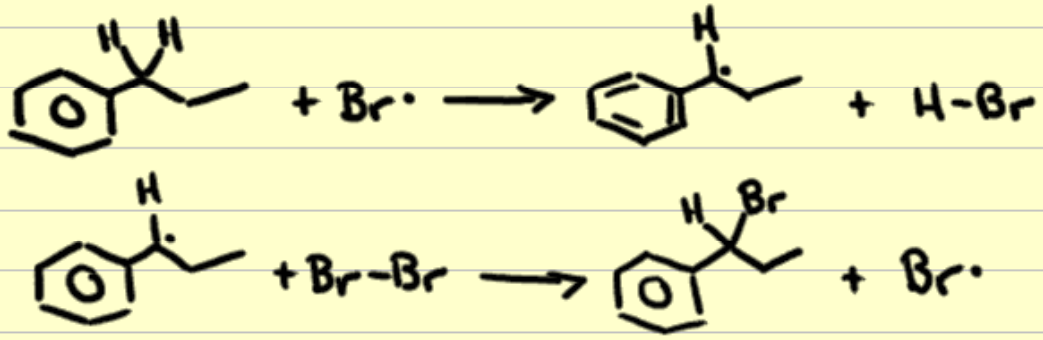


≡ IN·

OTHER POSSIBILITIES

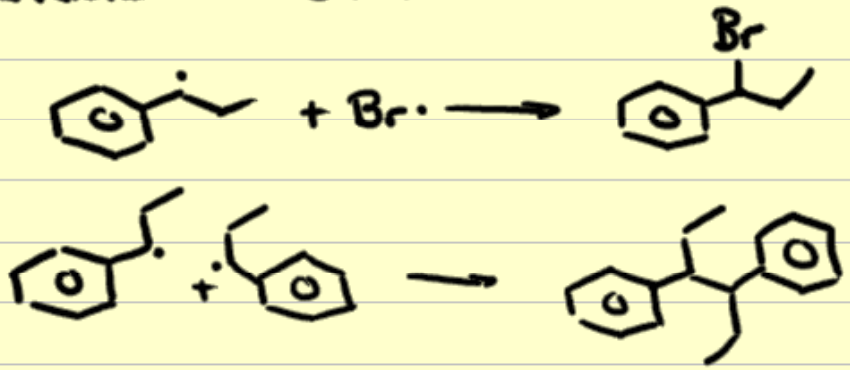


ii) PROPAGATION - CONSUMES SUBSTRATE & FORMS PRODUCT, BUT REGENERATES RADICAL.



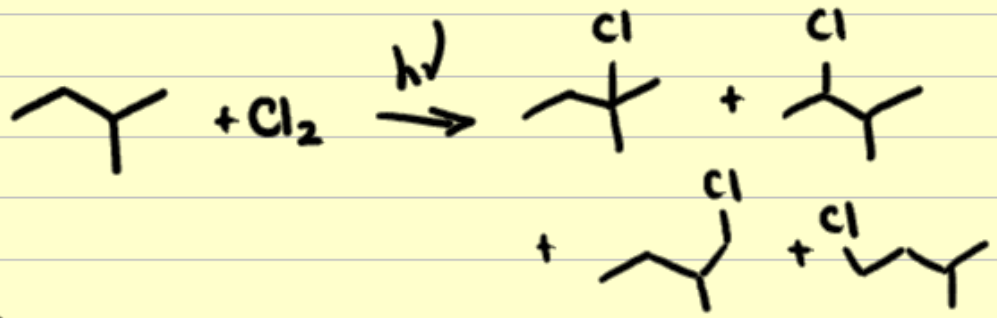
iii) TERMINATION - DESTRUCTION OF FREE RADICALS.

SEVERAL POSSIBILITIES -

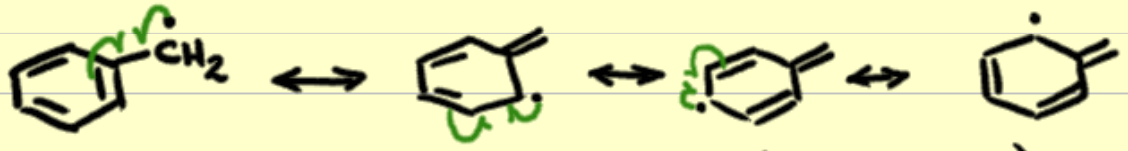


WHY BENZYLIC POSITION?

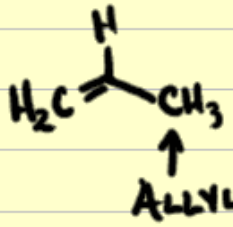
- RADICALS ARE HIGH ENERGY SPECIES
  - RADICAL HALOGENATION LOTS OF THINGS
  - V. UNSELECTIVE.



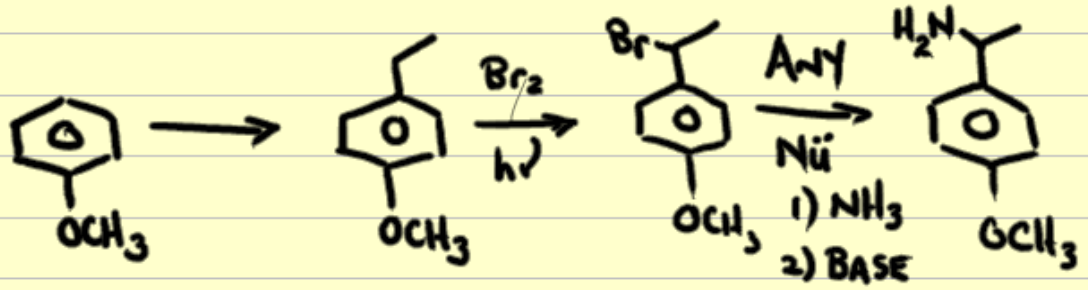
BUT



V. STABILIZED AT BENZYLIC (OR ALLYLIC) SITE



SO, MAKES FUNCTIONALIZATION OF MANY TYPES V. EASY



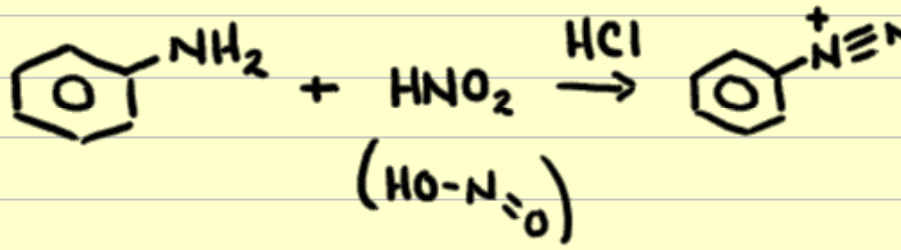
RADICAL CHLORINATION AT BENZYLIC SITE CAN BE DONE SIMILARLY.

235 Notes

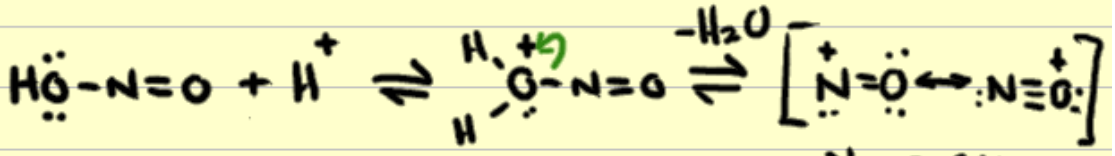
Notebook: jgreen1263's notebook
Created: 11/13/2009 2:45 PM **Updated:** 1/29/2013 11:14 AM

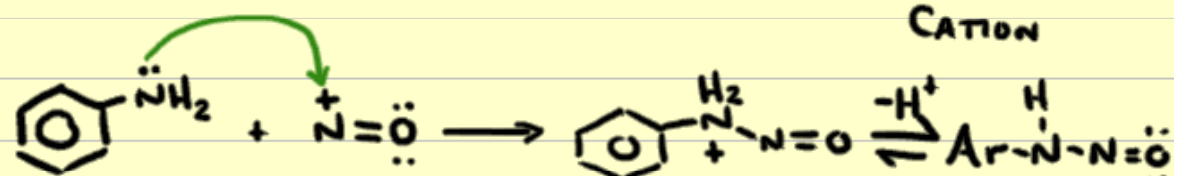
CHEM. 235 - LECTURE 7

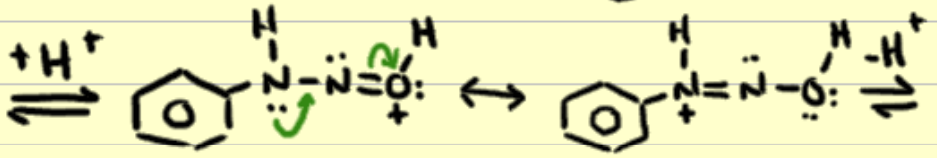
5) DIAZONIUM SALTS - SANDMEYER REACTION



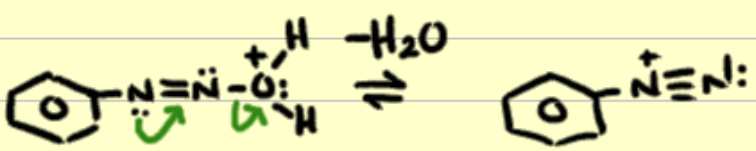
MECHANISM.







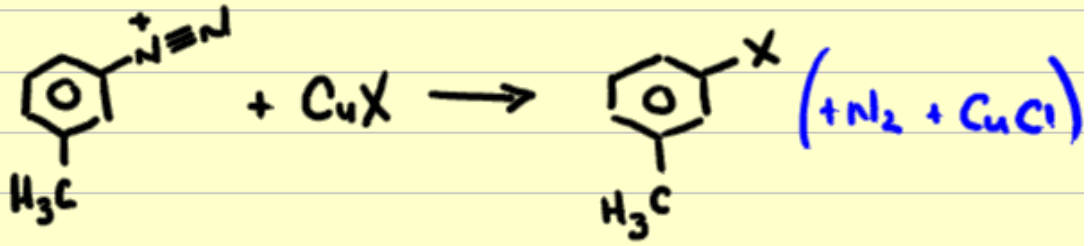
Note: I missed this +H⁺ in class



Very Reactive Species

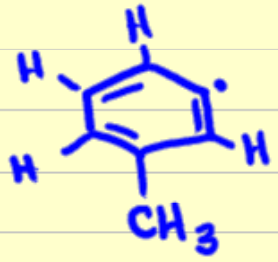
- Alkyl Diazonium Salts are usually Uncontrollable
- Aryl Ones Still Very Reactive

A) Reactions with Cu^{+1} Salts

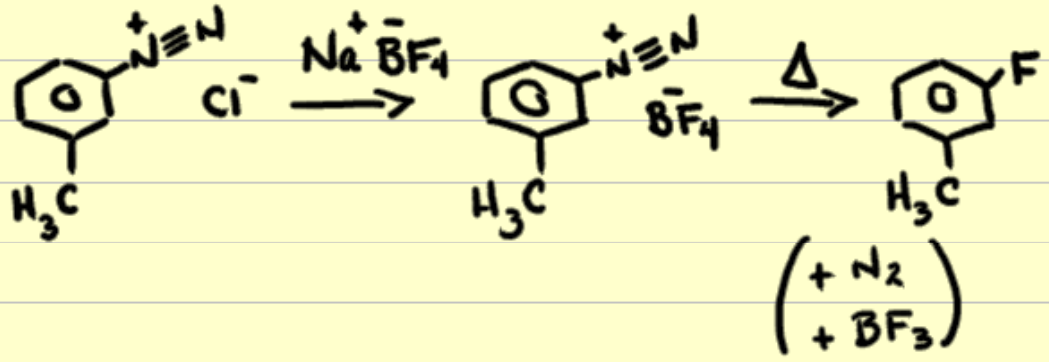


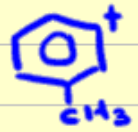
CuCl, CuBr, CuI, CuCN

Involves

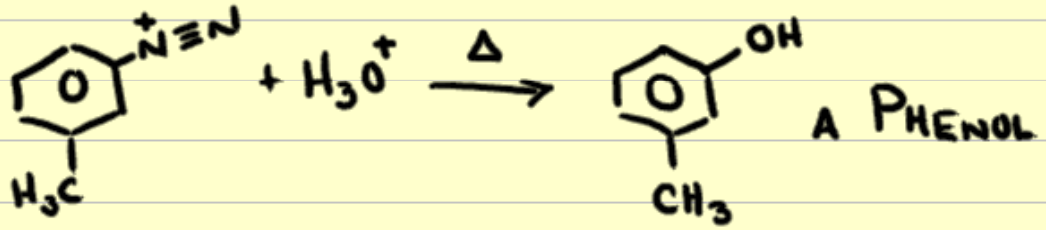


B) Schiemann Rxn.



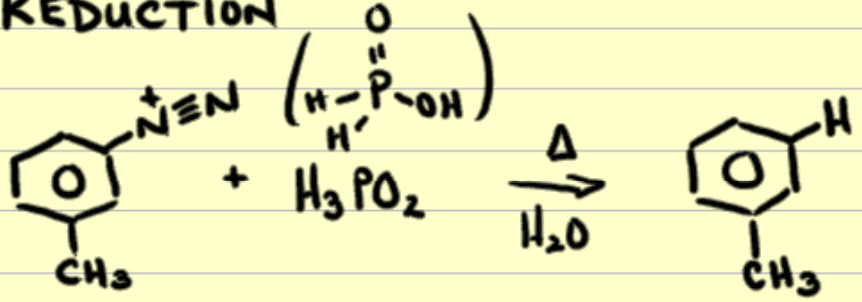
VIA  - DIAZONIUM SALTS ARE THE ONLY WAY THAT THESE ARE ACCESSIBLE

C) PHENOL SYNTHESIS



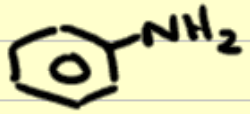
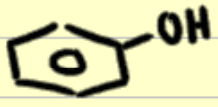
A PHENOL

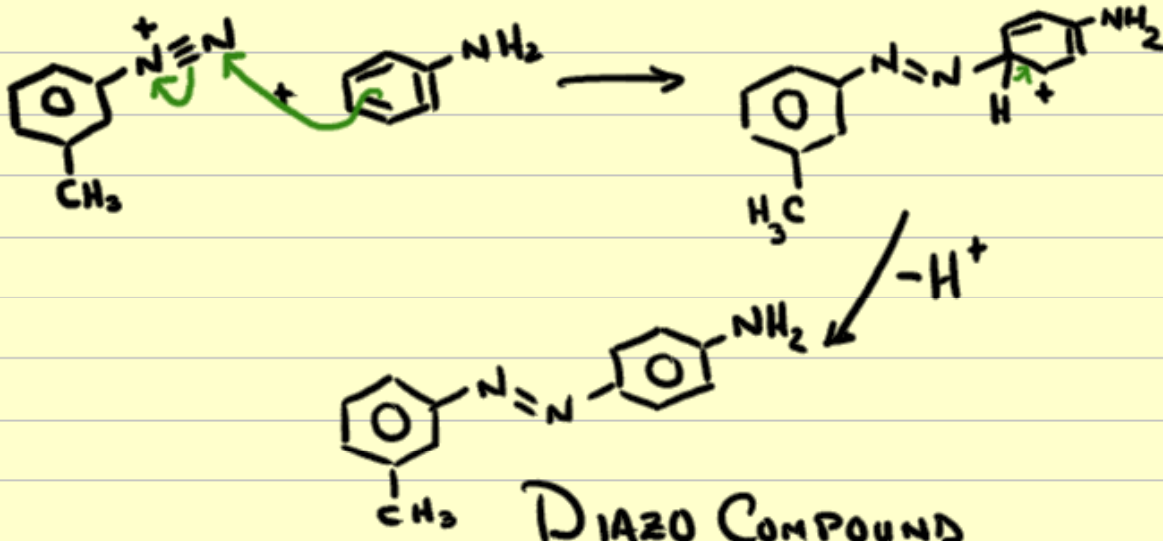
D) REDUCTION



E) DIAZO COUPLING.

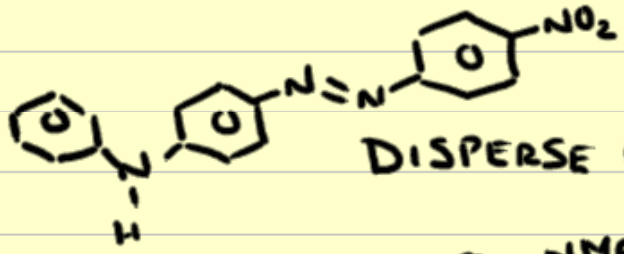
- THEY WILL REACT WITH BENZENES THAT ARE VERY ELECTRON RICH

I.E. ONLY  OR 

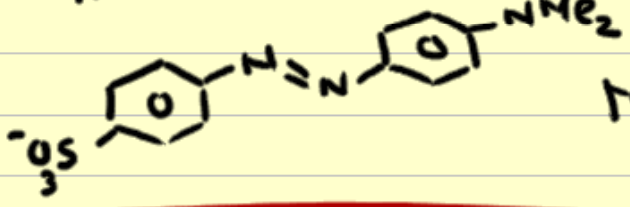


DIAZO COMPOUND
(MOSTLY PARA TO NH_2 OR OH)

MANY OF THESE ARE DYES - BRIGHTLY COLOURED



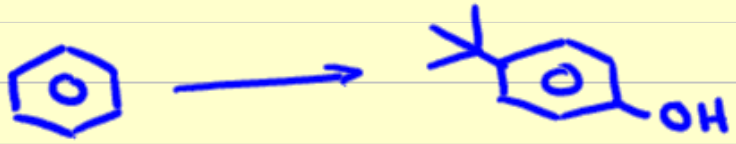
DISPERSE ORANGE 1

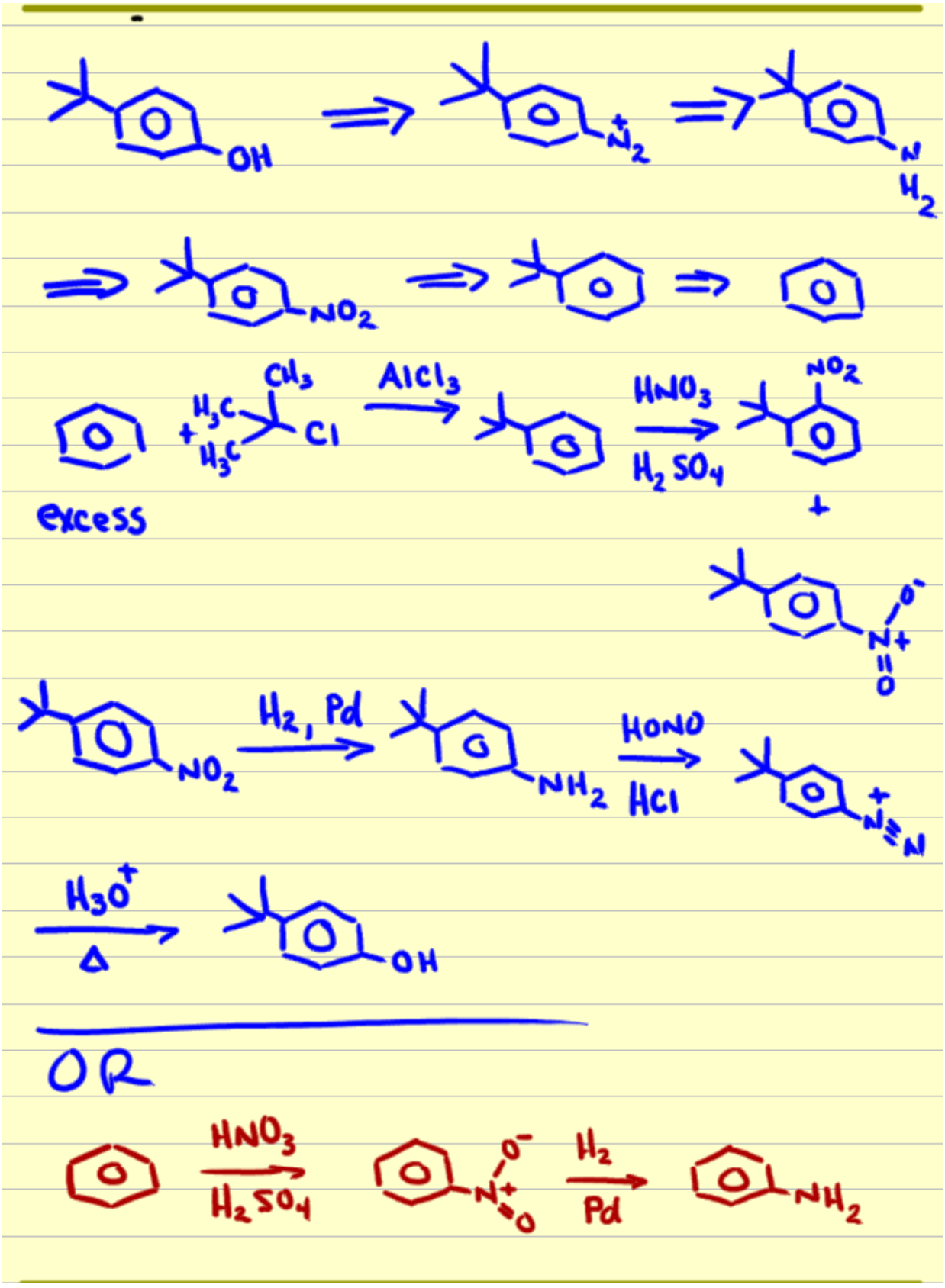


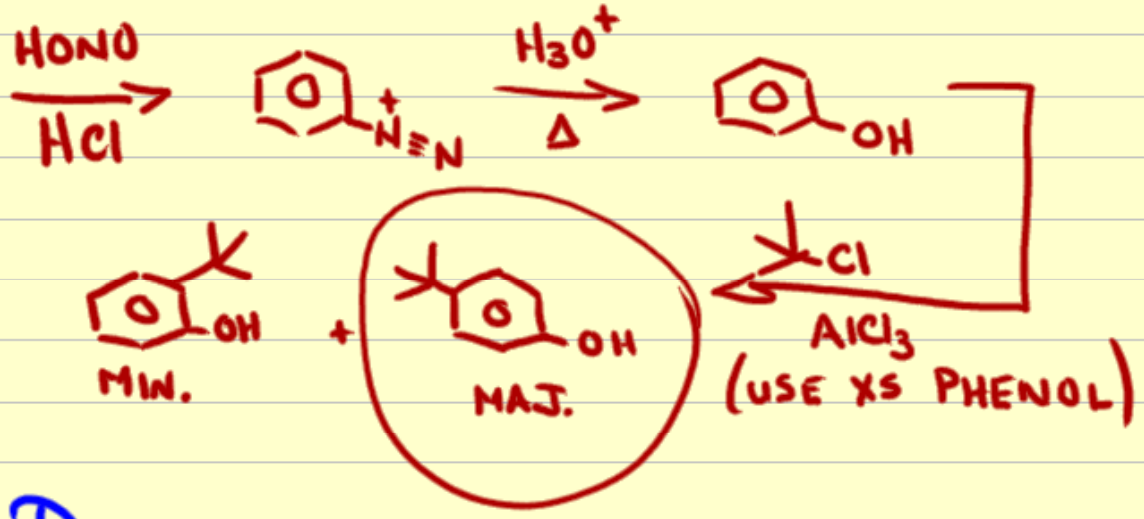
METHYL ORANGE

END OF TEST #1 MATERIAL

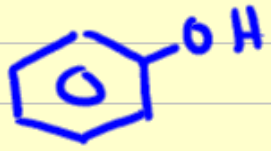
EXAMPLE OF A QUESTION



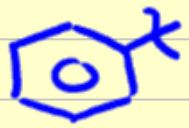

OH
N_2^+
NH2
NO_2
CH_3
H_3C
H_3C
Cl
$AlCl_3$
HNO_3
H_2SO_4
NO_2
excess
H_2, Pd
NO_2
NH_2
HONO
HCl
N_2^+
H_3O^+
Δ
OH
OR
HNO_3
H_2SO_4
H_2
Pd
NH_2



PHENOLS



PHENOL



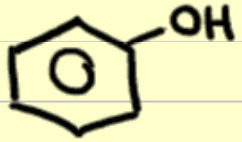
PHENYL SUBSTITUENT

235 Notes

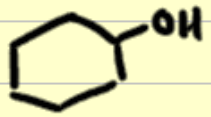
Notebook: jgreen1263's notebook
Created: 11/13/2009 2:45 PM **Updated:** 1/31/2013 11:20 AM

CHEM. 235 - LECTURE 8

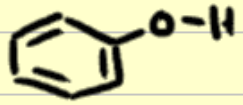
PHENOLS



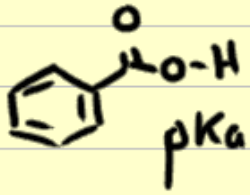
RELATIVELY ACIDIC



pKa 17

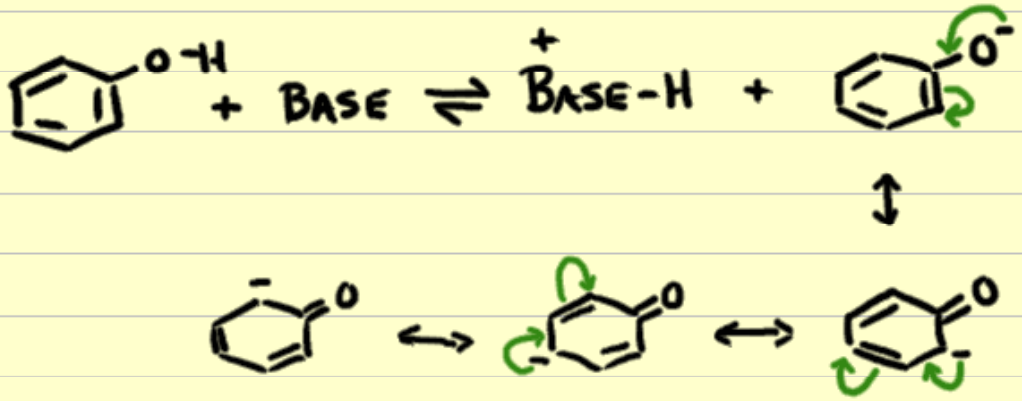


pKa ~10

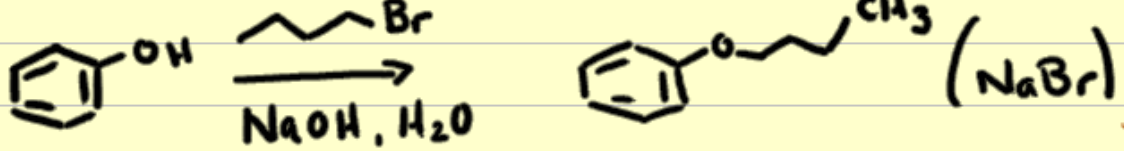


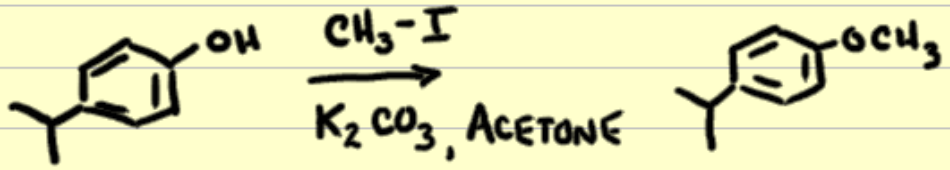
pKa 4-5

HALF WAY BETWEEN ALCOHOL & ACID IN ACIDITY



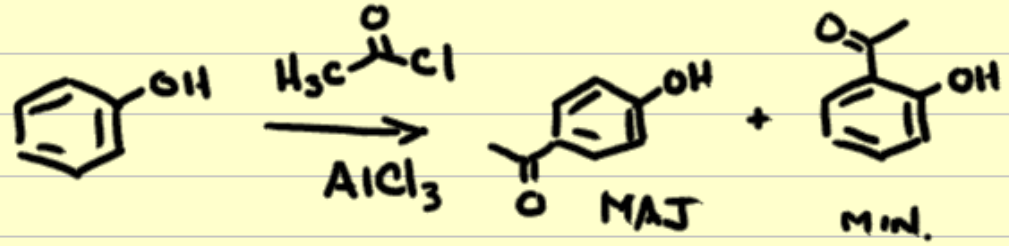
1) ALKYLATION OF PHENOLS



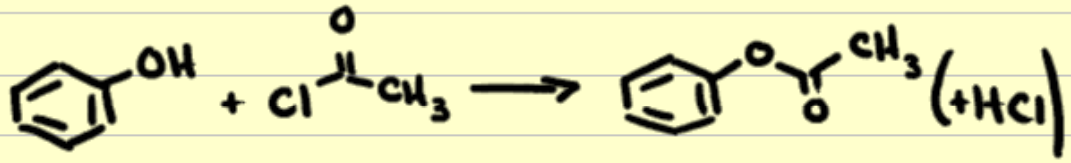


2) Acylation of Phenols

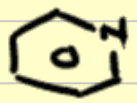
- Can Acylate on Carbon or Oxygen
- If Lewis Acid used, Rxn Goes on Carbon



- If No Lewis Acid - O Acylation

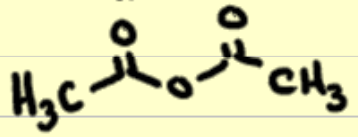


(Note: Weak Base Added to Consume HCl)

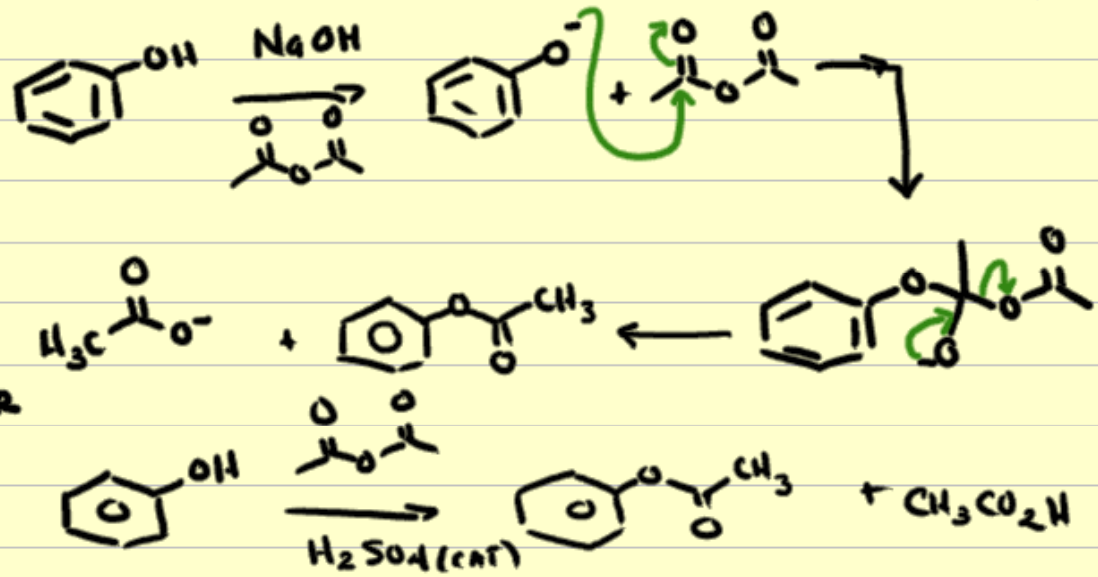


Pyridine

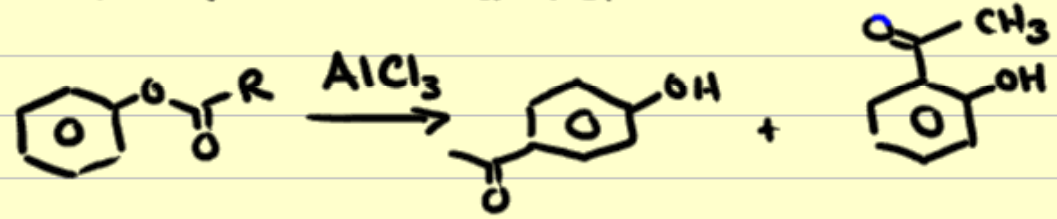
Could Also use An Anhydride



But Need Added Base or Acid to Make it Go.

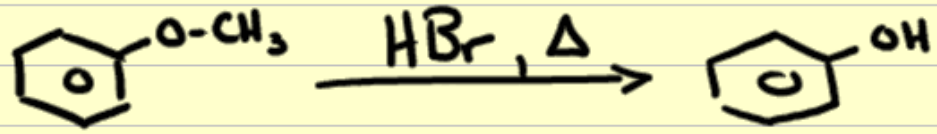


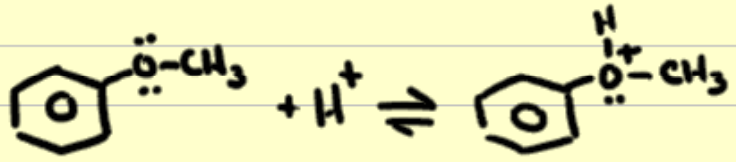
- THESE ESTERS CAN BE CONVERTED TO C-ACYLATION PRODUCTS.

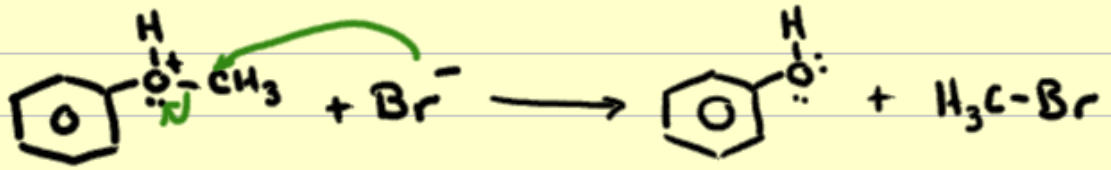


KNOWN AS FRIES REARRANGEMENT.

- CAN WE DE-ALKYLATE PHENOLIC ETHER?

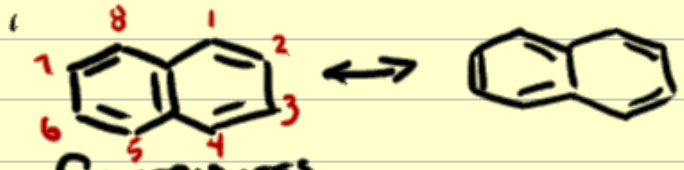


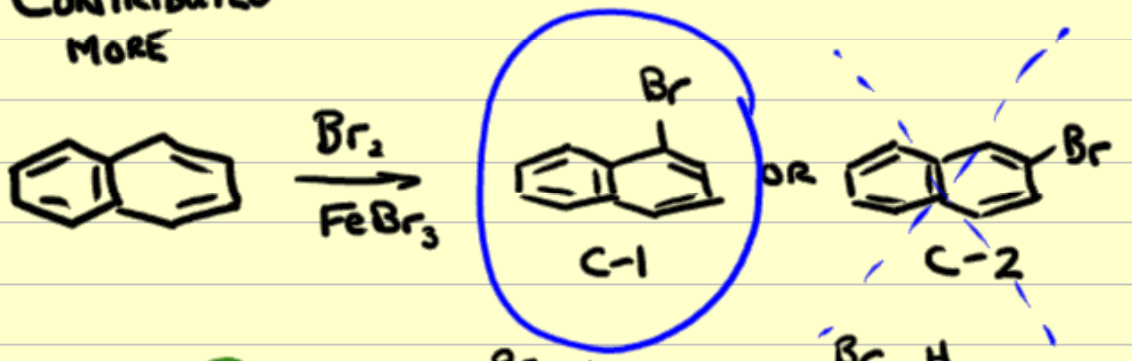
MECH 

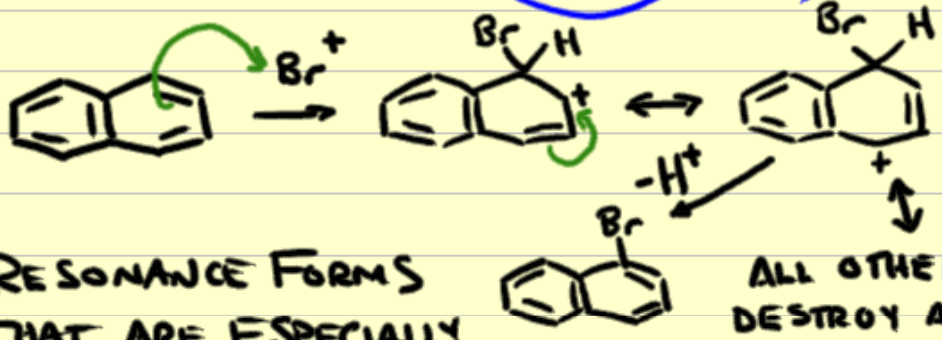


Other Aromatic Systems

Naphthalene



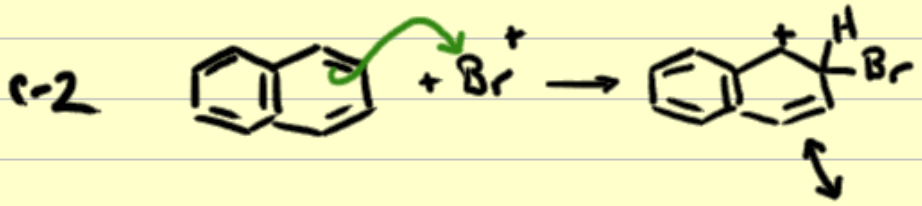




C-1

2-Resonance forms that are especially good.

All others destroy aromatic nature of both rings

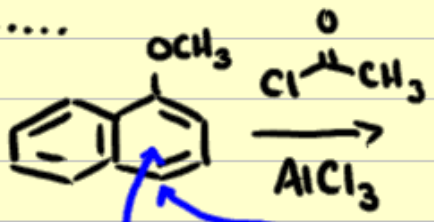


C-2

1 ESP. GOOD RESONANCE FORMS.

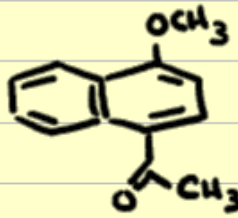
ALL OTHER RESONANCE FORMS DESTROYS BOTH RINGS' AROMATICITY

So.....

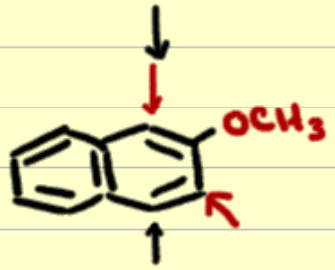


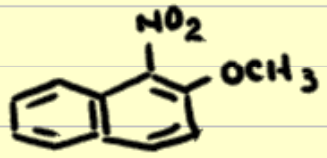
MORE e^- RICH

WINS IN EVERY WAY



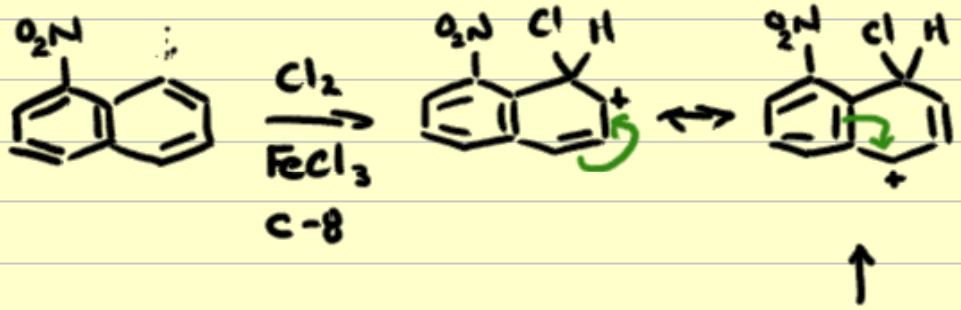
BOTH p- AND 'C-1 TYPE'



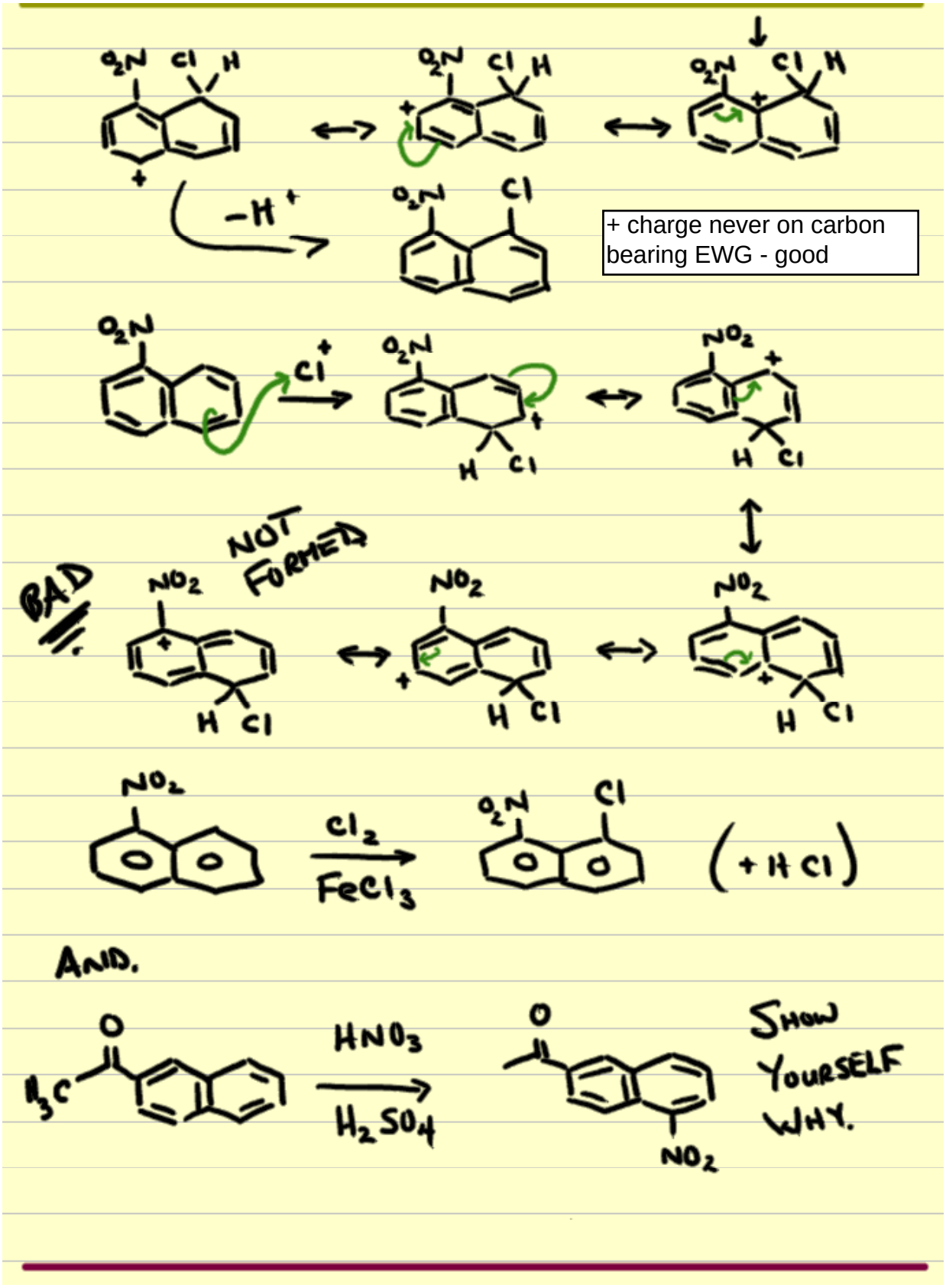


BOTH ORTHO AND C-1 TYPE

WHAT ABOUT



C-8

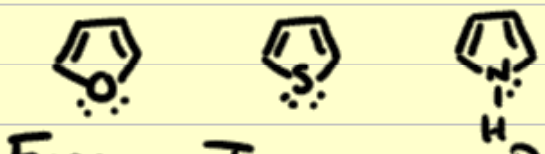

+ charge never on carbon bearing EWG - good
BAD
NOT FORMED
AND.
SHOW YOURSELF WHY.

235 Notes

Notebook: jgreen1263's notebook
Created: 11/13/2009 2:45 PM **Updated:** 2/5/2013 11:20 AM

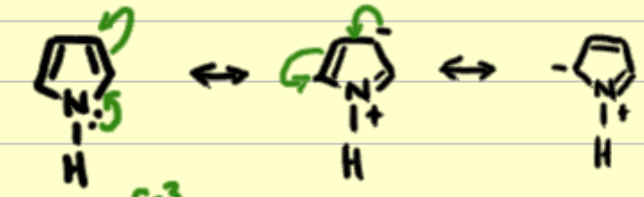
CHEM. 235 - LECTURE 9

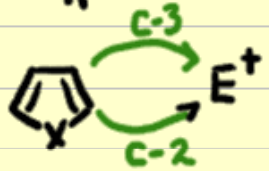
π - EXCESSIVE HETEROCYCLES

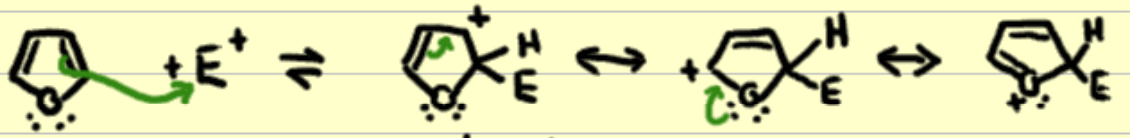


FURAN THIOPHENE PYRROLE

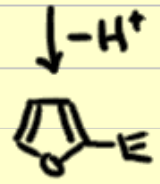
- ALL MORE REACTIVE THAN BENZENE





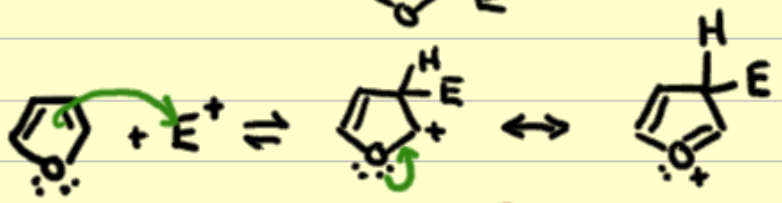


C-2



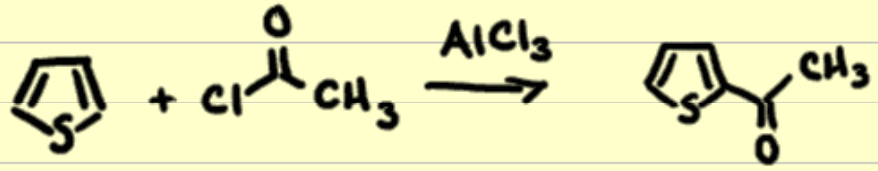
3 RESONANCE FORMS

C-3

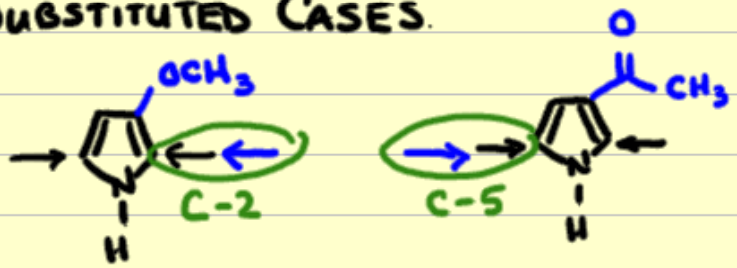


2 RESONANCE FORMS

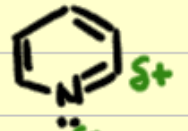
∴ C-2 SUBSTITUTION PREFERRED STRONGY IN THESE SYSTEMS



SUBSTITUTED CASES.



π-DEFICIENT HETEROCYCLES.

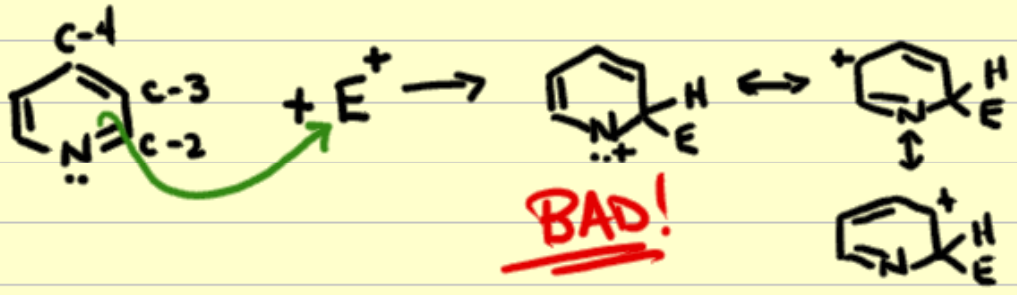


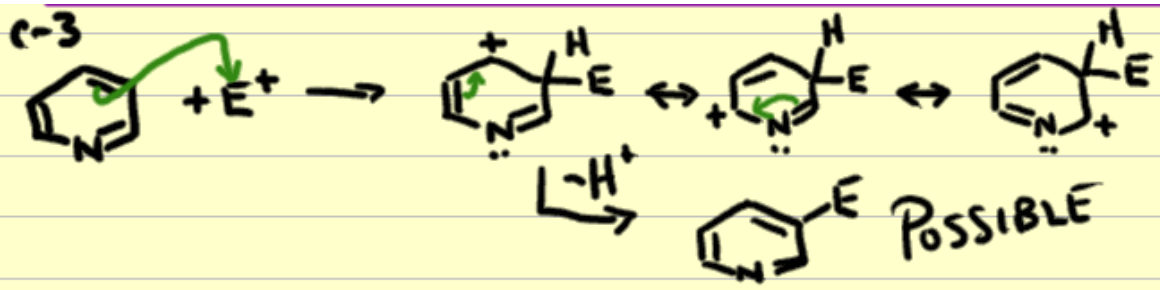
PYRIDINE

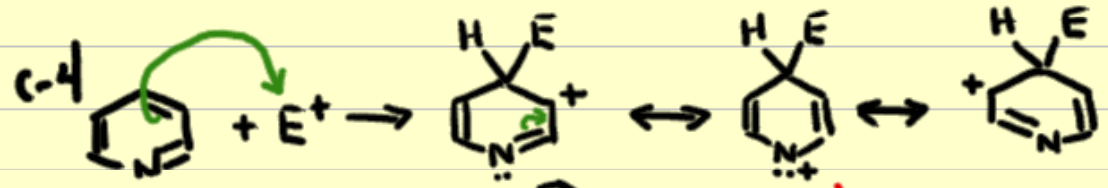
C'S RELATIVE ELECTRON DEFICIENT

∴ MUCH LESS REACTIVE THAN BENZENE

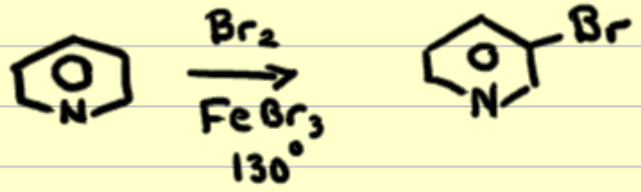
- OFTEN, RXN WON'T GO
- WHEN IT DOES GO





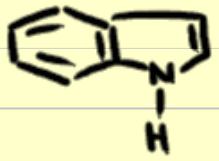


C-4 DISFAVOURED. BAD!!



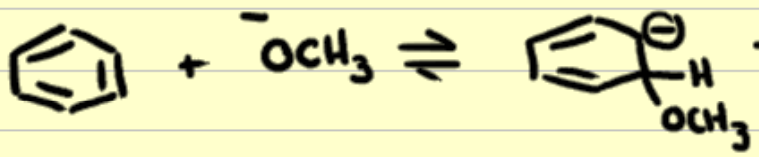
C-3 WINS.

WE'VE LEFT OUT



INDOLE

NUCLEOPHILIC AROMATIC SUBSTITUTION - IS THIS POSSIBLE?



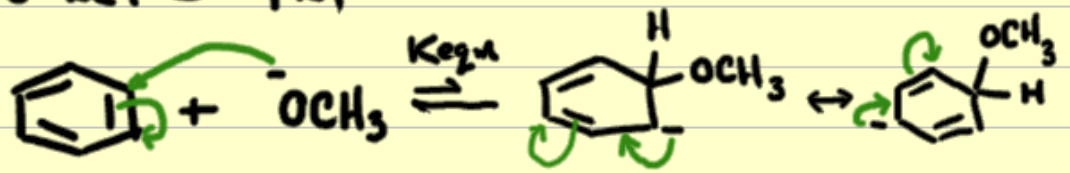
235 Notes

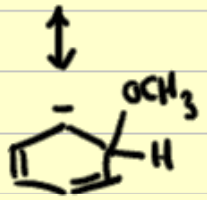
Notebook: jgreen1263's notebook
Created: 11/13/2009 2:45 PM **Updated:** 2/12/2013 11:22 AM

CHEM. 235 - LECTURE 10

NUCLEOPHILIC AROMATIC SUBSTITUTION

- LESS COMMON THAN ELECTROPHILIC SUBSTITUTION, BUT STILL FREQUENTLY SEEN
- SO LET'S TRY





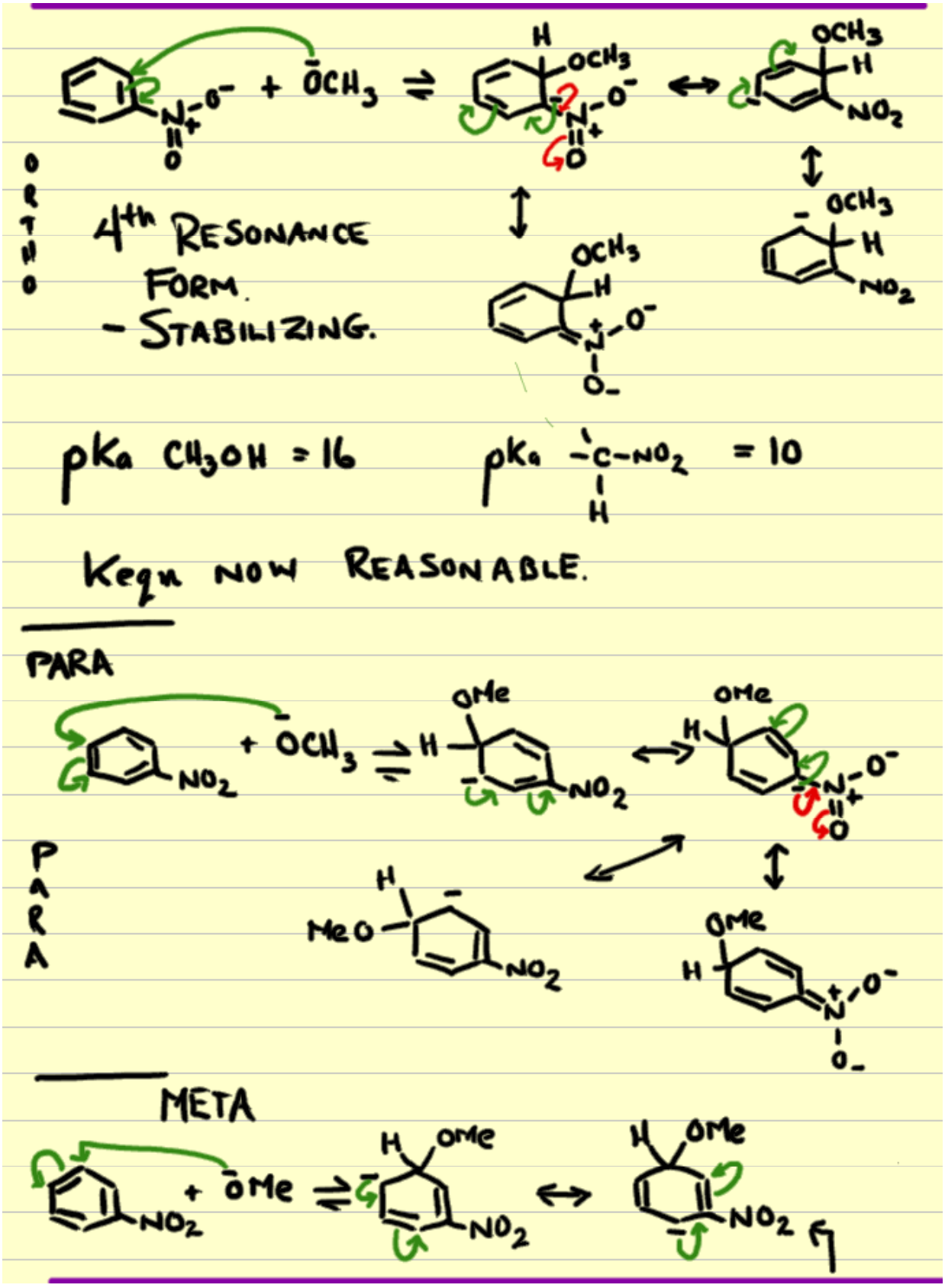
CONSIDER Keqm
- STILL DESTROYING AROMATIC

- pKa $CH_3OH \approx 16$ pKa  = 35

- DISFAVOURED SERIOUSLY

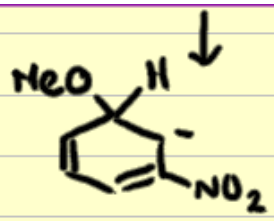
$\therefore K_{eqm} \ll\ll\ll\ll 1 \approx 0$

- SO LET'S PUT A VERY ELECTRON WITHDRAWING GROUP ON THE BENZENE $-NO_2$


ORTHO
4th RESONANCE FORM.
- STABILIZING.
pKa CH3OH = 16
pKa -C-NO2 = 10
H
Keqn NOW REASONABLE.
PARA
PARA
META

NEVER ON C WITH NO_2

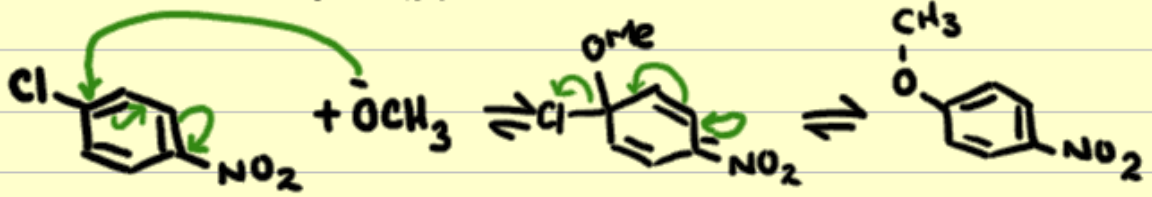
$\therefore$ NOT SAME STABILIZATION



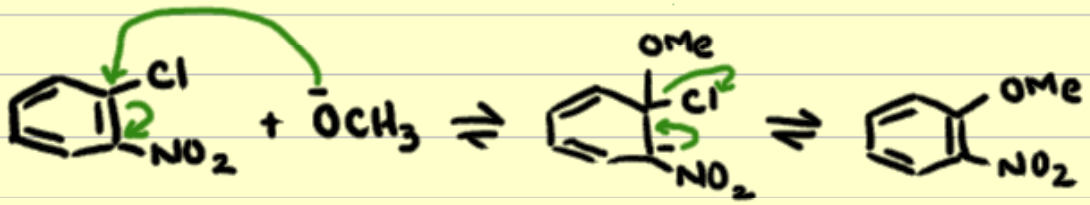
ISSUE #2

H^- IS A TERRIBLE LEAVING GROUP

- WE NEED SOMETHING BETTER, LIKE A HALOGEN.



VIABLE + Cl^-



VIABLE + Cl^-

- BUT NOT META -

$\therefore$ NUCLEOPHILIC AROMATIC SUBSTITUTION (S_NAr) RXN.

- TWO STEPS, BUT 1ST STEP IS THE SLOW, RATE DETERMINING ONE

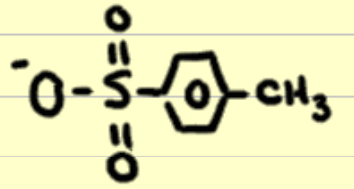
- 1ST STEP - DESTROYS AROMATICITY, COSTS 120KJ/mol ∴ TOUGHER.

- 2ND STEP - GET AROMATICITY BACK ∴ EASIER, FAST.

CONSEQUENCES ON LEAVING GROUP

FROM 230 COURSE X^- LEAVING GROUP

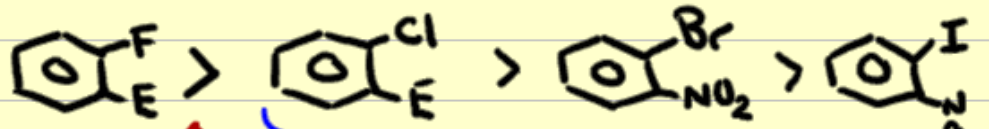
$$I^- > Br^- > Cl^- \gg F^-$$



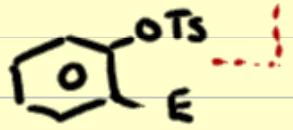
TOLUENESULFONATE (TOSYLATE ≡ ^-OTs)

$\approx Br^-$

- SINCE 1ST STEP IS SLOW IN S_NAr, WHAT'S CRITICAL IS THE ELECTRONEGATIVITY OF X

∴ 

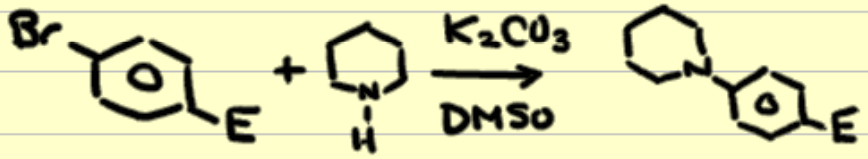
CLOSE



BETWEEN Ar-F & Ar-Cl

How About Other EWG's

- Let's Compare in A Standard Rxn.



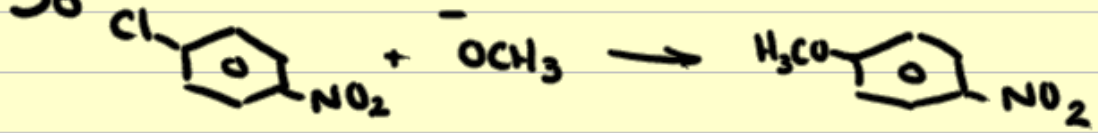
Relative Rate for E =

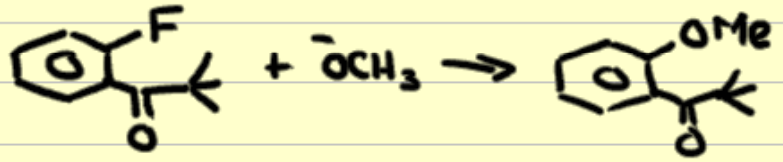
$-NO_2$	$-S(=O)(=O)-CH_3$	$-C\equiv N$	$-C(=O)CH_3$	$-CF_3$
100	5.3	3.1	1.3	? Too Low

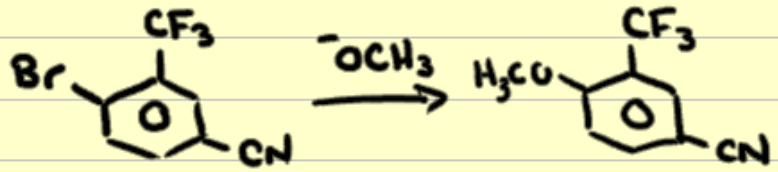
- Nitro is the Best - will work with All Halide / ^-OTs Leaving Groups

- The other EWG's Work with F^- Leaving, or There Must be A 2nd EWG (o-/p-) to Halide / ^-OTs

So





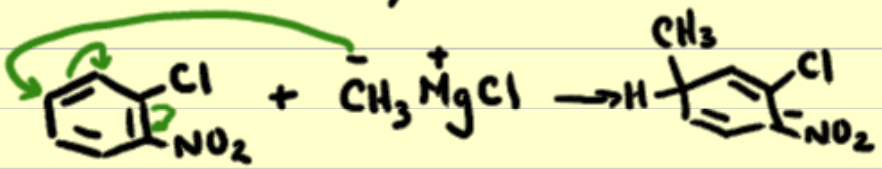


NUCLEOPHILES - USUALLY HETEROATOM BASED

$\bar{N}H_2$ ($NaNH_2$), RO^- (HO^- TOO), $R\ddot{N}H_2$ (NEUTRAL), RS^-,

X^- (HALIDE), $^-N_3$ ($\bar{N}=\overset{+}{N}=N^-$)

- NOT GRIGNARS, ORGANOLITHIUMS.

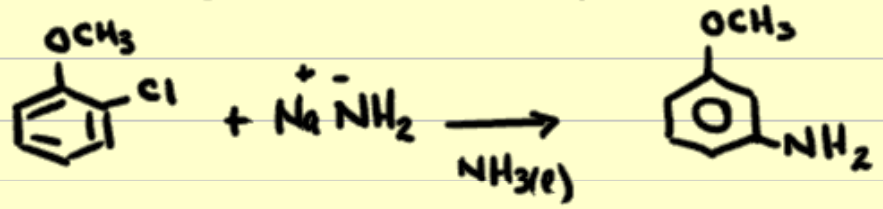


CAN'T GO ANY-WHERE

MESSY MIXTURE

BENZYNE MECHANISM.

- OCCASIONALLY SEE RXN THAT VIOLATES ALL OF THESE RULES



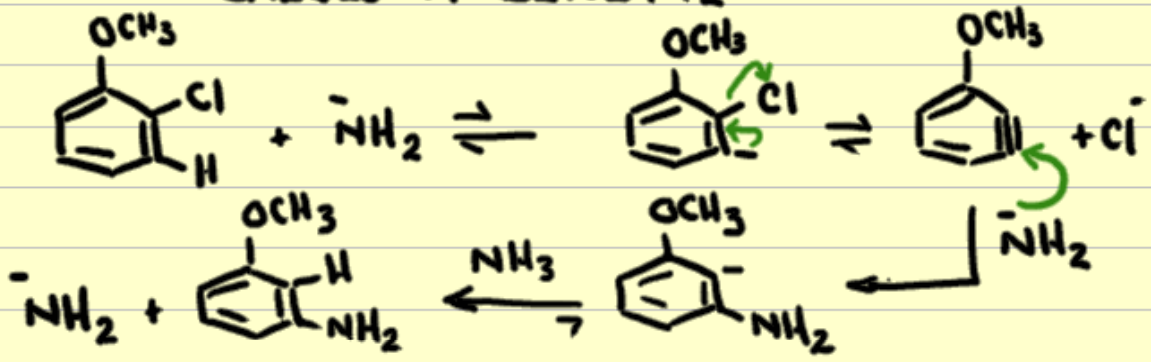
PROBLEMS

1) OCH_3 IS NOT AN EWG, IT'S EDG

2) NUCLEOPHILE DIDN'T GO IN WHERE THE LEAVING GROUP WAS

∴ MUST BE ANOTHER MECHANISM AT PLAY.
- FORSHADOWS ELIMINATION RXNS.

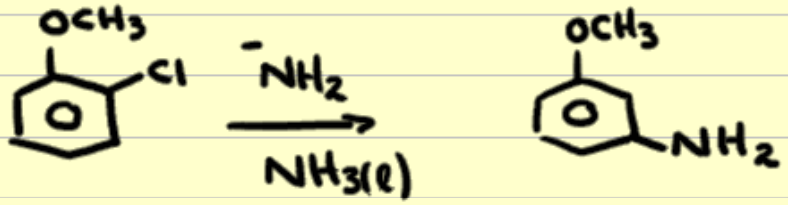
- INVOLVING A HIGH ENERGY SPECIES CALLED A BENZYNE



235 Notes

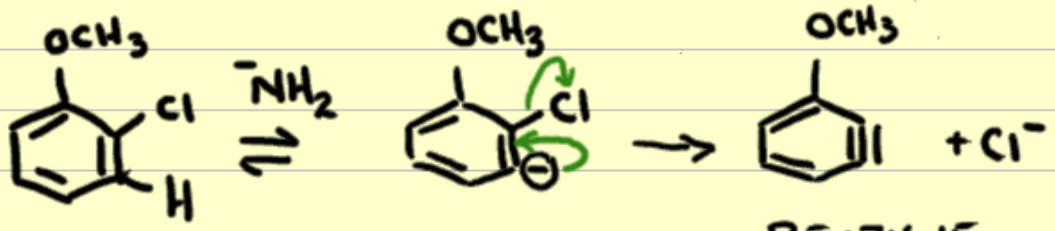
Notebook: jgreen1263's notebook
Created: 11/13/2009 2:45 PM **Updated:** 2/14/2013 11:17 AM

CHEM. 235 - LECTURE 11



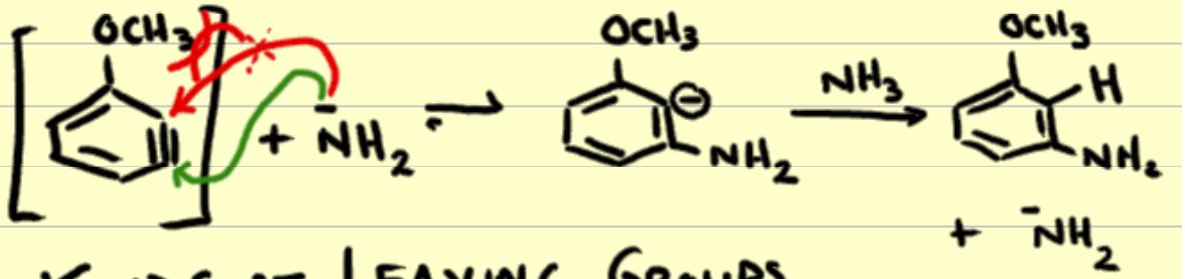
VIA BENZYNE MECHANISM.

MECHANISM

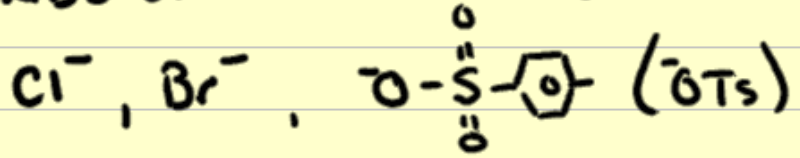


BENZYNE

BENZYNE - HIGH ENERGY INTERMEDIATE DUE TO ANGLE STRAIN ON TRIPLE BOND
- LASTS ONLY FRACTIONS OF A SECOND.
- REACTS IN THIS CASE WITH AMIDE ION



KINDS OF LEAVING GROUPS

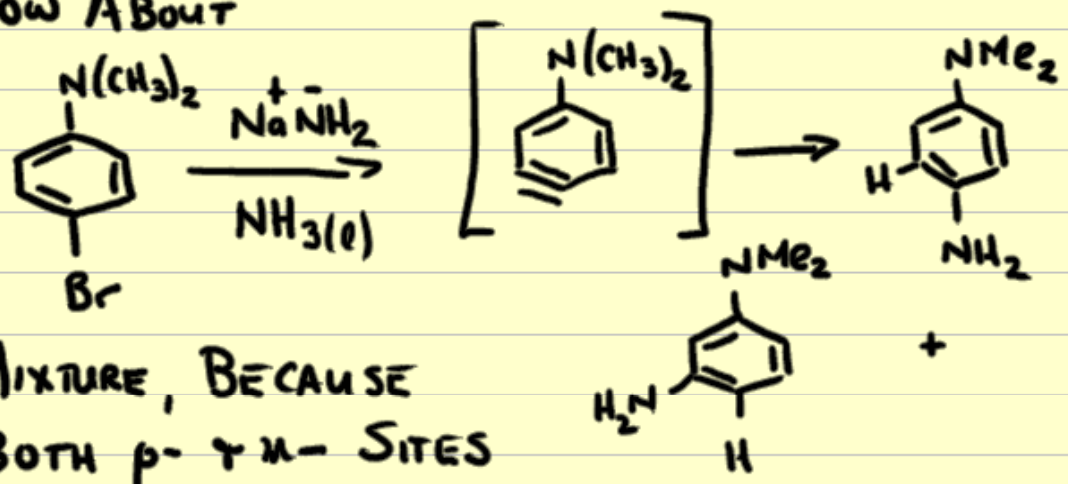


BASE / NUCLEOPHILE

$^{\ominus}NH_2$ OR $^{\ominus}NR_2$ AMIDE IONS

$^{\ominus}OH$ OR $^{\ominus}OR$ UNDER KILLER CONDITIONS 300 °C

HOW ABOUT



MIXTURE, BECAUSE BOTH p- & m- SITES ARE ACCESSIBLE STERICALLY.

AMINES.

DERIVATIVES OF NH_3

- MADE BY REPLACING H's BY OTHER R's - PROPERTIES. SIMILAR

NAMING - SUFFIX "AMINE"

$CH_3CH_2CH_2CH_2NH_2$

BUTANAMINE (OR BUTYLAMINE)

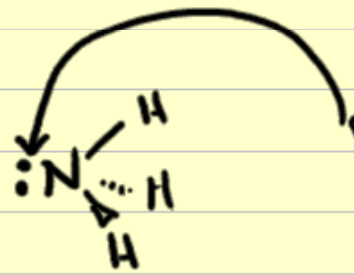
PRIMARY VS SECONDARY VS TERTIARY
1° 2° 3°

H_3C-NH_2 $H_3C-NH-CH_3$ $H_3C-N(CH_3)-CH_3$

VS ALCOHOLS

1° H_3C-CH_2-OH 2° $H_3C-CH(CH_3)-OH$

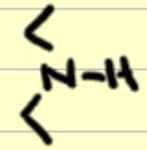
3° $H_3C-C(CH_3)_2-OH$

CHEMISTRY  RULES ALL.

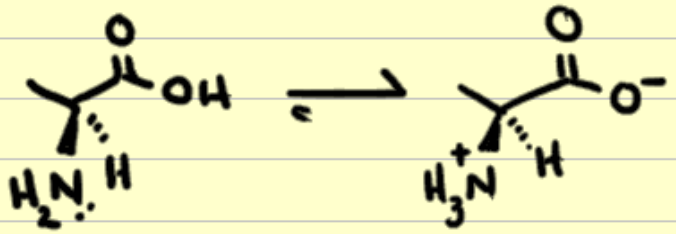
V. WILLING TO SHARE IT'S LONE PAIR

∴ BASIC AND NUCLEOPHILIC EVEN THOUGH THEY'RE NEUTRAL

pK_aH'S ALL IN 9's & 10's

	NH_3	CH_3NH_2	
pK_aH	9.3	10.7	10.98

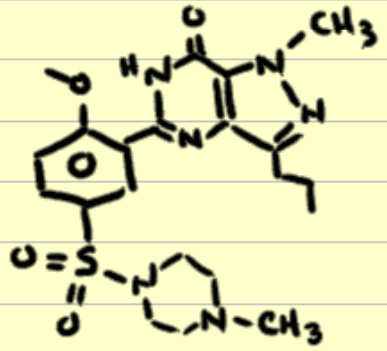
ADDITIONAL ALKYL GROUP MAKE AMINE MORE BASIC (SLIGHTLY)



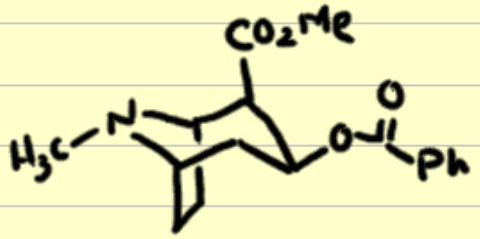
ALANINE

INCREDIBLE COMMON

- MANY HAVE BIOLOGICAL IMPORTANCE

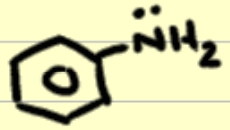


VIAGRA



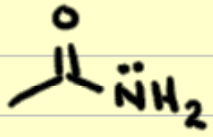
COCAINE

- IF THE LONE PAIR IS CONJUGATED TO π SYSTEM, AMINE IS LESS BASIC



pK_{aH} 4.6

$pK_{aH} = 0$

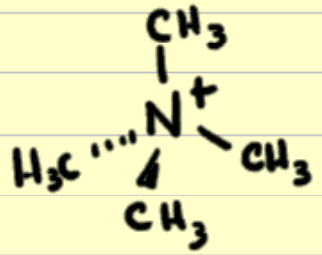


$pK_{aH} = -1.5$

- NEXT TO sp^2 C'S ALSO REDUCES BASICITY.

$pK_{aH} = 5.3$

-



EASILY AVAILABLE QUATERNARY (4°) AMMONIUM SALTS

235 Notes

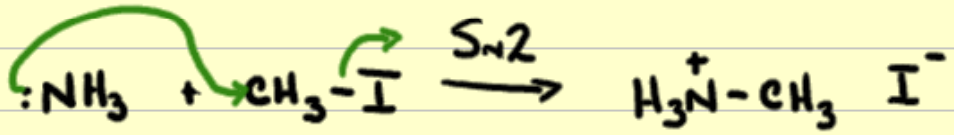
Notebook: jgreen1263's notebook
Created: 11/13/2009 2:45 PM **Updated:** 2/26/2013 11:16 AM

CHEM. 235 - LECTURE 12

AMINES

$:NR_3 + H^+ \rightleftharpoons H-\overset{+}{N}R_3$

$:NR_3$ ALSO NUCLEOPHILIC



SYNTHESIS OF AMINES

1) USING S_N2 ABILITY OF SIMPLE AMINES

$NH_3 \rightarrow\rightarrow H_3C-NH_2$

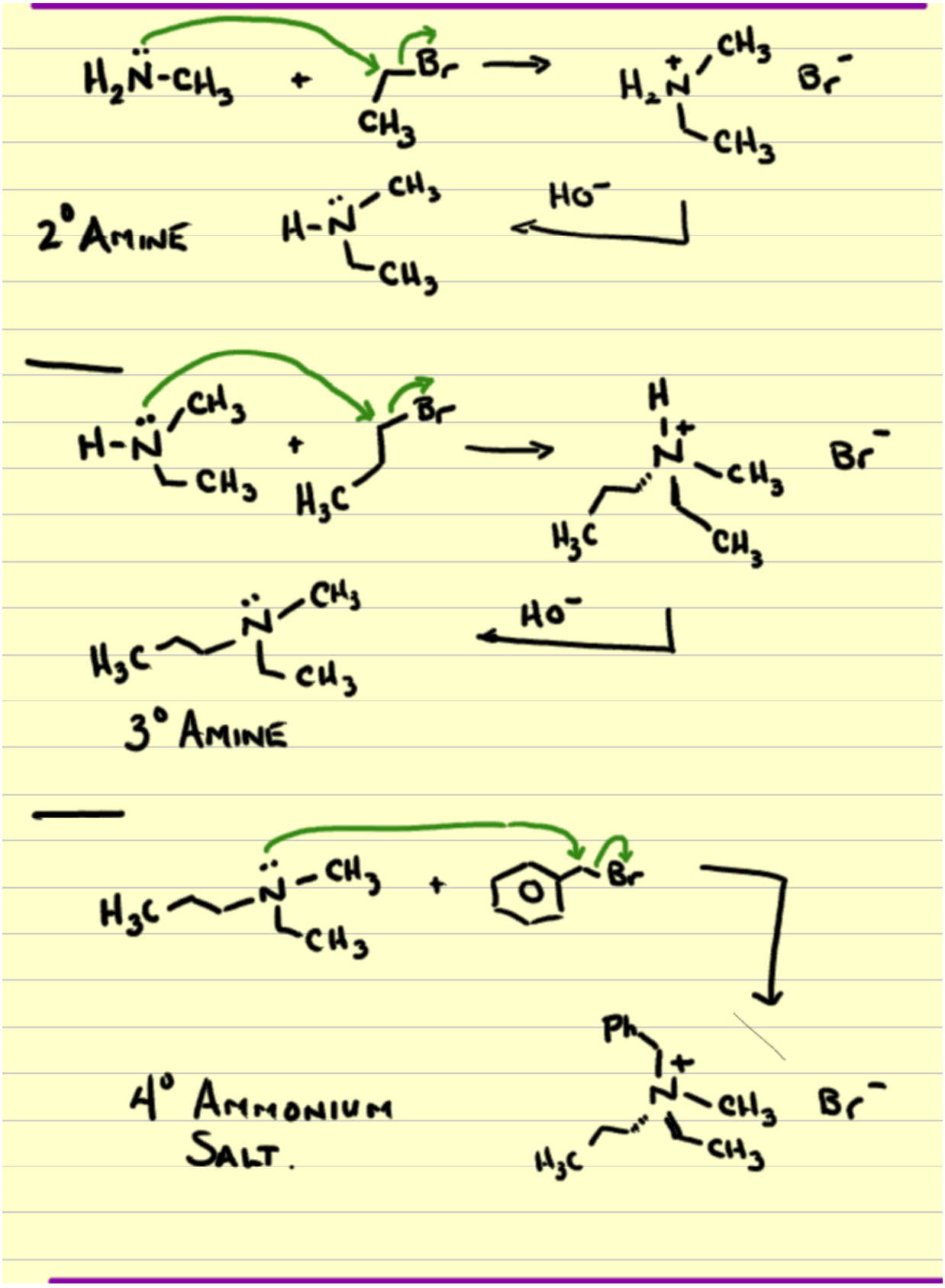
$NH_3 + CH_3I \rightarrow H_3\overset{+}{N}-CH_3\ I^-$

$\downarrow HO^-$

H_2N-CH_3 $(+ H_2O, + I^-)$

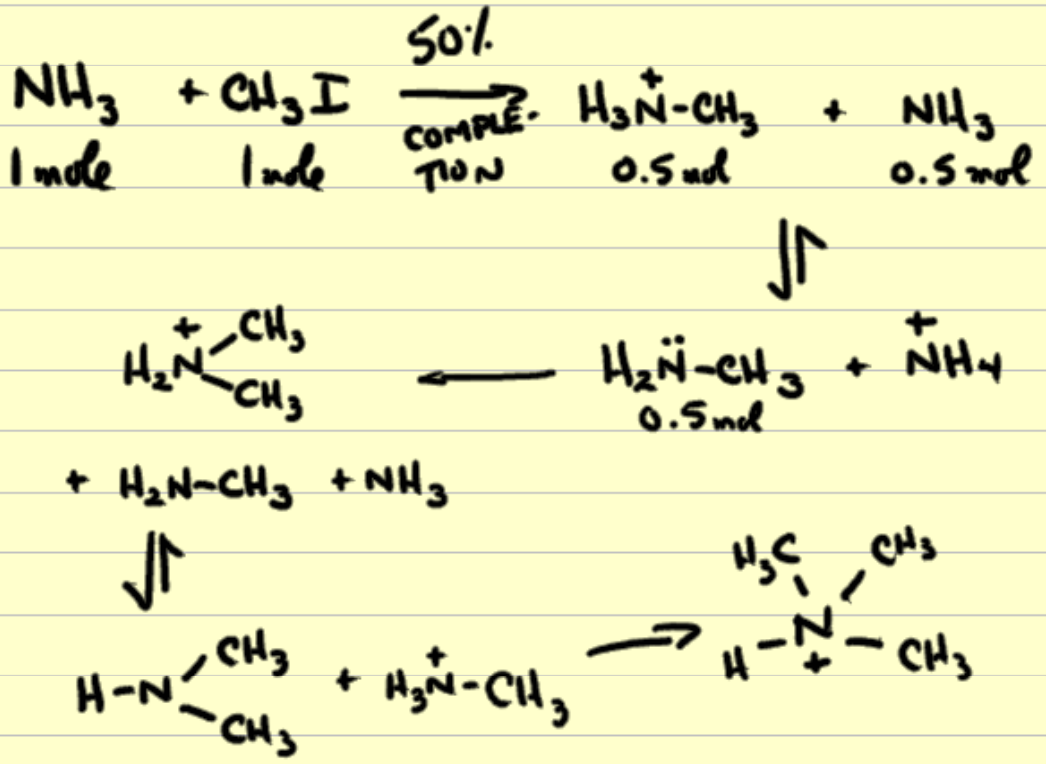
1° AMINE

SIMPLEST WAY OF MAKING MORE SUBSTITUTED AMINES FROM LESS SUBST. ONES

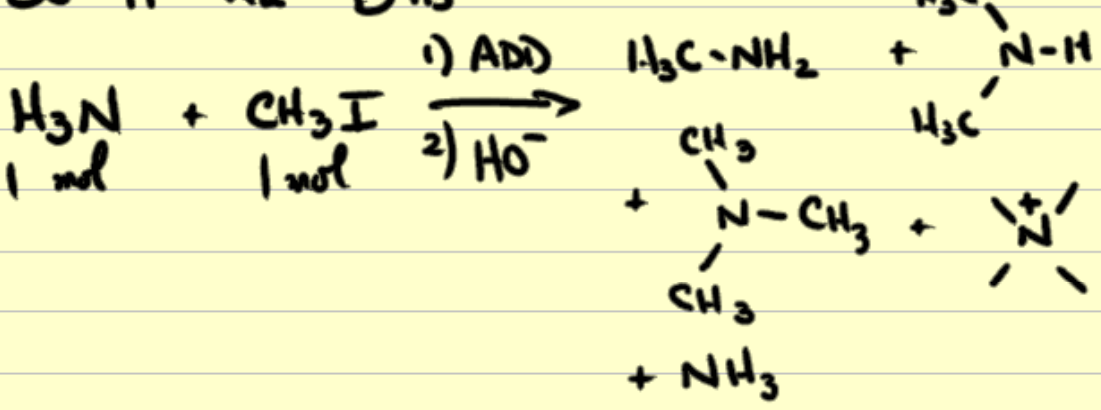

2° Amine
3° Amine
4° Ammonium Salt.

Problem w/ This Approach

- Amines are Better Nucleophiles as we Progress in Above Path
  - ∴ Polyalkylation is an Issue

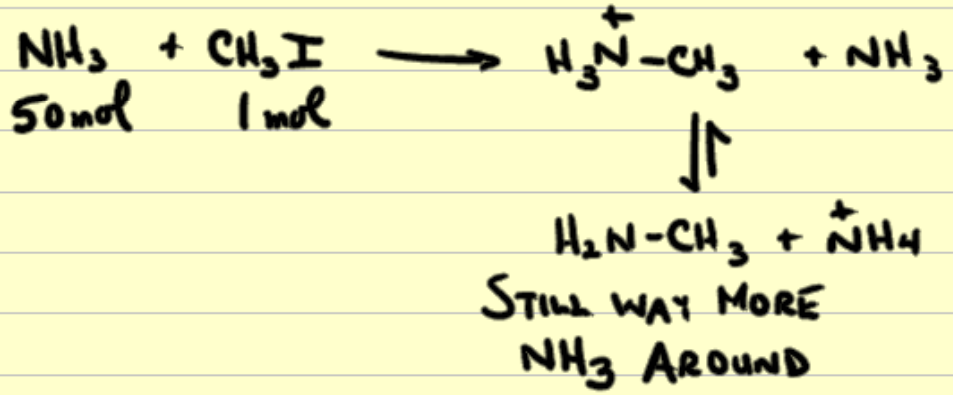


So if we Did

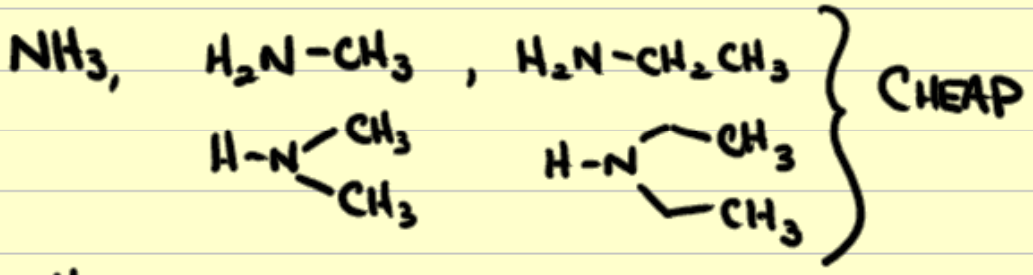


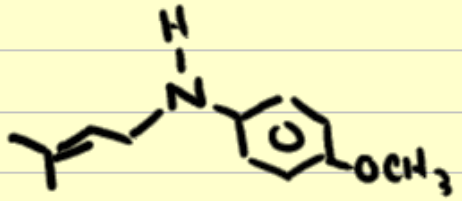
Solution

1) If Amine is Cheap
Use it in Excess



Still way more NH_3 Around

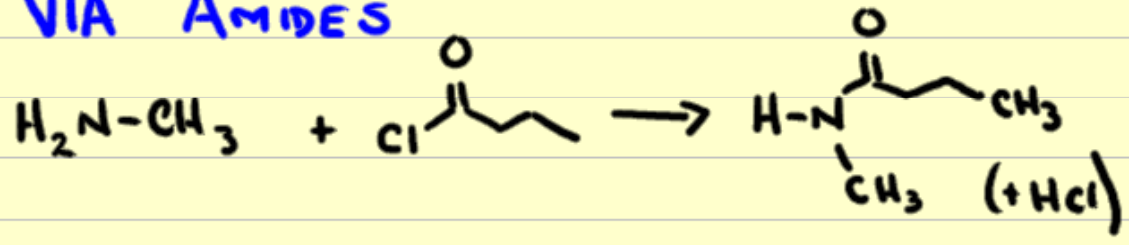


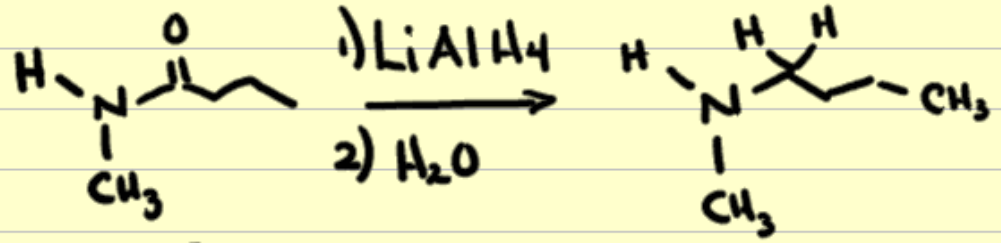


Not Cheap

Solution #2

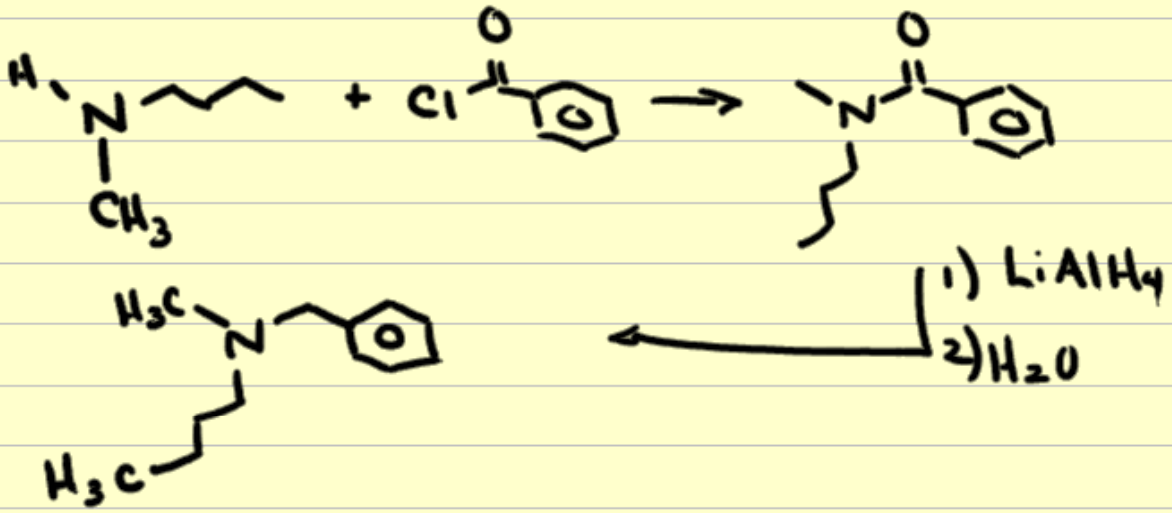
2) Via Amides





NON-BASIC
NON-NUCLEOPHILIC

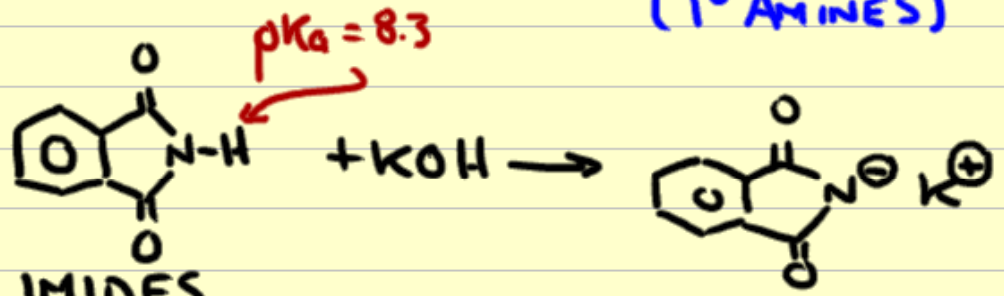
GOOD FOR "ANYTHING"
EXCEPT CH_3 INCORP.



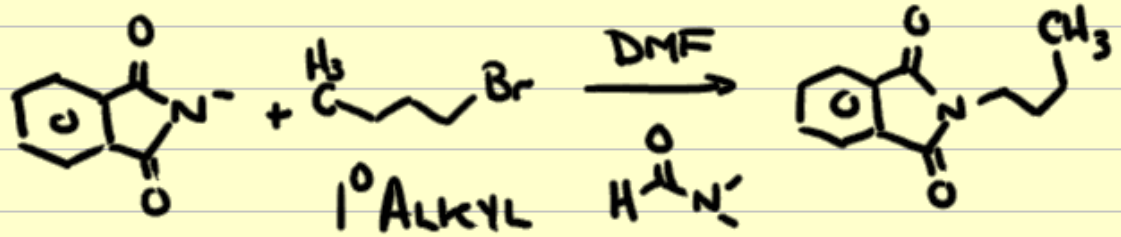
SOLUTION #3

GABRIEL SYNTHESIS

FOR R-NH_2
ONLY
(1° AMINES)

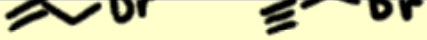


IMIDES



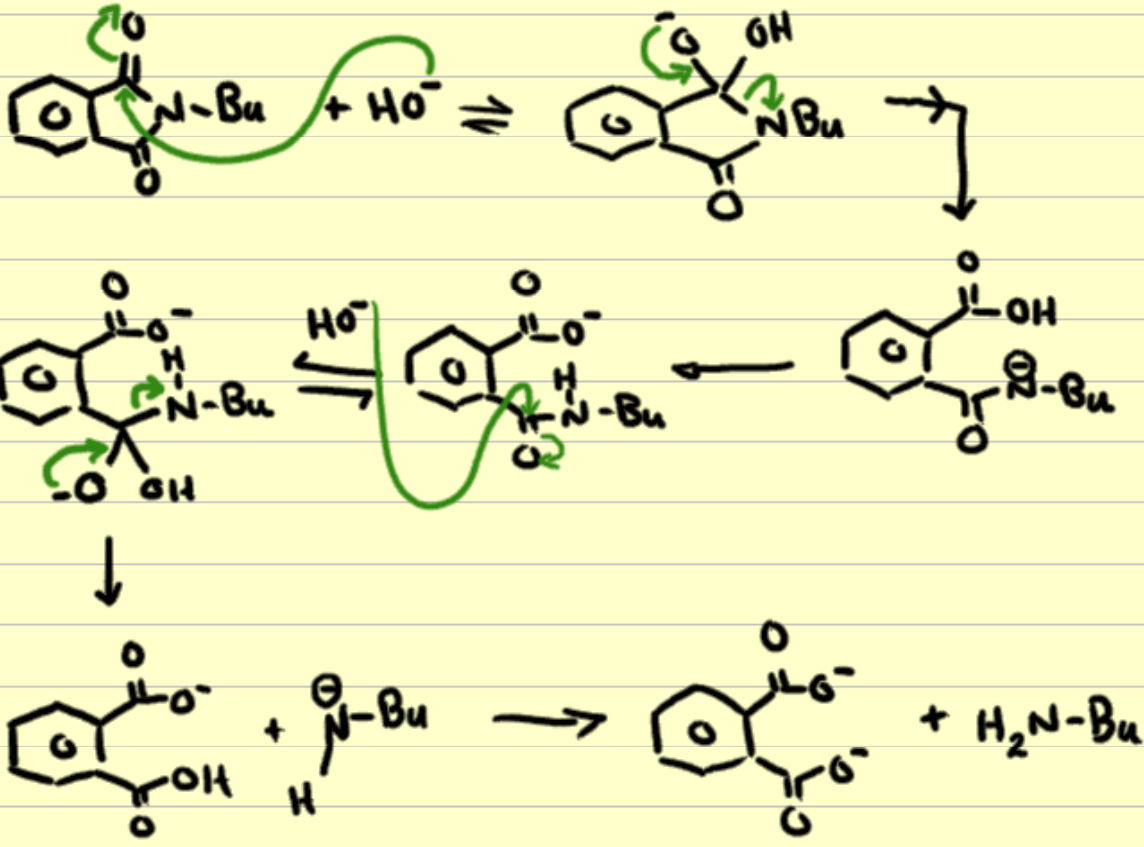
1° ALKYL

MUST BE 1°, BENZYLIC, ALLYLIC, PROPARGYLIC



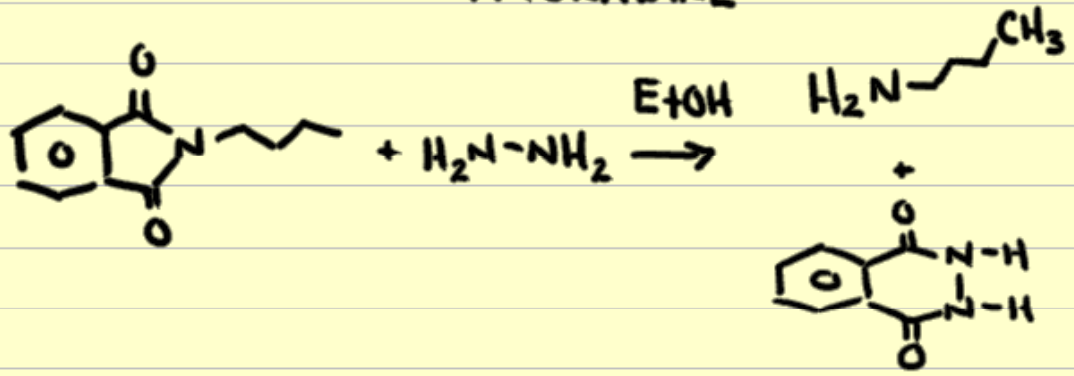
TO GET AMINE
MUST HYDROLYZE IMIDE

- CAN USE ACID OR BASE



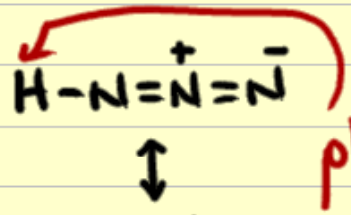
MORE OFTEN H_2N-NH_2 USED

HYDRAZINE



SOLUTION # 4

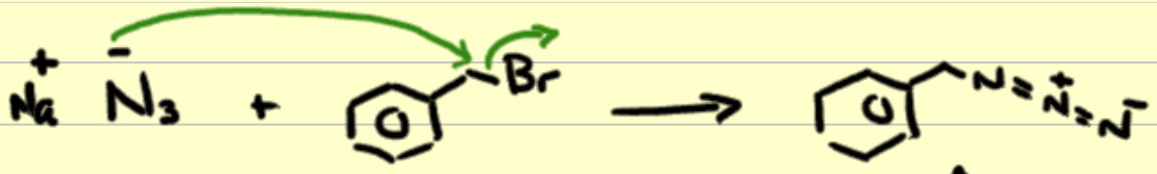
AZIDE ION



pKa = 4.6

$Na^+ \ ^-N_3$

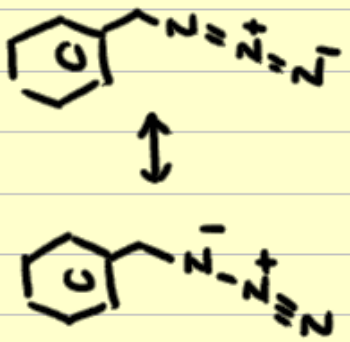
DECENT AS Nü



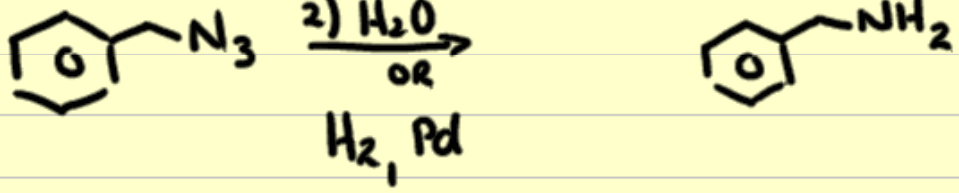
S_N2 REACTIVE

ALKYL HALIDE

PSEUDOHALIDE



Azides are also susceptible to reduction



235 Notes

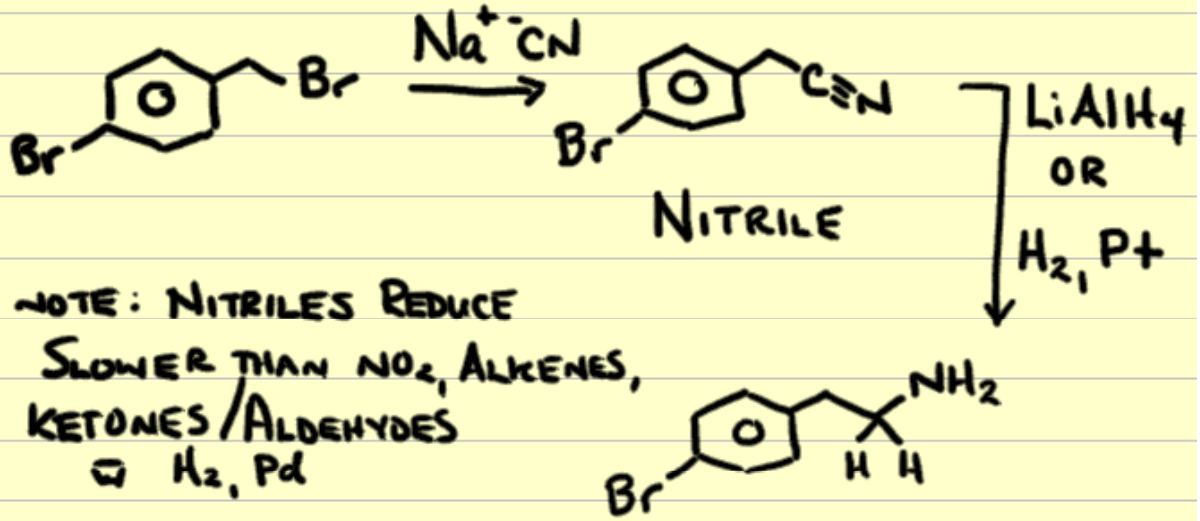
Notebook: jgreen1263's notebook
Created: 11/13/2009 2:45 PM **Updated:** 2/28/2013 11:18 AM

CHEM. 235 - LECTURE 13

5) USE OF CYANIDE ION

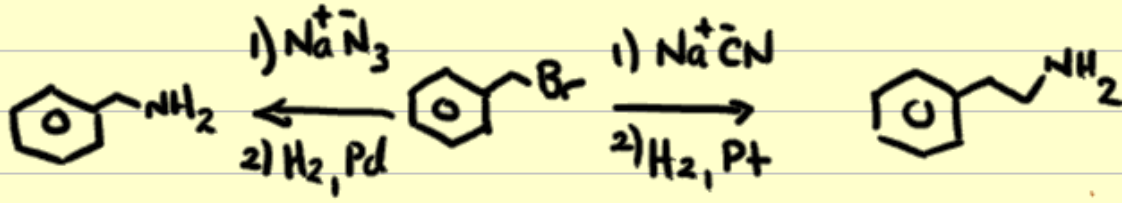
$Na^+ {}^-C{\equiv}N$ ← base — $H{-}C{\equiv}N$ (pKa = 9.2)

^-CN GOOD NUCLEOPHILE AT CARBON



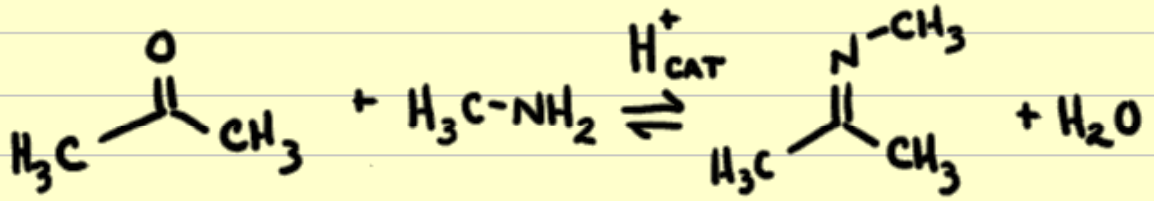
NOTE: NITRILES REDUCE SLOWER THAN NO_2, ALKENES, KETONES/ALDEHYDES @ H_2, Pd

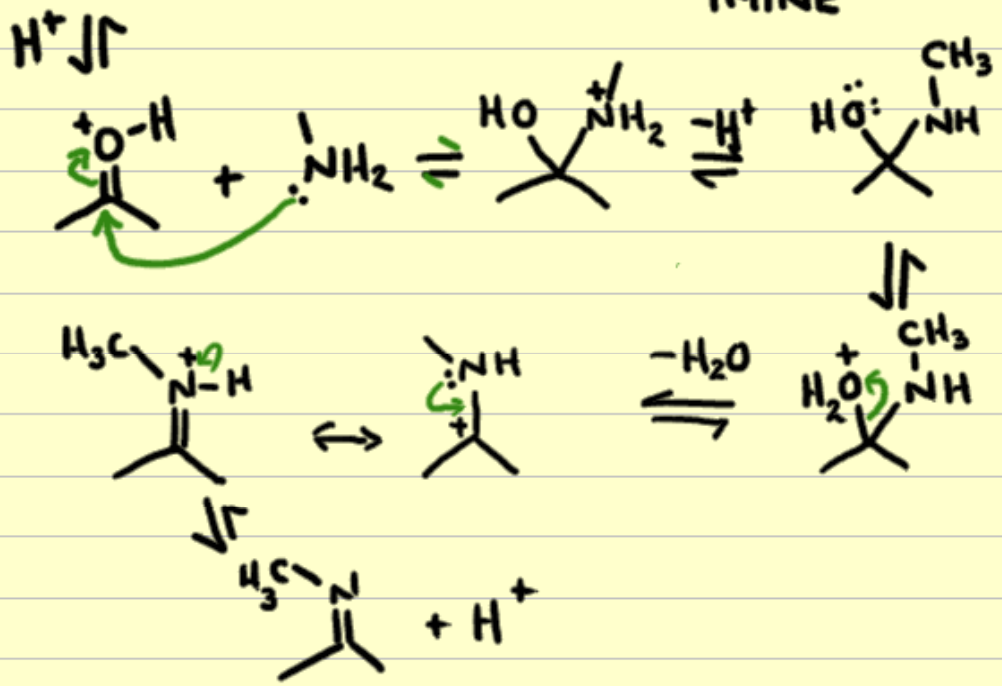
- ADVANTAGE - ADDS EXTRA CH_2 ALONG WITH THE NH_2 FUNCTION



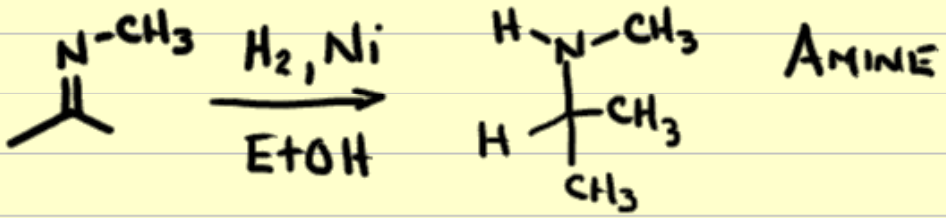
6) Reductive Amination

- Ketones/Aldehydes + RNH_2 React to Form Imines





Among Other Things You Can Reduce the C=N Bond.

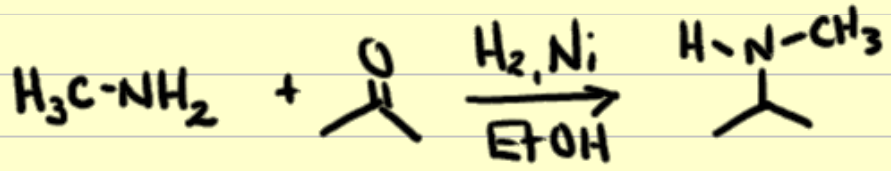


OTHER REDUCTANTS H_2, Pd

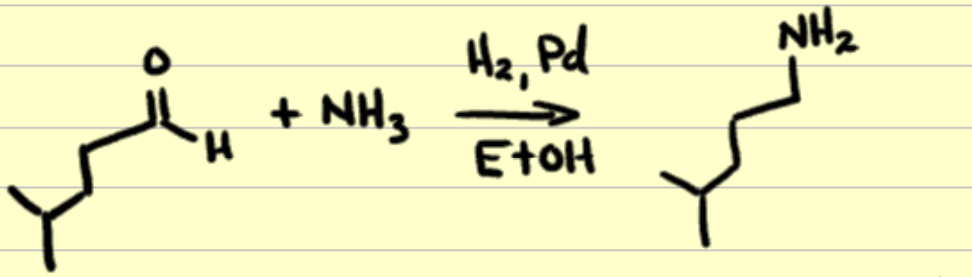
$Na^+ \bar{B}H_3CN$

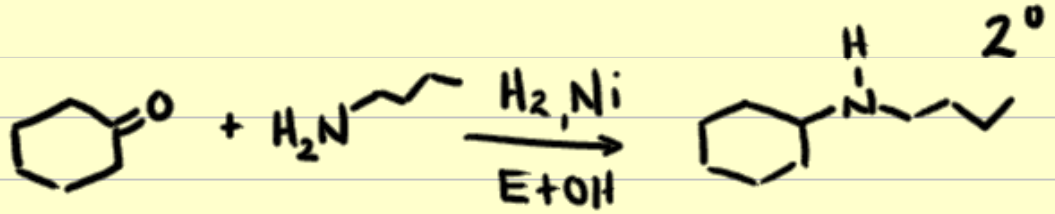
(SODIUM CYANOBOROHYDRIDE)

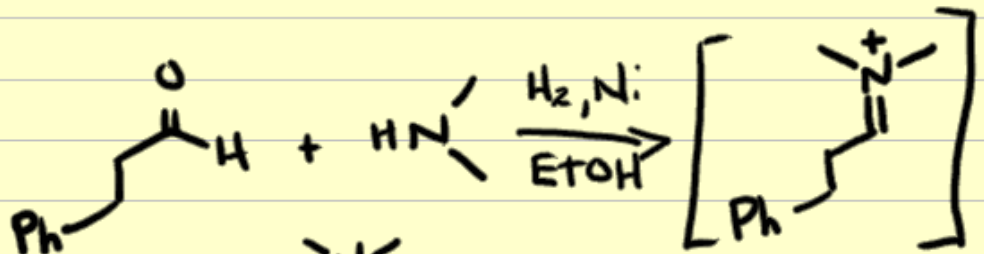
GOOD NEWS - BOTH RXNS. CAN BE DONE TOGETHER, IN ONE FLASK

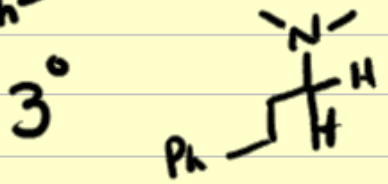


- USEFUL FOR 1°, 2°, OR 3° AMINES





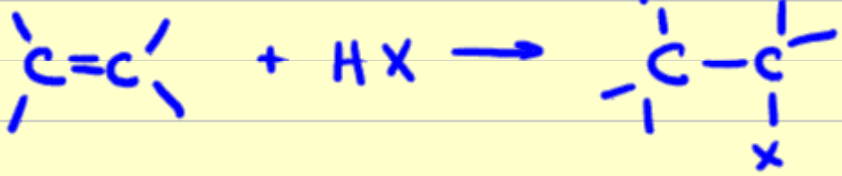




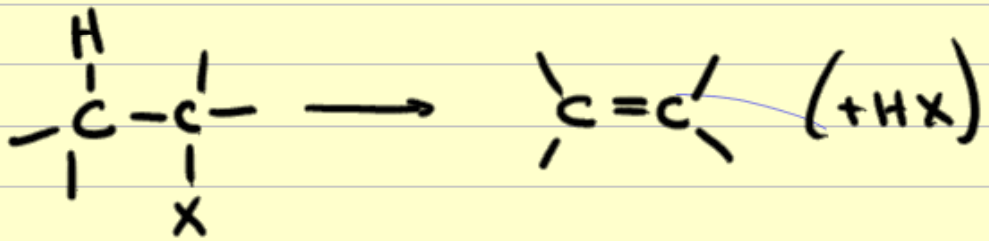
IMINIUM ION ALSO REDUCES

Elimination Reactions

Recall 230 — Addition Reaction



Now



Elimination Rxns.

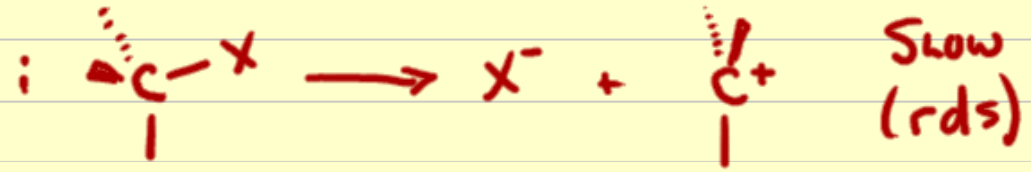
- Most important Alkene Prep method
- Probably for Alkynes Too

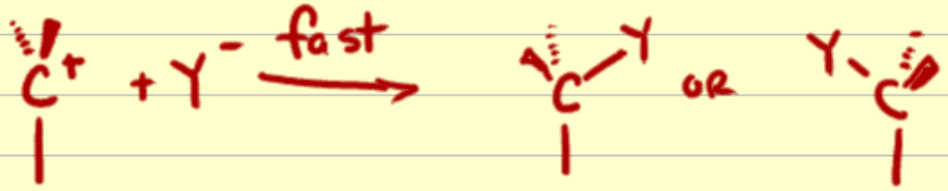
Mechanisms - 3 important ones

2 very well studied

E1 and E2 Mechanisms

Recall S_N1

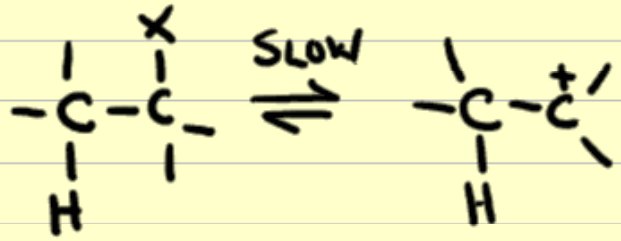


ii 

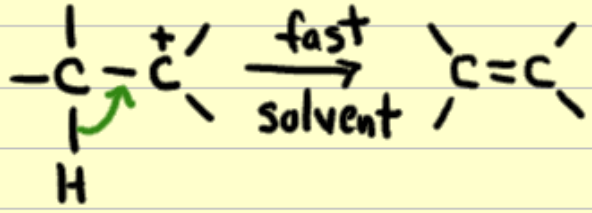
SN2

E1 ELIMINATION

- TWO STEP PROCESS

STEP 1 

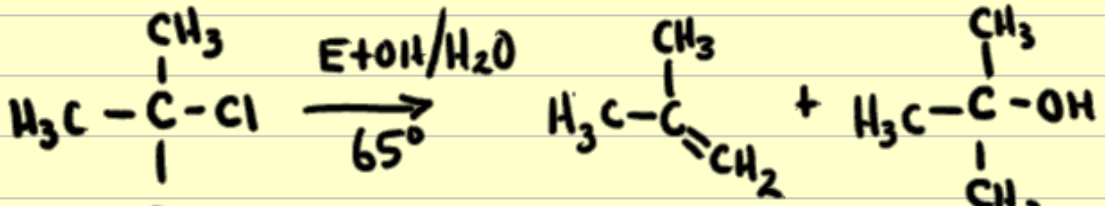
IONIZATION TO GIVE CARBOCATION

STEP 2 

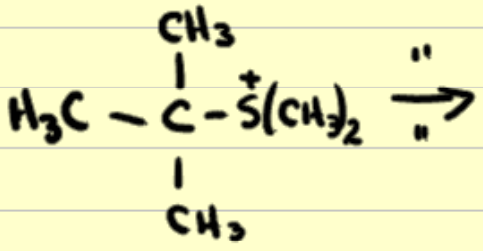
FEATURES

- TWO STEPS

- 1ST STEP SLOW
- 1ST ORDER KINETICS $v = k\left[\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{X}{C}}\text{-}\right]$ (H above C)
- 1ST STEP IDENTICAL TO S_N1 1ST STEP
- NO ADDED BASE (SOLVENT ACTS A BASE)



36.3% 63.7%

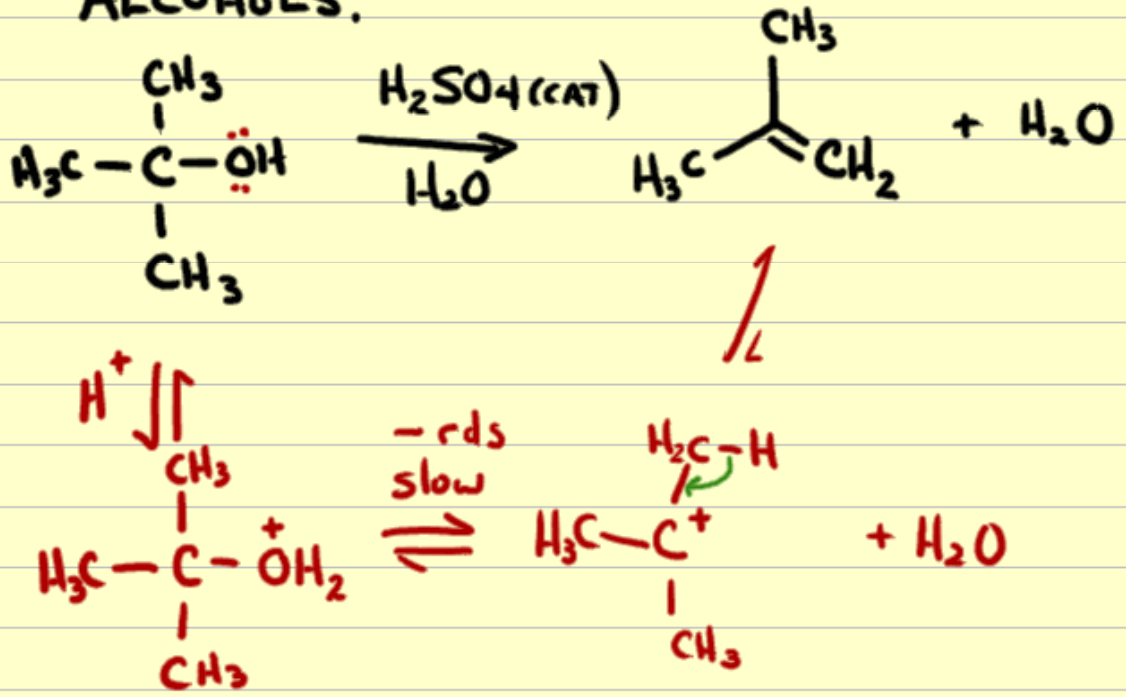


35.7% 64.3%

- TWO POINTS.
  - E1 ELIMINATIONS & S_N1 SUBSTITUTIONS OFTEN COMPETE.
  - IF YOU CHANGE LEAVING GROUP, AND THE SUBST./ELIMINATION RATIO STAYS THE SAME - EXCELLENT EVIDENCE THAT ELIMINATION WAS E1

Prototypical E1 Elimination

- Acid Catalyzed Elimination of Alcohols.



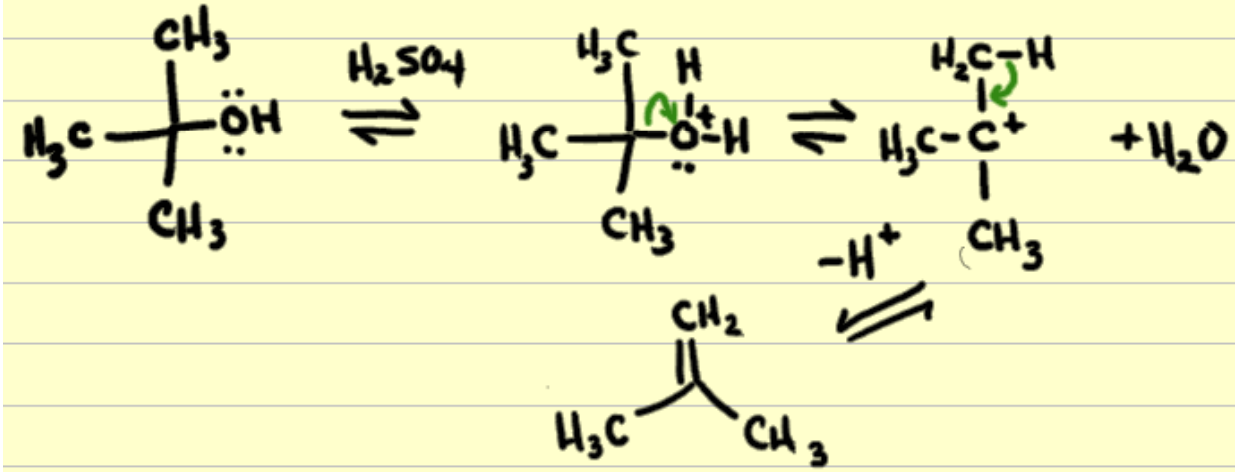
235 Notes

Notebook: jgreen1263's notebook
Created: 11/13/2009 2:45 PM **Updated:** 3/5/2013 11:24 AM

CHEM. 235 - LECTURE 14

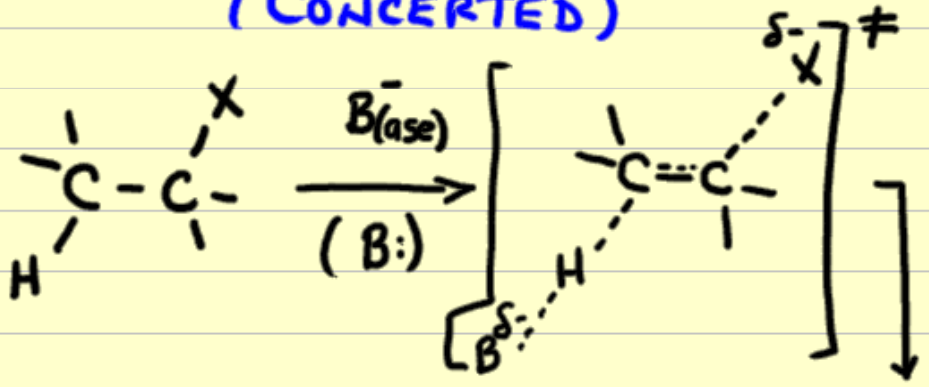
PROTOTYPICAL E1 ELIMIN.

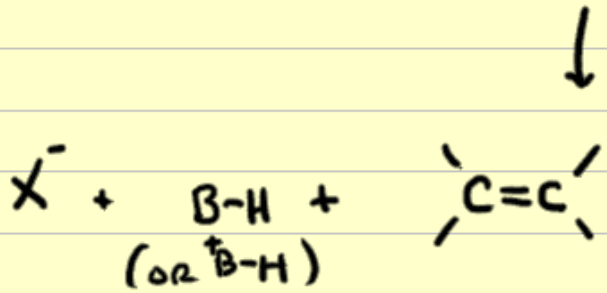
- ACID INDUCED (CATALYZED) ELIMINATION OF H_2O FROM ALCOHOL



E2 MECHANISM

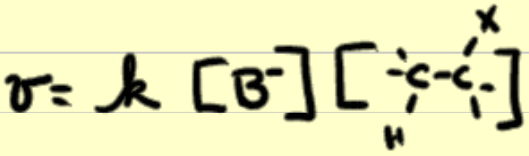
- ONE STEP - ALL BOND MAKING AND BREAKING AT THE SAME TIME (CONCERTED)





- FEATURES
  1) CONCERTED IN ONE STEP
     - PROTON ABSTRACTION BY BASE
     - DOUBLE BOND FORMATION
     - LOSS OF X^-

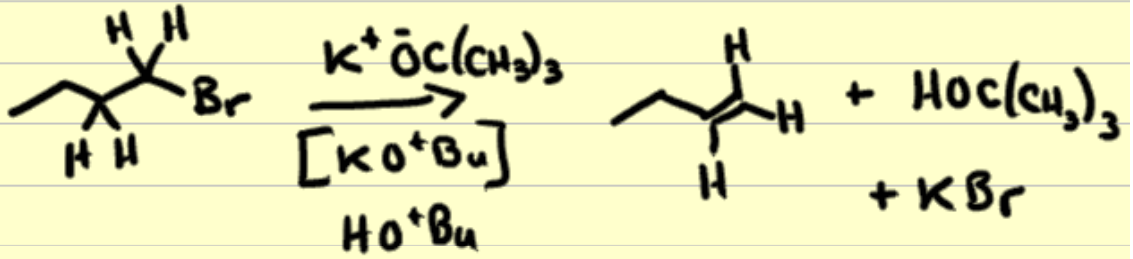
  2) SECOND ORDER KINETICS



E2

ELIMINATION — BIMOLECULAR

PROTOTYPICAL E2 EXAMPLE



$K^+ \bar{O}C(CH_3)_3$ / $[KO^tBu]$

HO^tBu

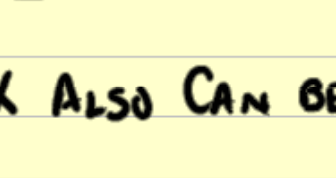
$+ HOC(CH_3)_3$

$+ KBr$

-BASE INDUCED ELIMINATION OF ALKYL HALIDES

X OFTEN HALIDE

I > Br > Cl >> F

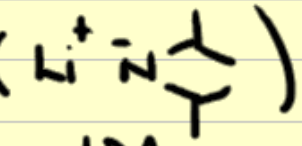
X ALSO CAN BE  ≡ -OTs

ROUGHLY ≈ Br

BASE: MOST COMMON ARE THINGS LIKE

ALKOXIDES $^{\ominus}OR$ (KO^tBu, $NaOEt$)

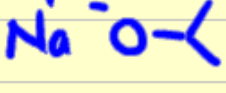
HYDROXIDE $^{\ominus}OH$

AMIDE ION $^{\ominus}NR_2$ ()

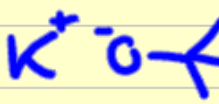
LDA

AMINES $:NR_3$

ASIDE

 SODIUM ISOPROPOXIDE

NaO^iPr

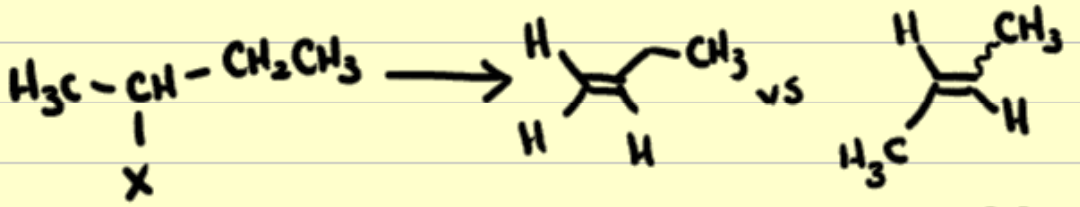
 POTASSIUM tert-BUTOXIDE

OR $K\,OBu\text{-}t$

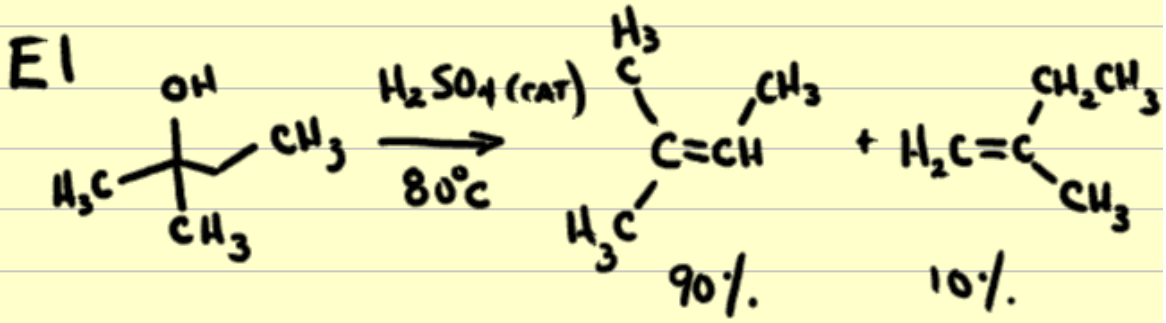
KO^tBu

REGIOCHEMISTRY.

- TWO POSSIBLE SITES OFTEN



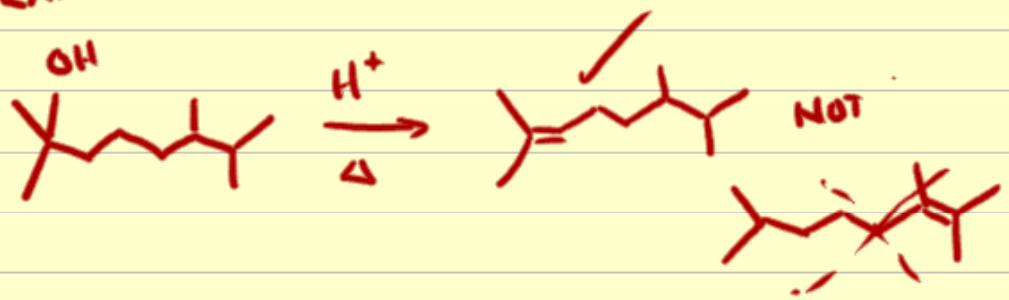
E1



- CATIONIC INTERMEDIATE ELIMINATES TO FORM THE MORE STABLE ALKENE POSSIBLE
  - MORE SUBSTITUTED ALKENE NORMALLY

- OPERATING UNDER ZATSEV RULE

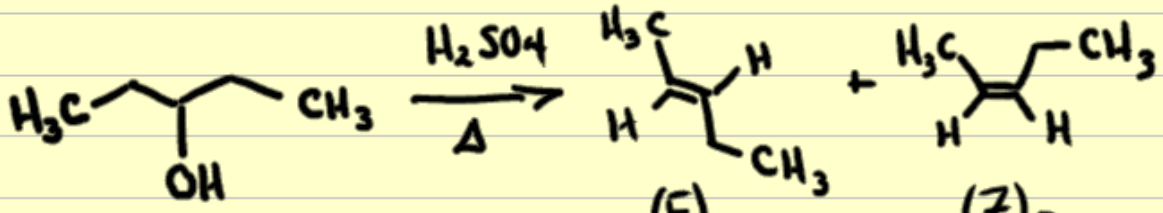
MEANS



- ALSO ANSWERS THE STEREOCHEMISTRY QUESTION - SINCE MOST STABLE ALKENE IS FORMED.

I.E. WHERE LARGEST GROUPS ARE TRANS- TO EACH OTHER

∴ (E)- ISOMER USUALLY

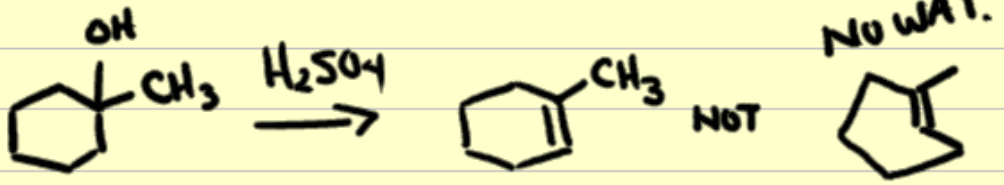


(E)- : (Z)-

87 : 13

- CALLED STEREOSELECTIVE BECAUSE ONE STEREOISOMER IS FORMED MOSTLY

- MUST USE WITH SOME CARE.



NO WAY.

Z- (E)-

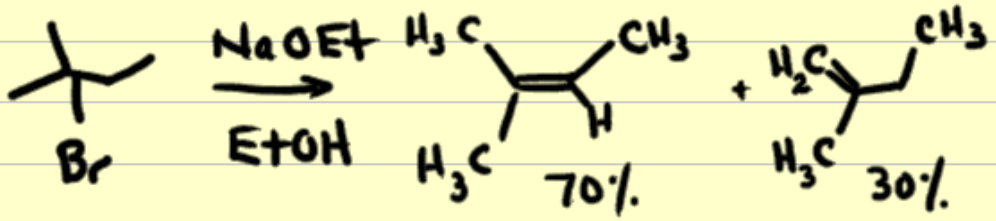
NOT IF ≥10 MEMB. RING.

E2 - Not a Clear Cut

- Depends on Leaving Group X
- Especially depends on Base

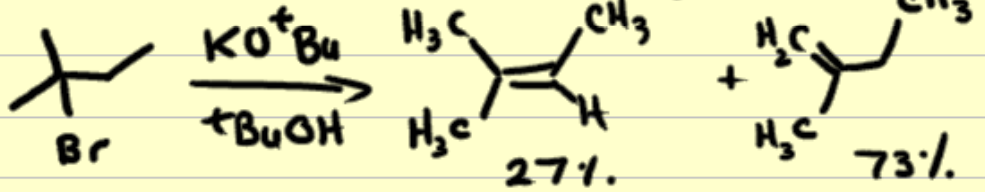
Less Bulky Base HO^-, MeO^-, EtO^-

- More towards Zaitsev (More Substituted Side)



- Bulky Bases KO^tBu or $Li^+ \overline{N}$

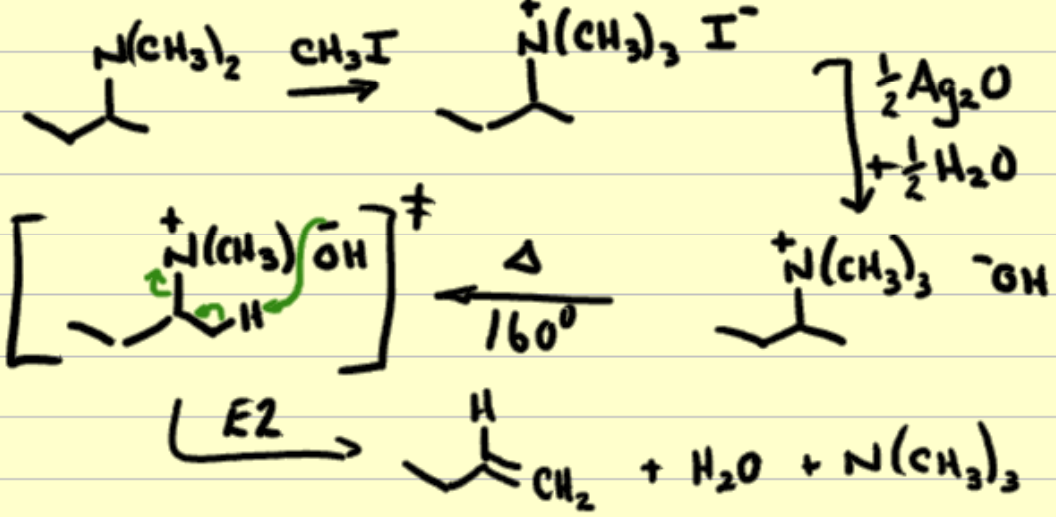
Elimination Prefers Less Substituted Side



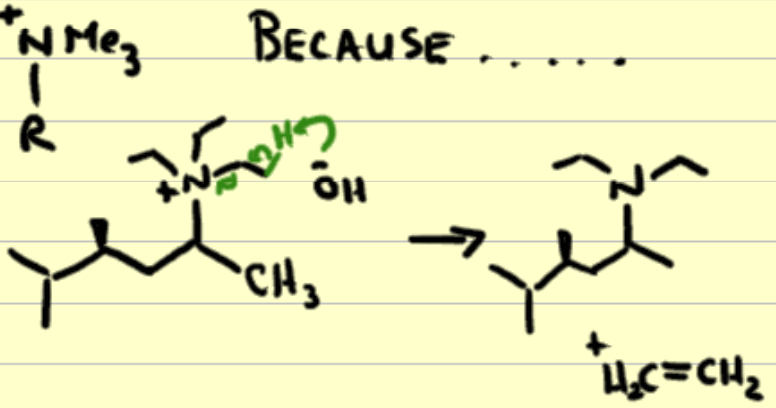
- Reason - Approach to more Subst. Side is getting too Sterically Hindered

- These Eliminations are Said to be Operating under the Hofmann Rule

- SPECIAL ELIMINATION PROTOCOL TO GIVE LESS SUBST. ALKENE
  - CALLED HOFMANN ELIMINATION



LESS SUBST. ALKENE RELIABLY

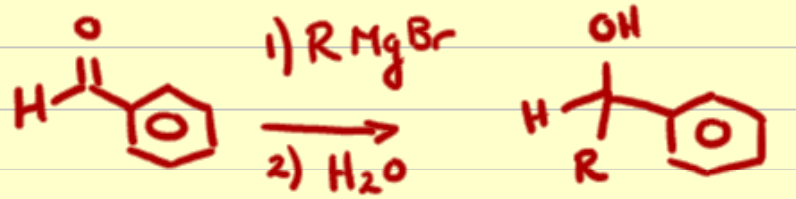
- ALWAYS  BECAUSE .....

235 Notes

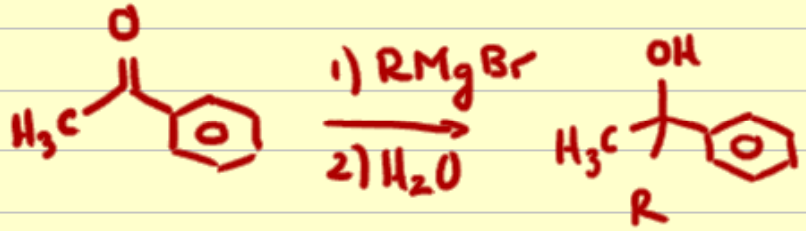
Notebook: jgreen1263's notebook
Created: 11/13/2009 2:45 PM **Updated:** 3/7/2013 11:21 AM

CHEM. 235 - LECTURE 15

ASIDE

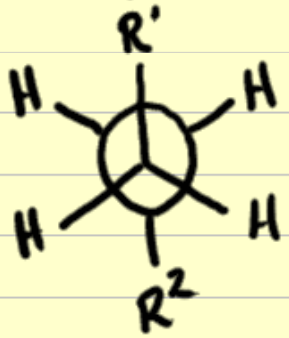


MAYBE TEST #2



E2 ELIMINATIONS - STEREOCHEMISTRY OF THE ELIMINATION

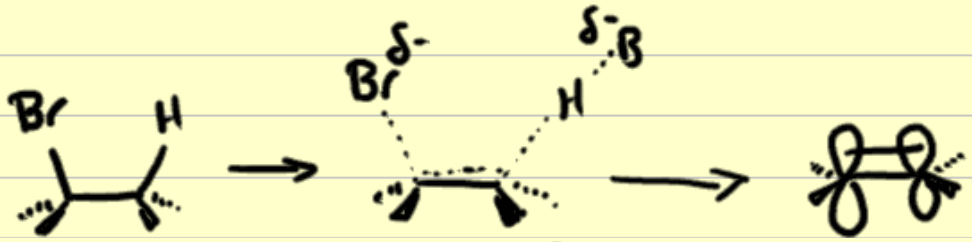
- VERY DISTINCT RELATIONSHIP BETWEEN THE TWO GROUPS BEING ELIMINATED (I.E. THE H & THE Br)
- HAVE AN ANTIPERIPLANAR ORIENTATION



- WHY? - sp^3 HYBRID C-H & C-Br BONDS ARE BECOMING p- ORIBTALS FORMING THE π-BOND

∴ MUST BE LINED UP

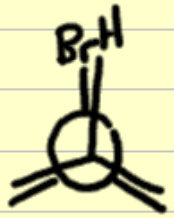
ANTIPERIPLANAR



SYNPERIPLANAR ALSO POSSIBLE, BUT

1)

ANTPERIPLANAR
- STAGGERED
LOWER E.



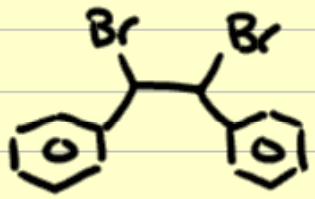
SYNPERIPLANAR
- ECLIPSED
HIGHER E.

2) 

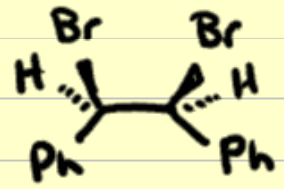
DONATION OF e⁻ DENSITY TO THE σ* (ANTIBONDING) ORBITAL OF C-Br WEAKENS THE BOND
- ASSISTS IN BREAKING THE BOND

THIS MEANS LOWER $\Delta G^{\ddagger}$ TRANSITION STATE
- NOT AVAILABLE FOR SYNPERIPLANAR ELIMINATION

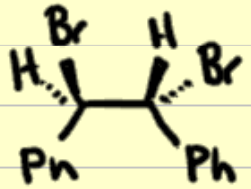
IMPLICATIONS



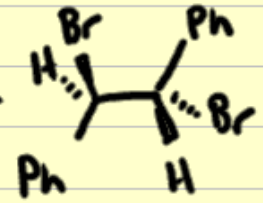
IS ACTUALLY 2 DIASTEREOMERS

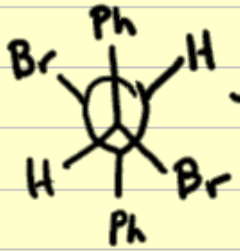


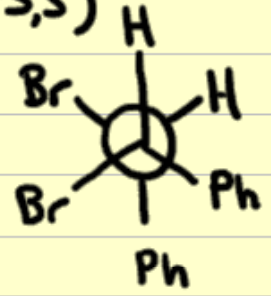
meso

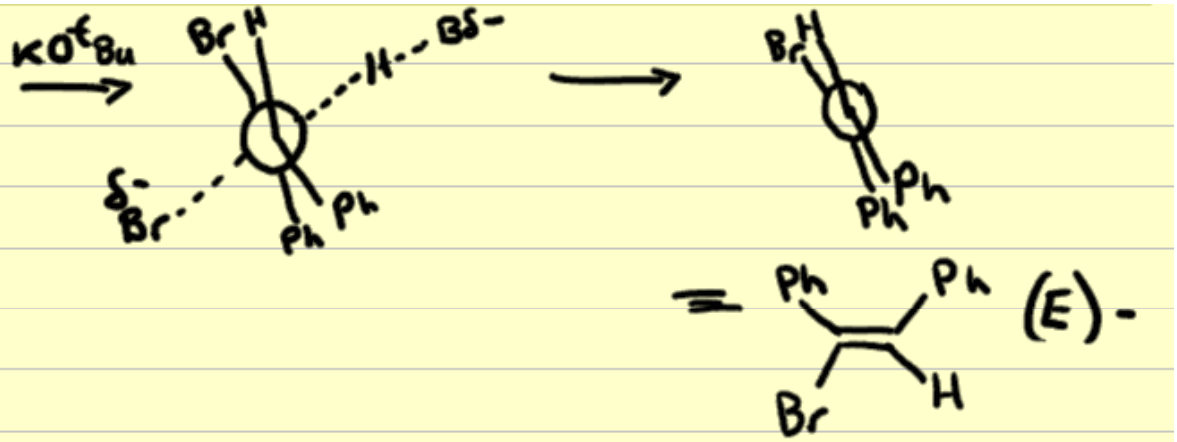


dl (R,R + S,S)

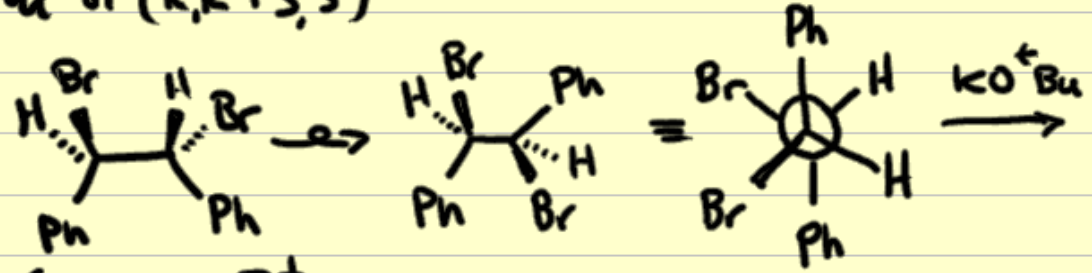
MESO ≡ 

≡ 





dl or (R,R + S,S)



∴ ONE DIASTEREOMER → (E)-
(meso, r,s)

OTHER DIASTEREOMER → (Z)-
(R,R or S,S)

- RXNS LIKE THESE ARE CALLED } STEREOSPECIFIC

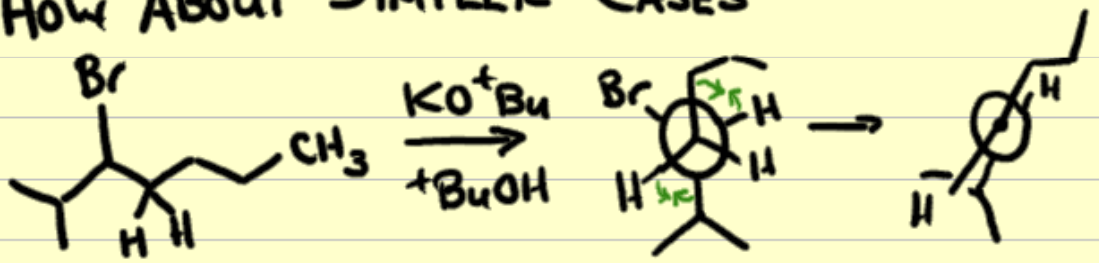
STEREOSPECIFIC MEANS THERE'S A PAIR (OR MORE) OF S.M. STEREOISOMERS AND A PAIR (OR MORE) OF PRODUCT STEREOISOMERS - AND -

ONE S.M. STEREOISOMER FORMS ONE PRODUCT STEREOISOMER

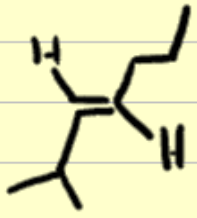
OTHER S.M. STEREOISOMER FORMS OTHER PRODUCT STEREOISOMER

COMPARE TO STEREOSELECTIVE
- JUST MEANS THAT ONE PRODUCT STEREOISOMER IS FORMED MOSTLY

HOW ABOUT SIMPLER CASES

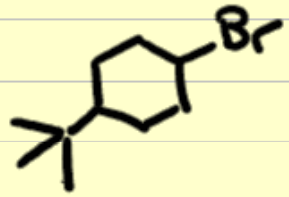


(E)- =

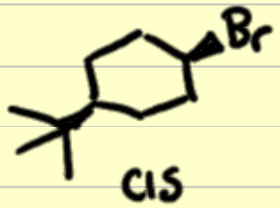


IN SIMPLER CASES MOST STABLE ALKENE STEREOCHEMISTRY WINS OUT.

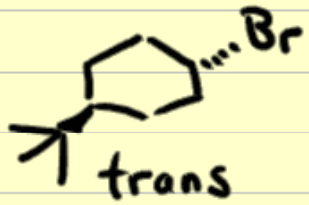
IN CYCLIC SYSTEMS (CYCLOHEXANES)



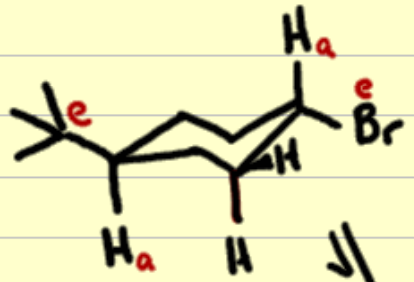
2 CPDS



CIS



trans



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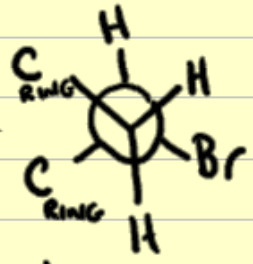
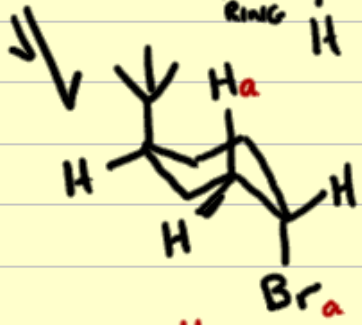
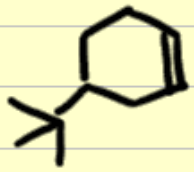


Br NOT ANTI TO ANY H



NaOEt
EtOH

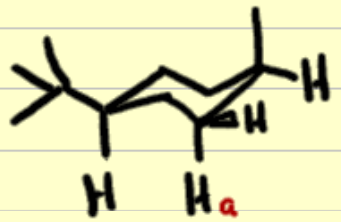


(+NaBr +EtOH)

NOW H_a & Br_a ARE ANTI

V. SLOW ELIMINATION, SINCE Br IS AXIAL ONLY A SMALL % OF TIME

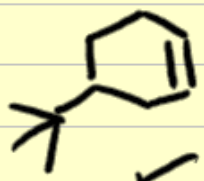
CIS



← ALREADY LINED UP

MOST STABLE CONFORMER

NaOEt
EtOH



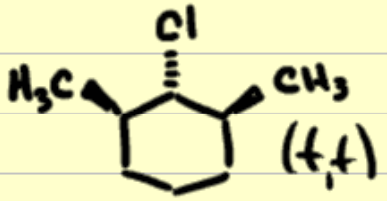
V. FAST

235 Notes

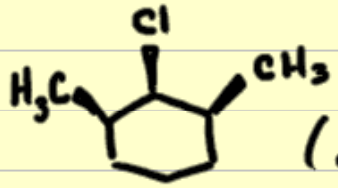
Notebook: jgreen1263's notebook
Created: 11/13/2009 3:45 PM **Updated:** 3/12/2013 11:21 AM

CHEM. 235 - LECTURE 16

A COUPLE MORE CASES



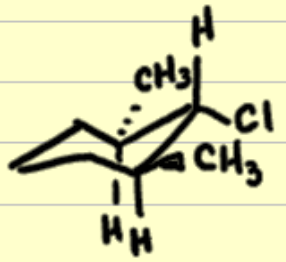
(t,t)

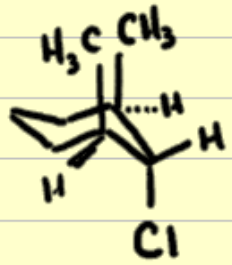


(c,c)

KO^tBu / ^tBuOH ?

t,t



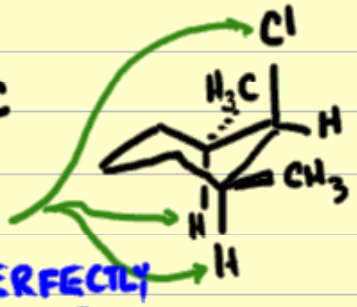


RXN. WILL BE V.V.V. SLUGGISH

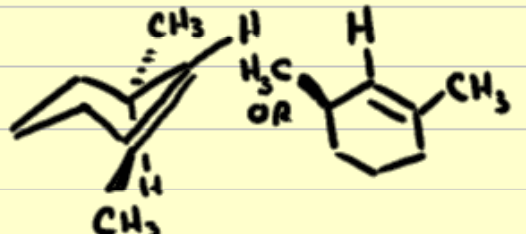
Cl NOT AXIAL

NO AXIAL H
ANTIPERIPLANAR TO Cl

c,c



KO^tBu



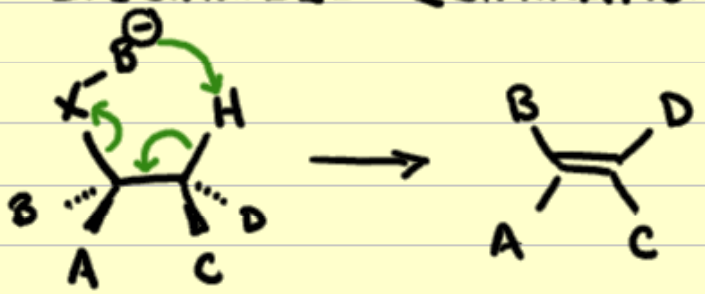
PERFECTLY ANTIPERIPLANAR - ELIMINATES (E2) FAST

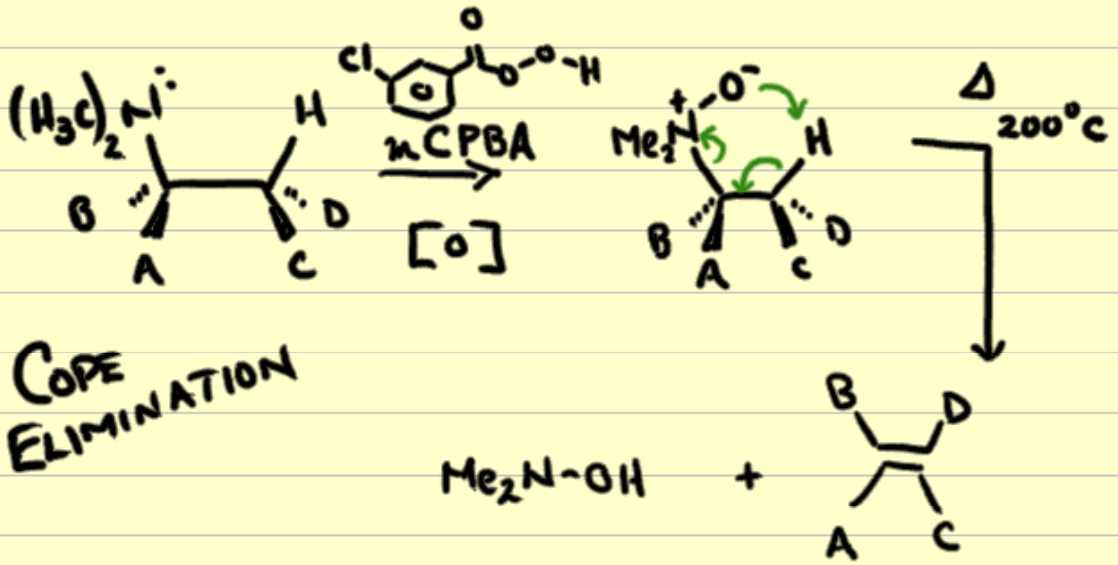
RAPID

CAN AN E2 EVER BE SYN (PERIPLAR)?

– YES

SPECIALIZED ELIMINATIONS.





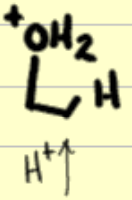
END OF TEST #2 MATERIAL

E1 vs. E2 Eliminations

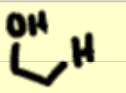
- Often competitive, often cases which have some E1 and some E2
  - How do we evaluate?
- Consider a number of factors.

Leaving Group

E1 - $\ddot{X}$ must leave all on its own
∴ must be very good or better



- Leaving group is H_2O
∴ Alcohols never E2



- I^-, Br^-, Cl^-, NR_3, ^-OTs certainly can do E1

E2 - Has to be a decent leaving group but base is helping

- Never an alcohol

BASE - E1 NO BASE (SOLVENT ACTING AS BASE)

E2 - MODERATE OR STRONG BASES

NR_3, ^-OH, ^-OR ($NaOEt$, KO^tBu), $LiN(^iPr)_2$ (LDA)

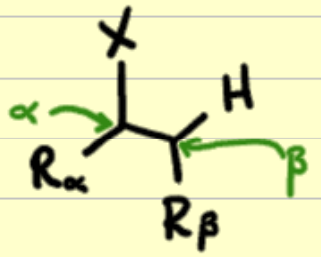
SOLVENT - E1 CATIONIC INTERMEDIATE STABILIZED BY POLAR SOLVENT

H_2O, CH_3OH, EtOH, MAYBE CH_3CN

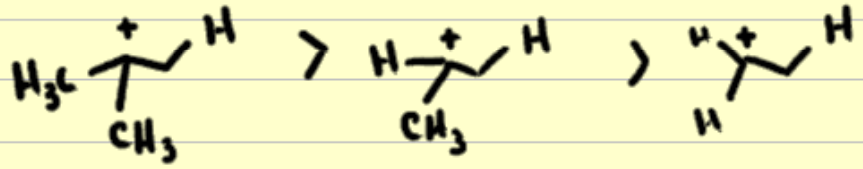
- E2 - NOT SO CRITICAL
  - POLAR SOLVENTS FINE
  - NON-POLAR SOLVENTS FINE, MAY BE MORE APPROPRIATE FOR THE BASE

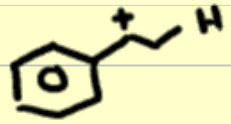
$H_3C-O-CH_3$ (Et_2O) THF

SUBSTRATE:



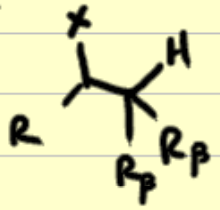
α- SITE - ADDITIONAL R_α'S TEND TO FAVOUR E1
- STABILIZE CARBOCATION




IS ALSO V. STABILIZED

SO R_α = ARYL ALSO FAVOURS E1

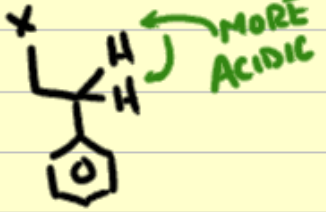
β- SITE



IF R_β IS ALKYL GROUP, WE HINDER BASE APPROACH TO THE H

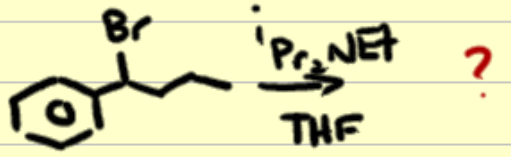
∴ SLOW E2
(∴ MORE E1 BY DEFAULT)

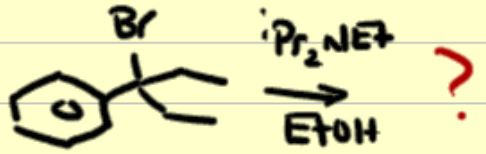
IF THE R_β's ARE ARYLS.

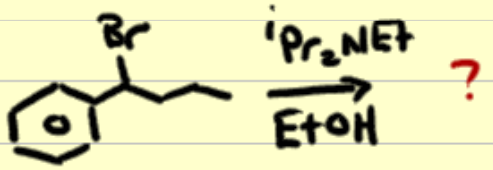


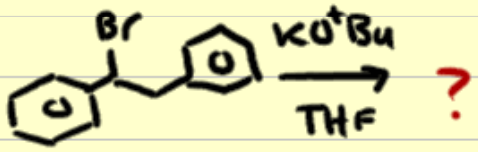
- H IS ACIDIFIED
∴ EASIER TO ABSTRACT
∴ SPEED UP E2

TYPICAL QUESTION

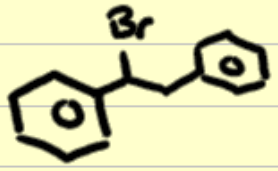




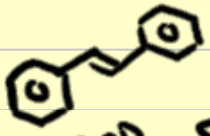




RANK THESE E1 vs E2 & WHY ?
- GIVE THE PRODUCTS



Ph GROUP α- MORE E1 TENDING, BUT THEY ALL HAVE THIS Br^- L.G. - E1 OR E2 V.G. L.G.

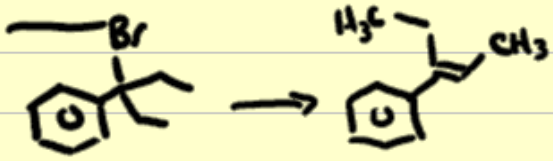


BASE - KO^tBu IS STRONG BASE ⟹ E2 FAVOURING

PROD. SOLVENT - NON POLAR ∴ E2 FAVOURING

β-ARYL - SPEEDS UP E2

∴ PRETTY HIGHLY E2 - MOST OF ALL

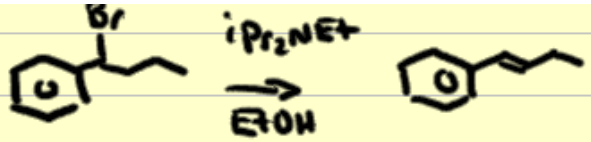


MOST E1 CHARACTER

3° & BENZYLIC HALIDE ∴ V. CATION FAVOURING ⟹ E1

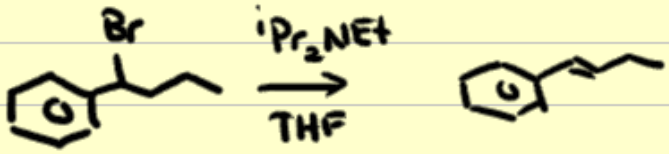
POLAR SOLVENT (EtOH) ⟹ CATION STABILIZING ⟹ E1

BASE NOT SO STRONG ∴ LESS E2 THAN ABOVE



- 2° + BENZYLIC ∴ NOT AS E1 AS 3° CASE
- BASE - MODERATE TO WEAK - E1 OR E2
- NO β-ARYL - NOT AS E2 AS KO^tBu CASE
- BUT POLAR SOLVENT ∴ MORE E1 THAN THF CASE

2ND MOST E1 CHARACTER



2° + BENZYLIC - NOT AS E1 AS 3° CASE
- NO β-ARYL ; NO STRONG BASE
  ∴ NOT AS E2 AS KO^tBu CASE
- SOLVENT (THF) NON-POLAR
  ∴ LESS E1, MORE E2 THAN CASE W EtOH

∴ 2ND MOST E2 CHARACTER

235 Notes

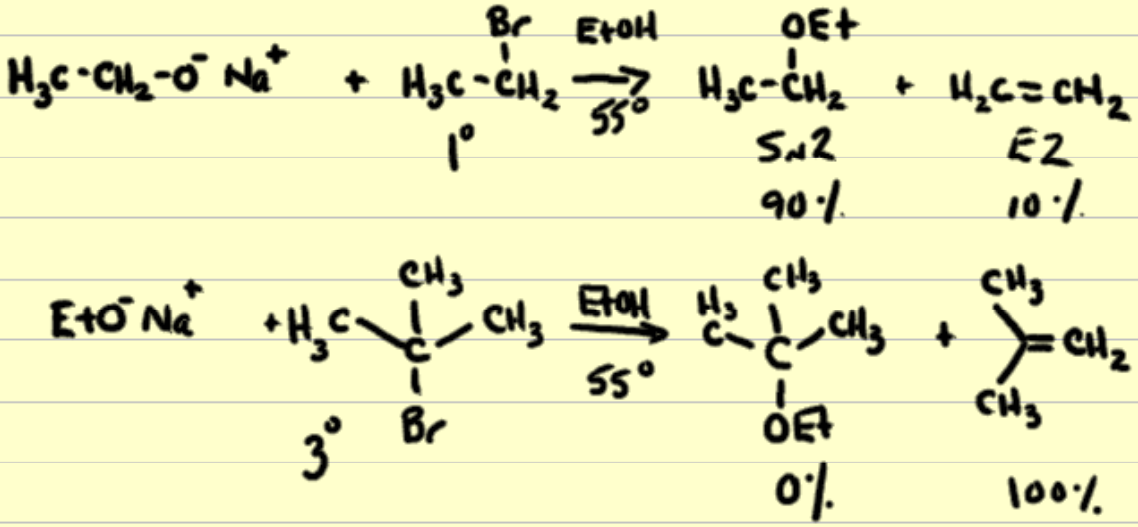
Notebook: jgreen1263's notebook
Created: 11/13/2009 3:45 PM **Updated:** 3/14/2013 10:48 AM

CHEM. 235 - LECTURE 17

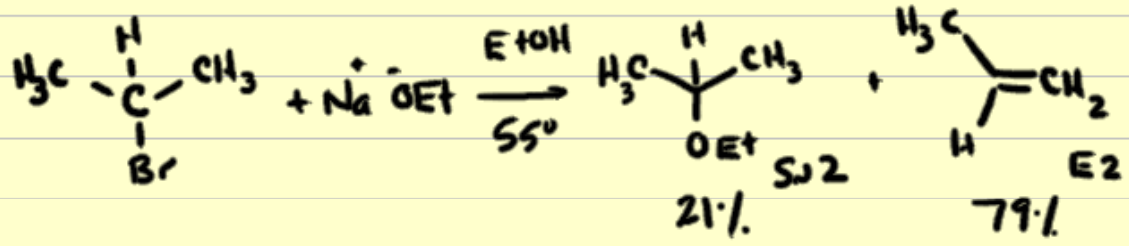
ELIMINATION VS SUBSTITUTION
E2 SN2

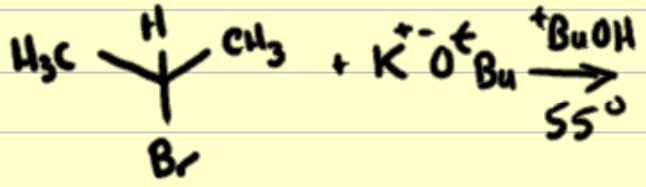
- STERICS OF RXN
- BASICITY OF Nu^- / BASE
- TEMPERATURE

- S_N2 HATES STERIC CROWED REAGENTS
  ∴ BULKIER SUBSTRATES $3^0 > 2^0 > 1^0$
  WILL TEND TO FAVOUR E2



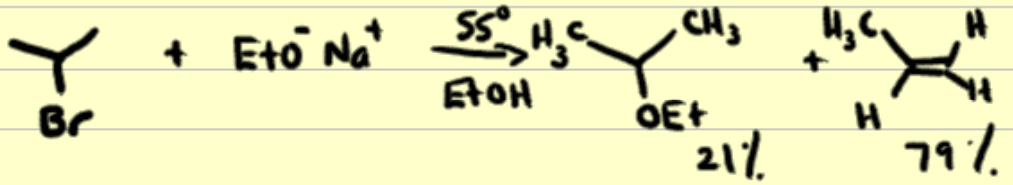
SAME FOR BASE / Nu⁻

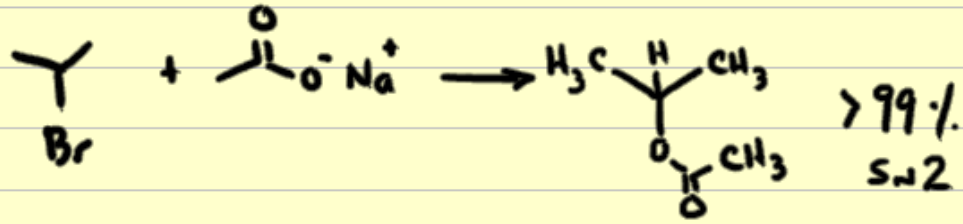




BASICITY OF BASE / Nu⁻

$EtO^- Na^+$	$H_3C-CO_2^- Na^+$	$H_3C-CH_2-S^- Na^+$
V. BASIC	NOT V. BASIC	NOT V. BASIC
V. GOOD Nu⁻	DECENT Nu⁻	V. GOOD Nu⁻





- MORE BASIC ⟹ E2
  LESS BASIC ⟹ SN2

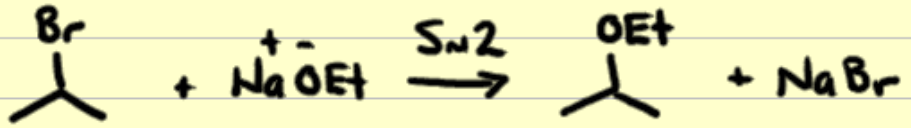
TEMPERATURE

- HIGHER TEMPS TEND TO ENCOURAGE ELIMINATION (E1 OR E2) OVER SUBSTITUTION

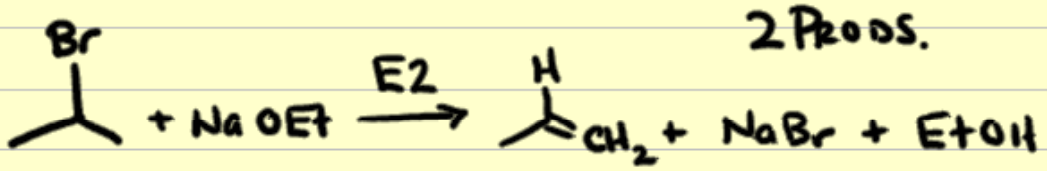
$$\Delta G = \Delta H - T\Delta S$$

ΔS IS RANDOMNESS - IF RXN PRODUCES MORE PRODUCTS, ΔS IS HIGHER

- SHOULD GET MORE FAVOURABLE AT HIGH T



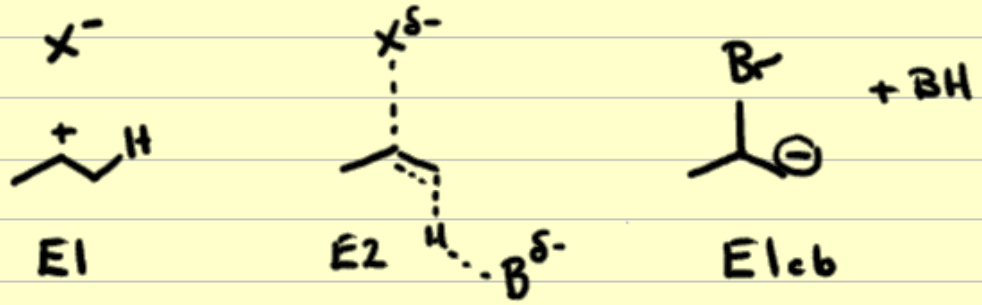
2 PRODS.



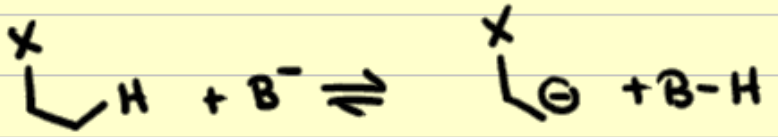
3 PRODS

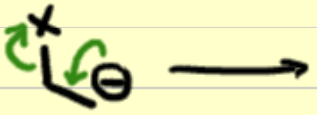
∴ FAVOURED MORE AT HIGH T.

FINAL MECH E1cb



TWO STEPS.

1) 

2) 

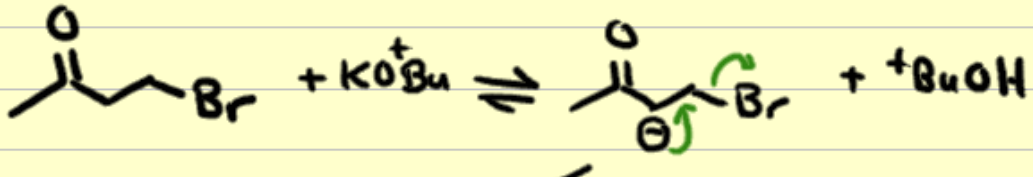
E1 CONJUGATE BASE

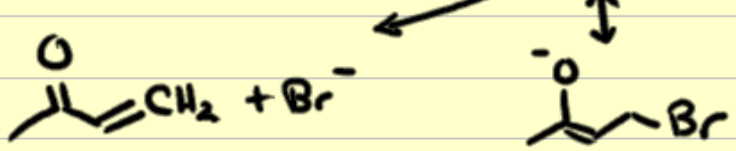
USUALLY 2ND STEP IS SLOW ONE

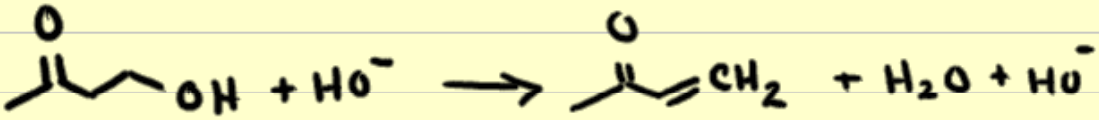
$$v = k\left[\text{X-L}^{\ominus}\right] \qquad \text{BUT } \left[\text{X-L}^{\ominus}\right] = K[B^-]\left[\text{X-L-H}\right]$$

$$v_{APPARENT} = k'\left[\text{X-L-H}\right][B^-]$$

95% OF TIME, THERE'S A REAL ACIDIFYING GROUP

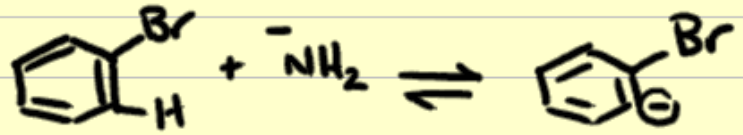




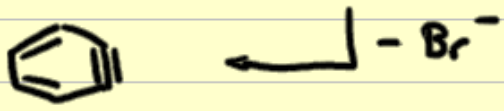
* 

ALDOL CONDENSATION

EXCEPTION (5%)



BENZYNE



Elcb

235 Notes

Notebook: jgreen1263's notebook
Created: 11/13/2009 3:45 PM **Updated:** 3/21/2013 11:21 AM

CHEM. 235 - LECTURE 18

- WHEN YOU GET A REACTION PRODUCT HOW DO YOU KNOW ITS IDENTITY?

- TEASER FOR S9-330/332

- WHAT WE NEED TO KNOW

1) WHAT IS THE MOLECULAR FORMULA $C_{17}H_{32}O$ OR SOMETHING ELSE?

- a) ELEMENTAL ANALYSIS.
  RATIO OF C:H:N:O:OTHERS

b) MASS SPECTROSCOPY
GIVES MOLAR MASS (MOLECULAR WEIGHT)

2) - WHERE IS EVERYTHING BONDED?

a) INFRARED SPECTROSCOPY (IR)

i.e.  ?, -CEN, OR C=C OR -C≡C-

 ? OR ONLY C-C 'S

b) Nuclear Magnetic Resonance Spectroscopy (NMR)

- Local Environment of H atoms & C atoms

1a) Elemental Analysis

-Burn a Carefully Weighed Sample of a Pure Compound

$C \rightarrow CO_2$ $\quad$ $N \rightarrow N_2$

$H \rightarrow H_2O$

Get Back a Report w

%C %H %N (%O)

To Convert into Molecular Formula

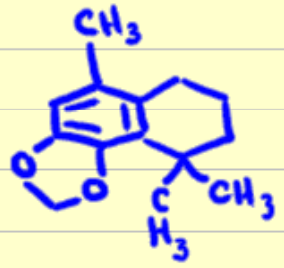
$$\frac{\%\,C}{12.011} \quad \frac{\%\,H}{1.007} \quad \frac{\%\,N}{14.007} \quad \frac{\%\,O}{15.999}$$

- Take These Results & Divide By Smallest of These #'s

$\Rightarrow$ Emperical Formula

EMPERICAL FORMULA MAY BE = MOLECULAR FORMULA OR IT MAY BE A MULTIPLE (×2 OR ×3)

TAKE



	C, 77.03%	H, 8.31%	O, 14.66%
	12.011	1.007	15.999
	= 6.41	8.25	0.916
÷	0.916	0.916	0.916
	= 7	9	1

m/e = 218

EMPERICAL FORMULA = C_7H_9O

COULD BE THE MOLECULAR FORMULA, OR IT COULD BE $C_{14}H_{18}O_2$ OR $C_{21}H_{27}O_3$ OR ....

TELL BY 16 - MASS SPECTROSCOPY.

- KNOCKS AN e^- OUT OF MOLECULE TO GIVE A RADICAL CATION ($M^{+\cdot}$)
- SENDS IT THROUGH A MAGNETIC FIELD

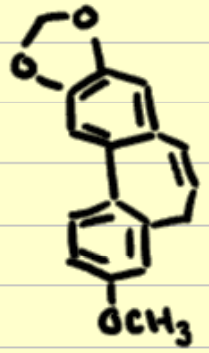
- How fast it bends towards magnet depends on mass/charge ratio
= m/e

Ideally m/e = molar mass

Note: in reality $M^{+\cdot}$ is decomposing at the same
∴ Usually highest m/e = Molar mass

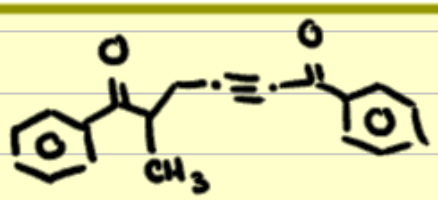
Above m/e (molecular ion) = 218

∴ $C_{14}H_{18}O_2$ is real molecular formula

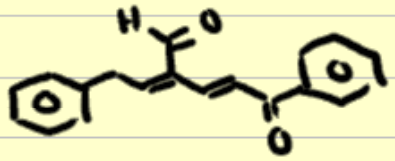


	C, 76.68%	H, 5.30%	O, 18.02%
÷	12.011 / 6.384	1.007 / 5.26	15.999 / 1.126
÷	1.126 / 5.670	1.126 / 4.67	1.126 / 1
×2	11.34	9.34	2
×3	17.01	14.01	3

m/e = 266 ∴ it's $C_{17}H_{14}O_3$

ONE MORE 

	C	H	O
	82.6 %	5.8 %	11.6 %
	12.011	1.007	15.999
=	6.88	5.8	0.725
÷	0.725	6.725	0.725
=	9.5	8	1
HOW ABOUT	C_{19}	H_{16}	O_2

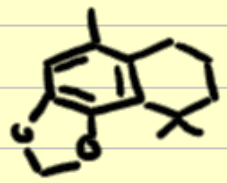
COULD ALSO BE 

- ALMOST NO INFORMATION ON STRUCTURE
  - EXCEPT A BIT

COMBINED # DOUBLE BONDS + # RINGS + 2x # TRIPLE BOND = INDEX OF HYDROGEN DEFICIENCY

$$IHD = \frac{2c + 2 - h - x + n}{2}$$

c = # OF C'S
h = # OF H'S
x = # OF Cl, Br, I, F
n = # OF N'S

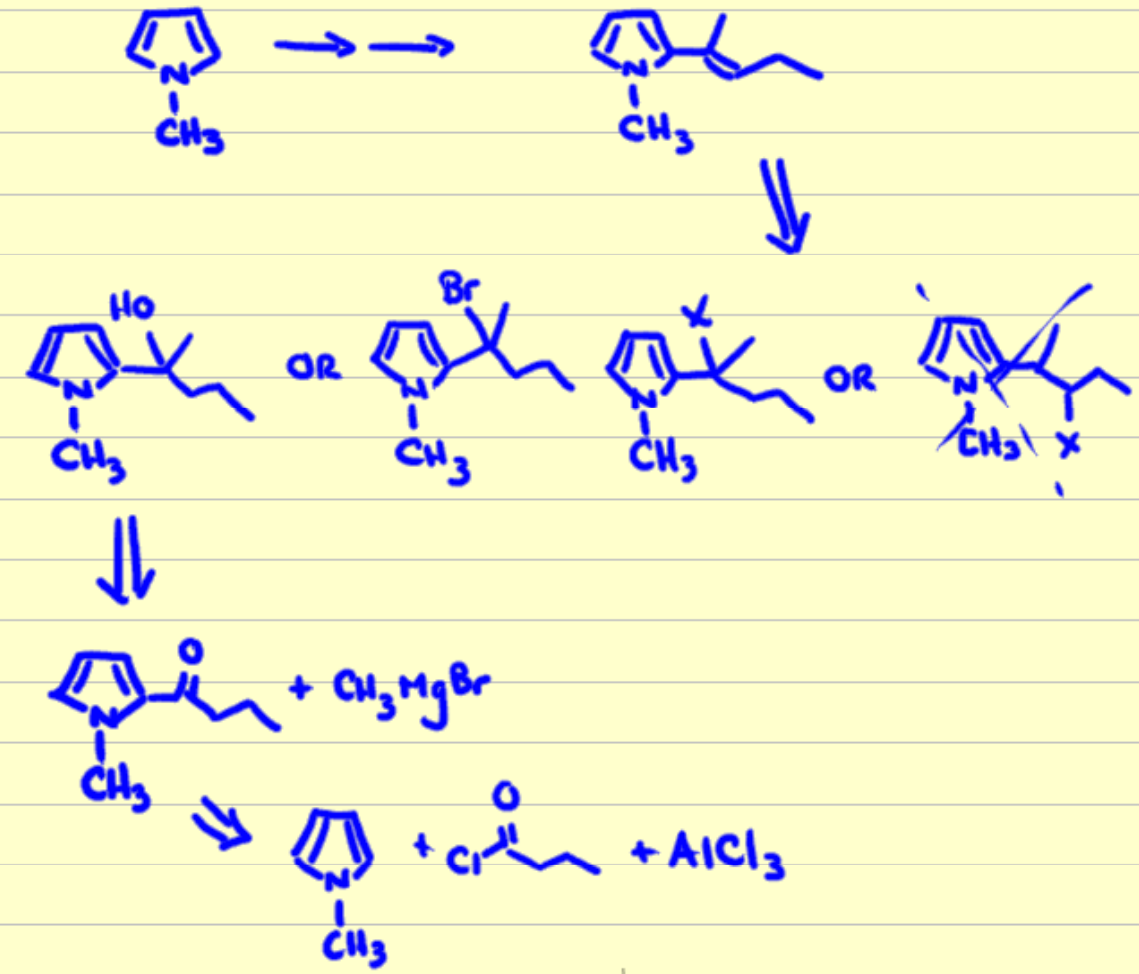


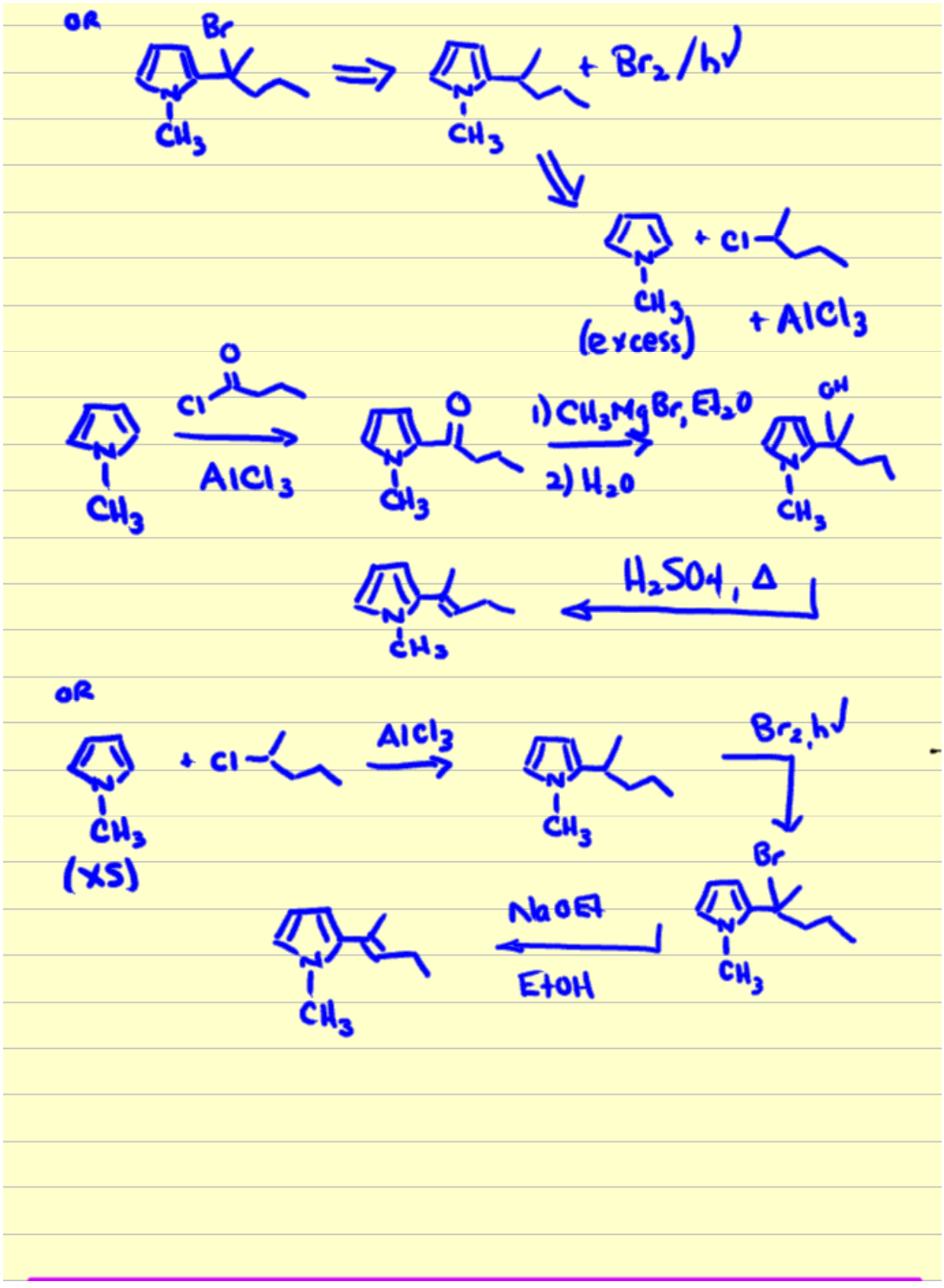
$C_{14}H_{18}O_2$

$$IHD = \frac{2(14)+2-18}{2} = \frac{28+2-18}{2}$$

$$= 6$$

IN THIS CASE, 3 RINGS
+ 3 "FORMAL" C=C 'S
6




OR
Br
CH3
+ Br2/hν
+ Cl
(excess)
+ AlCl3
O
Cl
AlCl3
1) CH3MgBr, Et2O
2) H2O
OH
H2SO4, Δ
OR
(XS)
NaOEt
EtOH

235 Notes

Notebook: jgreen1263's notebook
Created: 11/13/2009 3:45 PM **Updated:** 3/26/2013 11:20 AM

CHEM. 235 - LECTURE 19

SPECTROSCOPIC METHODS

1) NMR SPECTROSCOPY

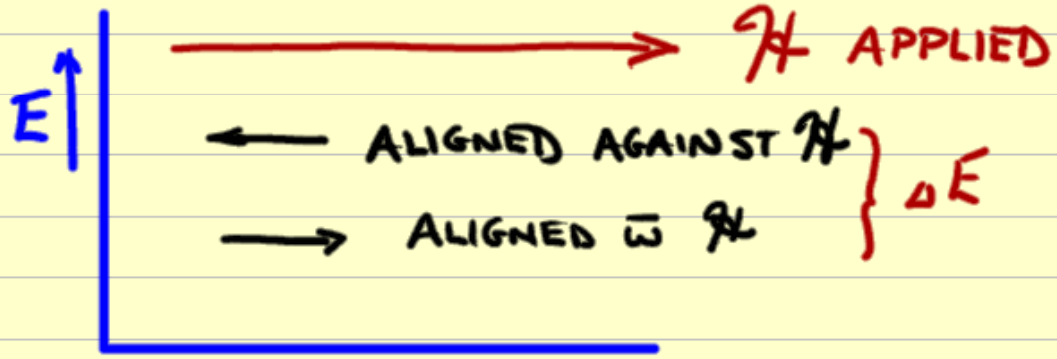
NMR - NUCLEAR MAGNETIC RESONANCE

- NUCLEI HAVE SPIN
  - EASIEST IS HYDROGEN WITH ONE PROTON, NO DEUTERIUM

^1H PROTON NMR SPECTROSCOPY.

- SPIN ½ NUCLEUS

- IN A MAGNETIC FIELD $\mathcal{H}$, A PROTON NUCLEUS WILL ALIGN EITHER WITH OR AGAINST THAT FIELD



- ΔE IS PROPORTIONAL TO APPIED $\mathcal{H}$

1.41 T = 60 MHz

7.05 T = 1.2×10^{-4} kJ/mol = 300 MHz

11.7 T = 2×10^{-4} kJ/mol = 500 MHz

- DIFFERENT ^1H NUCLEI ABSORB E AT APPROX. THE SAME ν, BUT THERE ARE SMALL DIFFERENCES

IN A 7.05 T MAGNET
- RANGE IS 3000 Hz

SO WE REPORT THEM AS $\frac{\Delta\nu}{\nu_{MAGNET}}$ IN ppm

ppm = parts per million

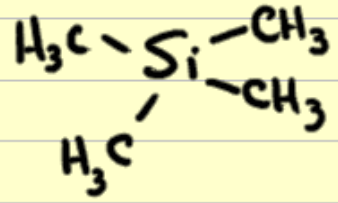
$$\frac{3000\ Hz}{300 \times 10^6\ Hz} = 10\ ppm$$

RANGE FOR 95% OF ^1H NUCLEI

- Since $\Delta E \propto$ Applied Field
- This Range in ppm, Stays the Same

Called Chemical Shift

- Call one Compound 0 ppm as a Reference



Tetramethylsilane ≡ TMS

- Every other ^1H is Said To Be 1 Shifted Relatine to TMS

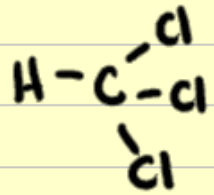
= δ

- Where do these Shifts Occur?

- H's w/ a Lot of Electron Density Around Them are Shielded From the Applied Field → Give Low δ
  Referred to as Upfield

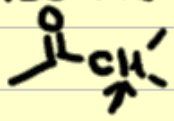
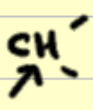
- H's without much electron density around them - not a shielded from applied B_0
  ∴ larger δ
  ∴ downfield

H_3C-CH_3 0.8 ppm



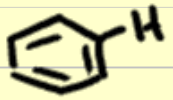
7.26 ppm

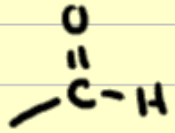
General Ranges for δ

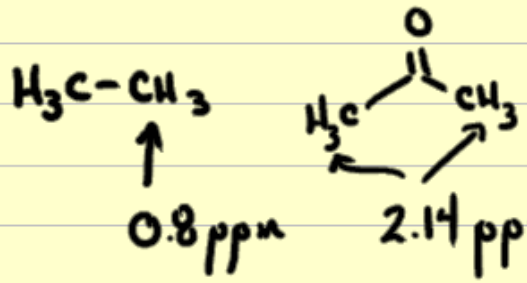
	δ (ppm)
- Simple Alkanes $CH_3-CH_2-CH_2-$	~1
- Alkyl one atom away from a heteroatom $HO-CH_2-CH_3$ or next to multiple bond $C=C-CH$	1-2
- Alkyls next to carbonyls or amines  	2-3

- ALKYLS NEXT TO RO-CH 3-4.3
  OR HALIDE X-CH

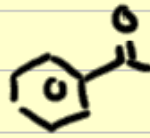
- VINYL C=C(H) 4.8-7.3

- AROMATIC H'S  6.8-8.5

-  ALDEHYDES 9-10



OH'S + NH'S
- VARY WITH SOLVENT, CONCENTRATION, TEMPERATURE
- DUE TO H BONDING
  ∴ V. WIDE RANGES



11-14 ppm

R~NH$_2$ 0.5-5.0 ppm

- How to Read NMR Table

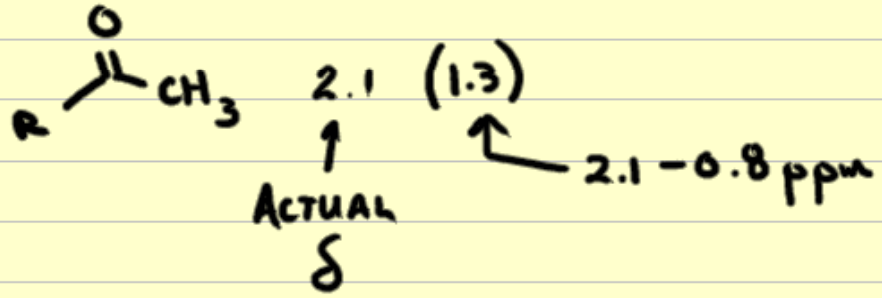
see NMR table page or web page now

Divided into Chemical Shifts by CH_3 (methyl) CH_2 (methylene) and CH (methine) next to a Functional Group

and

Shifts for CH_3, CH_2, CH that are one atom removed from a Functional Group

- In both tables, the number in brackets is the δ (chemical shift) subtracted from base δ (i.e. No Functional Group)

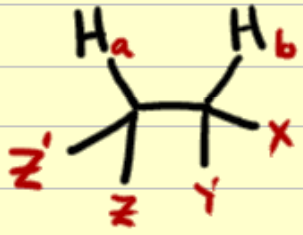


235 Notes

Notebook: jgreen1263's notebook
Created: 11/13/2009 3:45 PM **Updated:** 3/28/2013 11:20 AM

CHEM. 235 - LECTURE 20.

- SPLITTING OF ^1H NMR RESONANCES
THE n+1 RULE

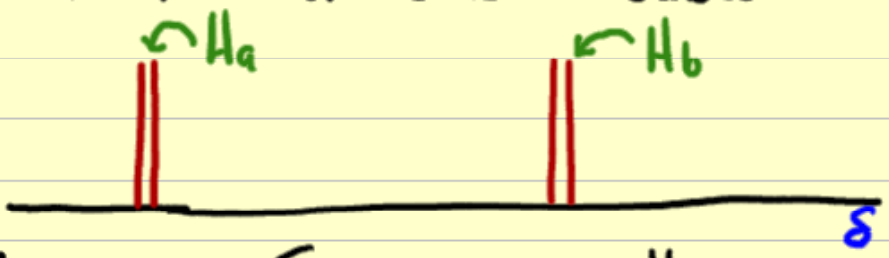


FOR Ha TWO POSSIBLE SITUATIONS:

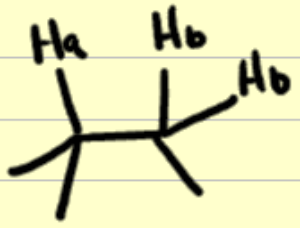
i) Hb IS ALIGNED W APPLIED FIELD
ii) Hb IS ALIGNED AGAINST

∴ TWO V. SLIGHTLY DIFFENT ENVIRONMENTS FOR Ha - EXISTS AS A DOUBLET

∴



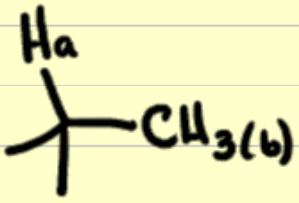
- ANALOGOUS SITUATION FOR Hb



Hb SHOULD GIVE A DOUBLET, JUST AS ABOVE

For Ha 3 Possibilities

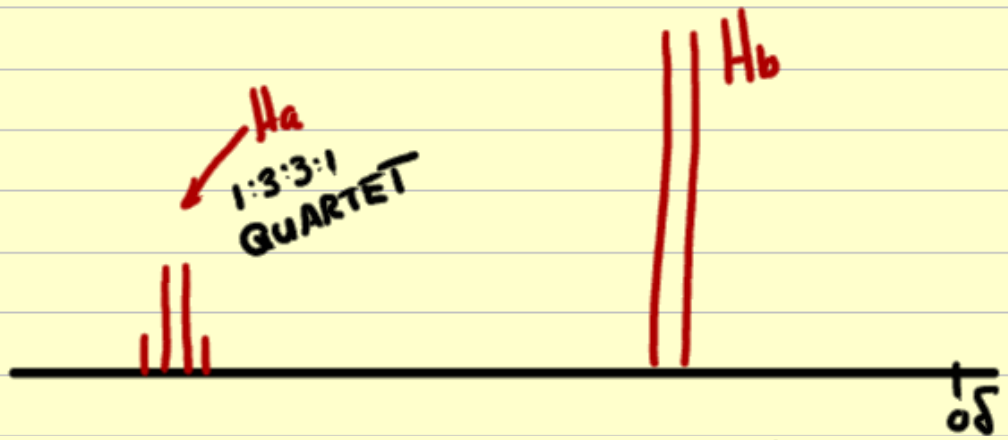
- Both Hb's with
- One Hb with; One Against — 2x as possible
- Both Hb's Against Field



Hb is a Doublet, Just Like Above, But Still More Intense

Ha 4 Possibilities

	Amount
- All 3 Hb's with Field	1
- Two with Field, One Against	3
- One with Field, Two Against	3
- All 3 Hb's Against Field	1



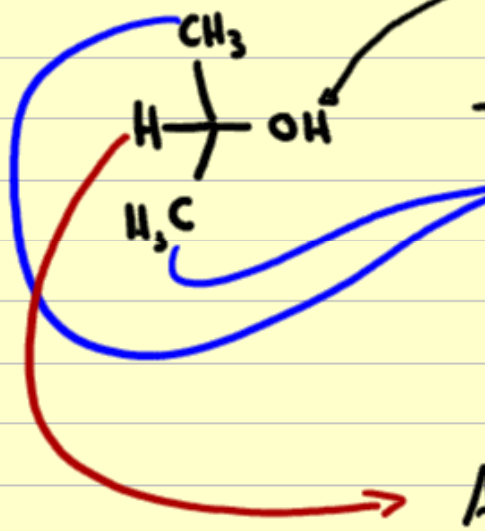
TO REMEMBER INTENSITIES, USE PASCAL'S TRIANGLE

```
          1        ← 0 H'S NEXT DOOR
        1 1        ← 1 H
      1 2 1        ← 2 H
    1 3 3 1        ← 3 H
  1 4 6 4 1        ← 4 H
1 5 10 10 5 1      ← 5 H
```

INTEGRALS

- FINALLY, THE AREA UNDERNEATH THE ^{1}H NMR RESONANCES CORRESPONDS TO THE # OF H ATOMS IT REPRESENTS

CALLED THE INTEGRAL.



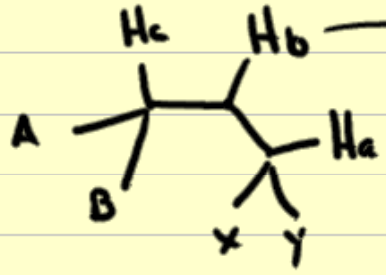
OH'S & NH USUALLY DON'T PARTICIPATE IN SPLITTING
- DUE TO H BONDING

CHEMICALLY IDENTICAL

∴ DOUBLET (CAUSED BY H-c)

AREA = 6

APPEARS AS 7 LINES (SEPTET), A=1

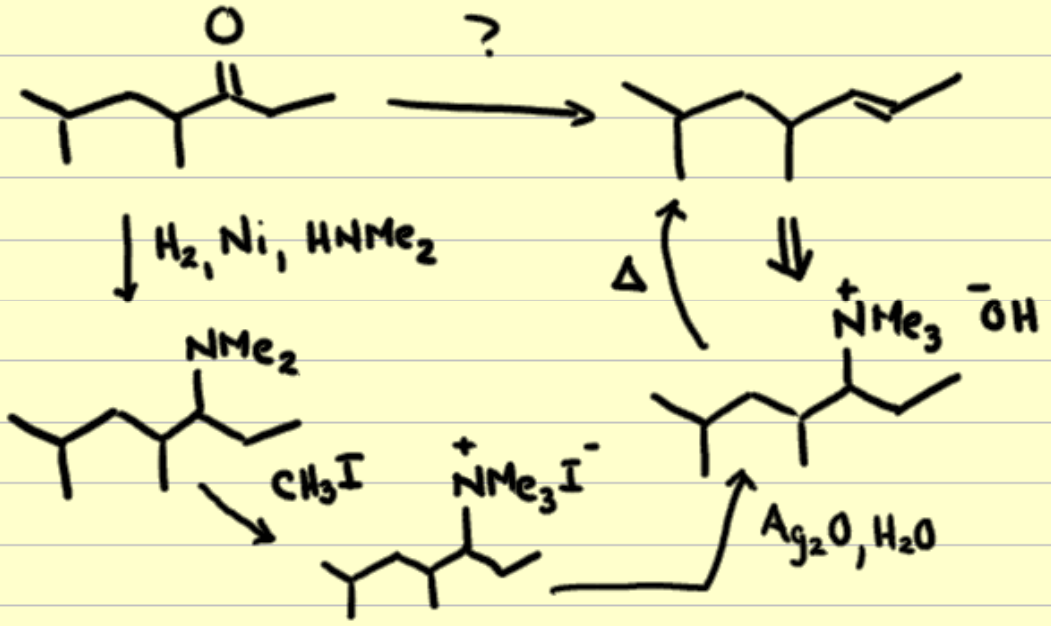


SINCE Hc & Ha ARE NOT IDENTICAL

Hb APPEARS AS A DOUBLET OF DOUBLETS

- ALTHOUGH IT MIGHT LOOK LIKE A TRIPLET

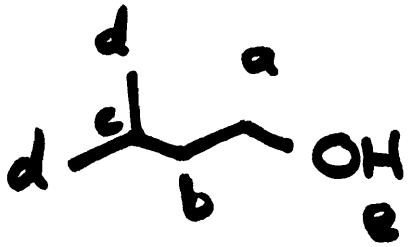
2011 EXAM



NMR ROUNDUP

- δ's ARE PREDICTABLE
- AREAS CORRESPOND TO # OF H's
- SPLITTING (n+1 RULE) TELLS US ABOUT H's NEXT DOOR

EXAMPLES



PREDICT

a CH_2 A=2, δ=3.4, triplet (t)

b CH_2 A=2, δ=1.5, doublet of triplets (dt) (expect multiplet)

c CH, A=1, δ=1.6, triplet of septets = multiplet

d 2 CH_3, A=6, δ=0.8, doublet (d)

e OH, A=1 δ=0.5–5.5 singlet but often broad.

OBSERVED

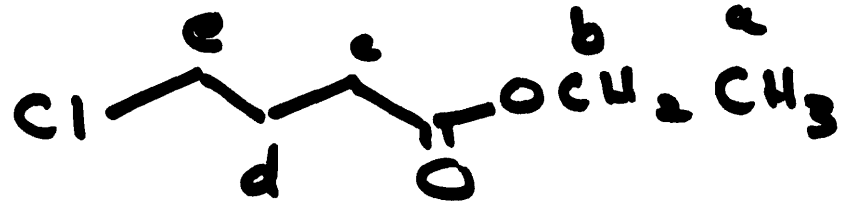
a δ 3.65, A=2, triplet - decent agreement

b δ 1.45, A=2, apparent quartet but really doublet of triplets - good

c δ 1.7, A=1, multiplet - good agreement

d δ 0.9, A=6, doublet - good agreement

e δ 2.25, A=1, br singlet - fits



PREDICT

a. CH_3, A=3, δ=1.3, ~~quartet~~ triplet

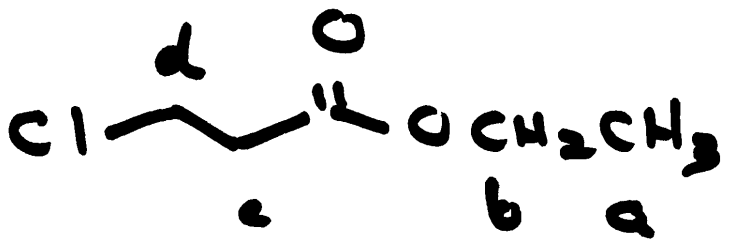
b. CH_2, A=2, δ=4.1, quartet

V. DIAGNOSTIC FOR AN ETHYL ESTER

c. CH_2, A=2, δ=2.2, triplet

d. CH_2, A=2, δ=1.8+(0.5)=2.3, triplet of triplets (m)

e. CH_2, A=2, δ=3.4, triplet



a A=3, δ= 1.3, triplet

b A=2, δ= 4.1, quartet

c A=2, δ= 2.2 + (0.6) = 2.8, triplet

d A=2, δ= 3.4 + (0.5) = 3.9, triplet

COMPARE TO COPY OF ^{1}H NMR ON WEB SITE.

---

^{13}C NMR. NOT TESTED ON FINAL.

^{12}C NUCLEUS HAS NO NUCLEAR SPIN

^{13}C IS ACTIVE I = ½

- PROBLEM 1% ABUNDANCE
- INHERENTLY WEAKER.
- "DECOUPLE" H NUCLEI FROM THE CARBONS. - INCREASES SIGNAL, ONLY SEE SINGLETS.
- DON'T INTEGRATE, AREAS NOT ACCURATE

- BUT, MUCH WIDER RANGE OF CHEMICAL SHIFTS, δ 20-220 ppm
- FUNCTIONAL GROUPS HAVE FAIRLY DIAGNOSTIC δ'S.

	δ
- C=O 's	170 - 210 ppm
- C=C 's	120's + 130's
C≡C	80's + 100's
-C-C-	< 77 ppm

IR SPECTROSCOPY.

ABSOLUTELY ON FINAL

- BASED ON THE IDEA THAT BOND IS LIKE A SPRING
- WITH RIGHT FREQUENCY OF IRRADIATION, IT WILL STRETCH, OR BEND, OR TWIST.
- THAT ν (FREQUENCY) IS VERY CHARACTERISTIC OF THE FUNCTIONAL GROUP

235 Notes

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Created: 11/13/2009 3:45 PM **Updated:** 4/4/2013 11:27 AM

CHEM. 235 - LECTURE 22.

IR SPECTROSCOPY

ENERGY RANGES 8 - 40 kJ/mol

- LOWER ν THAN VISIBLE LIGHT
  - THEREFORE "INFRARED"
- UNITS ARE A FREQUENCY ν (BUT AN ODD ONE)

$1/\lambda$ (IN CM) $\therefore$ cm^{-1}

OFTEN CALLED 'WAVENUMBERS'

TYPICAL RANGE $4000\ cm^{-1}$ - $600\ cm^{-1}$

DEPENDS ON

1) PROCESS - STRETCH?, BEND?, TWIST?
2) STRENGTH OF BOND
3) MASS OF THE GROUPS AT END OF BOND

$\nu \propto \sqrt{\frac{1}{\mu}}$ FOR m_1—m_2 $\mu = \frac{m_1 \times m_2}{m_1 + m_2}$

μ = "REDUCED MASS"

C≡C	C=C	C-C
$2150\ cm^{-1}$	$1650\ cm^{-1}$	$1200\ cm^{-1}$

∴ STRONGER BOND, HIGHER ν

C-H	C-O	C-Br
$3000\ cm^{-1}$	$1100\ cm^{-1}$	$550\ cm^{-1}$

∴ HEAVIER THE ATOMS, THE LOWER THE ν

TWO HALVES OF SPECTRUM

WE CARE MOSTLY ABOUT

1) CHARACTERISTIC GROUP RANGE

$4000 - 1500\ cm^{-1}$

* - HIGHLY CHARACTERISTIC OF INDIVIDUAL FUNCTIONAL GROUPS

2) FINGERPRINT REGION

$1500 - 650\ cm^{-1}$

- COMPARING KNOWNS & UNKNOWNS BY OVERLAP, BUT DIAGNOSTIC FUNCTIONAL GROUP ν'S MUCH HARDER TO SEE

Note: Polarized bonds will tend to give more intense absorptions that non-polarized ones; i.e.,
nitriles > alkynes
C=O carbonyls > C=C alkenes

Characteristic Functional Group ν's

			ν (broad)	
OH (stretch)	Alcohol	R-OH	3600-3200 cm^{-1}	br (sometimes 2 bands)
	Carboxylic Acid	$R-\overset{O}{\overset{\|}{C}}-OH$	Centred at 3000 cm^{-1} V. broad	
NH	Amines	$R-\overset{R'}{\overset{\|}{N}}H$	~3300 cm^{-1} Weaker than OH	
C-H			~3000 cm^{-1}	
			< 3000 cm^{-1}	sp^3 C-H
			> 3000 cm^{-1}	sp^2 C-H
			~3300 cm^{-1}	sp C-H
C≡C	Alkynes		2150 cm^{-1}	Weaker than C≡N
C≡N	Nitrile		2250 cm^{-1}	More intense than C≡C
C=O	Carbonyls		1650-1820 cm^{-1}	often the most intense absorption in spectrum
		$-\overset{O}{\overset{\|}{C}}-Cl$	1800 cm^{-1}	
		$-\overset{O}{\overset{\|}{C}}-OR$	1740 cm^{-1}	
		$-\overset{O}{\overset{\|}{C}}-R(H)$	1710-1720 cm^{-1}	

now is a good time to look at the selected IR spectra link

$-\overset{O}{\overset{\|}{C}}-OH$ 1700 cm^{-1}

$-\overset{O}{\overset{\|}{C}}-NR_2$ 1660 cm^{-1}

NOTE: IF CONJUGATED TO C=C OR C≡C ✓ OF C=O IS LOWERED BY ~30 cm^{-1}

C=C ALKENES 1600-1650 cm^{-1}

BUT WEAKER THAN C=O

 1600 & 1500 cm^{-1}

END OF NEW MATERIAL

FINAL 2012 SPECTRAL Q (#7)

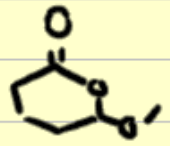
- 5 POSSIBLE COMPOUNDS TO SELECT FROM

C 54.53% H 9.15% O 36.32%

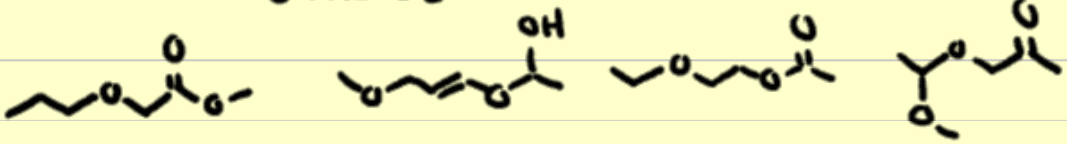
m/e = 132 (MASS SPECTRUM)

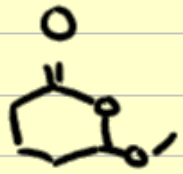
	C	H	O
	$\frac{54.53}{12.011}$	$\frac{9.15}{1.007}$	$\frac{36.32}{15.999}$
=	$\frac{4.54}{2.27}$	$\frac{9.08}{2.27}$	$\frac{2.27}{2.27}$
=	2	4	1

BUT $C_2H_4O_1$ IS m/e 44, BUT TRUE m/e IS 132



$\therefore$ $C_6H_{12}O_3$



CAN'T BE  - ELIMINATE FROM CONSIDERATION

OTHER 4 STILL IN PLAY.

WE WILL CONTINUE WITH IR, NMR ANALYSIS ON TUES APR 8 .....

235 Notes

Notebook: jgreen1263's notebook
Created: 11/13/2009 3:45 PM **Updated:** 4/9/2013 11:42 AM

CHEM. 235 - LECTURE 22+23

IR SPECTROSCOPY

ENERGY RANGES 8-40 kJ/mol

- LOWER ν THAN VISIBLE LIGHT
  - THEREFORE "INFRARED"
- UNITS ARE A FREQUENCY ν (BUT AN ODD ONE)

$\frac{1}{\lambda}$ (IN CM) ∴ cm^{-1}

OFTEN CALLED 'WAVENUMBERS'

TYPICAL RANGE 4000 cm^{-1} - 600 cm^{-1}

DEPENDS ON

1) PROCESS - STRETCH?, BEND?, TWIST?
2) STRENGTH OF BOND
3) MASS OF THE GROUPS AT END OF BOND

$\nu \propto \sqrt{\frac{1}{\mu}}$ FOR m_1—m_2 $\mu = \frac{m_1 \times m_2}{m_1 + m_2}$

μ = "REDUCED MASS"

C≡C	C=C	C-C
$2150\ cm^{-1}$	$1650\ cm^{-1}$	$1200\ cm^{-1}$

∴ STRONGER BOND, HIGHER ν

C-H	C-O	C-Br
$3000\ cm^{-1}$	$1100\ cm^{-1}$	$550\ cm^{-1}$

∴ HEAVIER THE ATOMS, THE LOWER THE ν

TWO HALVES OF SPECTRUM

WE CARE MOSTLY ABOUT

1) CHARACTERISTIC GROUP RANGE

$4000 - 1500\ cm^{-1}$

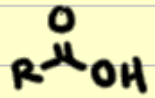
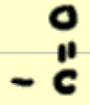
* - HIGHLY CHARACTERISTIC OF INDIVIDUAL FUNCTIONAL GROUPS

2) FINGERPRINT REGION

$1500 - 650\ cm^{-1}$

- COMPARING KNOWNS & UNKNOWNS BY OVERLAP, BUT DIAGNOSTIC FUNCTIONAL GROUP ν'S MUCH HARDER TO SEE

Characteristic Functional Group ν's

OH (stretch)	Alcohol	R-OH	3600-3200 cm^{-1} (broad) (sometimes 2 bands)	bc
	Carboxylic Acid		Centred at 3000 cm^{-1} V. broad	
NH	Amines		~3300 cm^{-1} Weaker than OH	
C-H			~3000 cm^{-1}	
			< 3000 cm^{-1}	sp^3 C-H
			> 3000 cm^{-1}	sp^2 C-H
			~3300 cm^{-1}	sp C-H
C≡C	Alkynes		2150 cm^{-1}	Weaker than C≡N
C≡N	Nitrile		2250 cm^{-1}	More intense than C≡C
C=O	Carbonyls		1650-1820 cm^{-1}	Often the most intense absorb-tion in spec-trum
			1800 cm^{-1}	
			1740 cm^{-1}	
			1710-1720 cm^{-1}	

$-\overset{O}{\overset{\|}{C}}-OH$ 1700 cm^{-1}

$-\overset{O}{\overset{\|}{C}}-NR_2$ 1660 cm^{-1}

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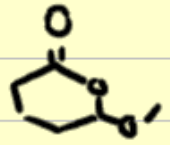

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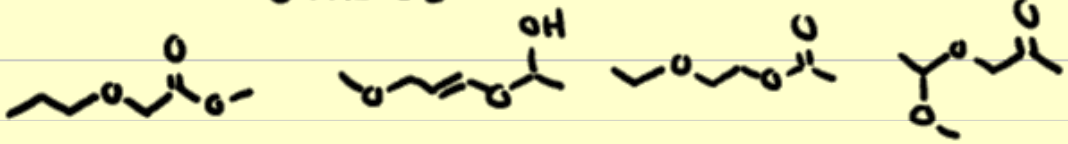
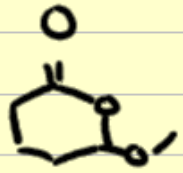


CAN'T BE  - ELIMINATE FROM CONSIDERATION

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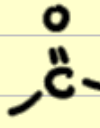
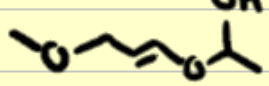
CONT'D

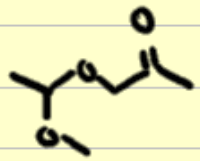
IR SPECTRUM 2978 cm^{-1} & 1742 cm^{-1}

2978 cm^{-1} $\sqrt{}$ C-H sp^3 C-H

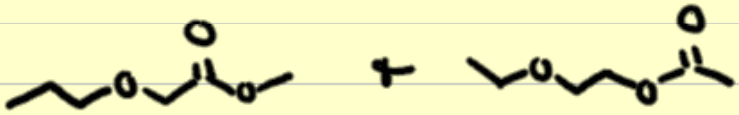
1742 cm^{-1} $\sqrt{}_{C=O}$ ESTER 

ELIMINATES  NO $\sqrt{}_{O-H}$ = 3400 cm^{-1}

NO $\sqrt{}_{C=C} \simeq$ 1660 cm^{-1}

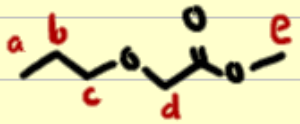
ALSO  EXPECT $\nu_{C=O}$ 1710 cm^{-1} (KETONE)

1742 cm^{-1} IS TOO FAR OFF



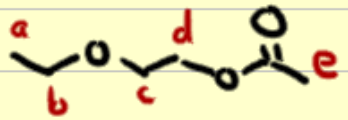
ON TO ^1H NMR

WE HAVE $\delta = 4.25$, t, A=2 $\quad \delta = 2.2$, s, A=3
$\delta = 3.7$, t, A=2 $\quad \delta = 1.2$, t, A=3
$\delta = 3.5$, q, A=2

LET'S TRY 

a $\delta = 0.8$, t, A=3 MAYBE ω $\delta = 1.2$, t, A=3
b $\delta = 1.5$, t of q, A=2 NOTHING TO MATCH
c $\delta = 3.4$, t, A=2 MAYBE ω $\delta = 3.7$, t, A=2
d $\delta = 3.4 + (1.0) = 4.4$, s, A=2 FAILS

∴ THIS ISN'T IT.

SO LET'S TRY 

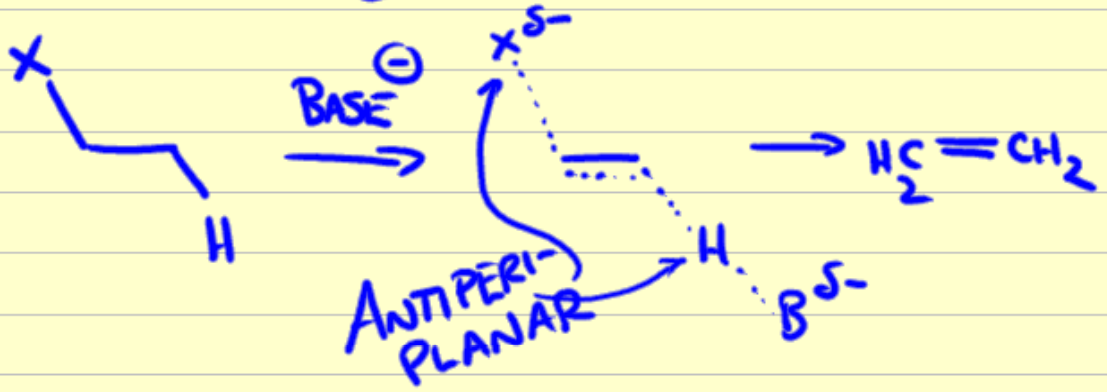
a $\delta = 1.2$, t, A=3 MATCHES $\delta = 1.2$, t, A=3
b $\delta = 3.4$, q, A=2 MATCHES $\delta = 3.5$, q, A=2
c $\delta = 3.4 + 0.4 = 3.8$, t, A=2 MATCHES $\delta = 3.7$, t, A=2

d $\delta = 4.1 + (0.3) = 4.4$, t, A=2 GOOD MATCH @ $\delta = 4.25$, t, A=2

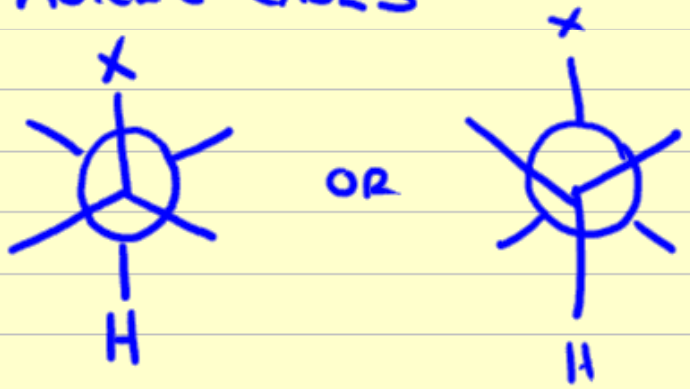
e $\delta = 2.0$, S, A=3 OR MATCH @ $\delta = 2.2$, S, A=3

THIS IS IT.

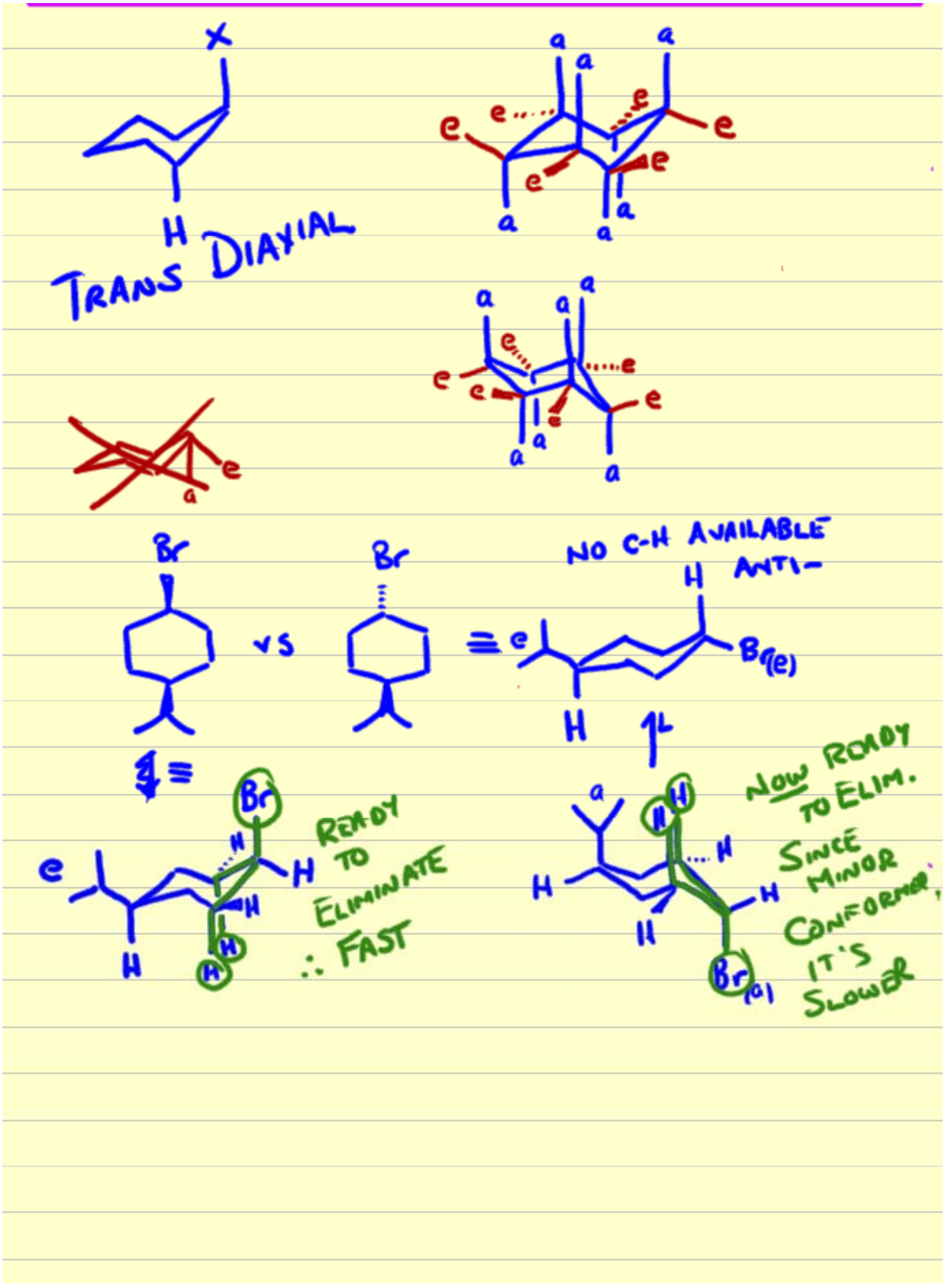
REVIEW - E2 ELIMINATION AND STEREOCHEMISTRY

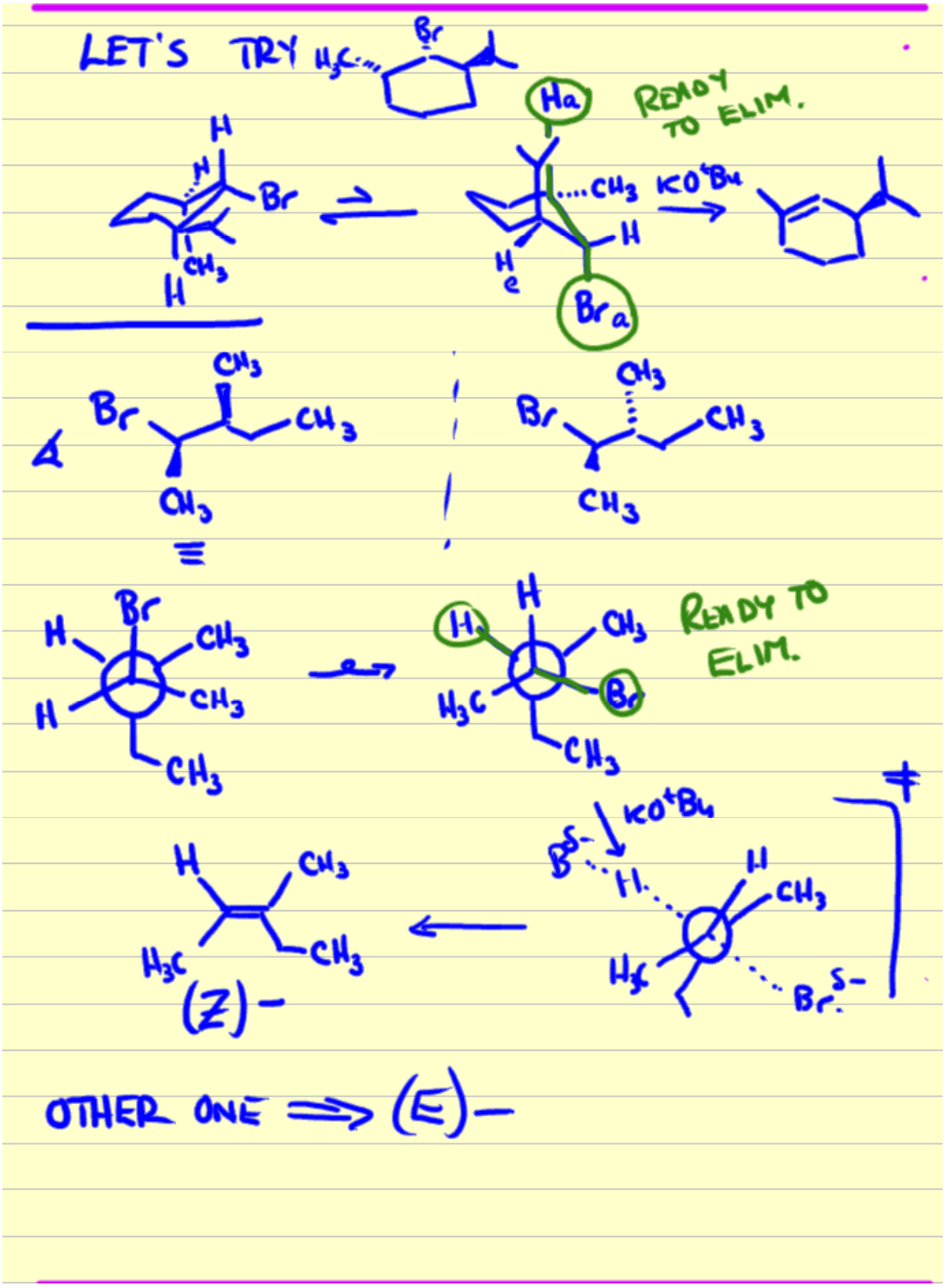


IN ACYCLIC CASES



IN CYCLIC CASES


X
H
TRANS DIAXIAL
a
e
Br
vs
NO C-H AVAILABLE
ANTI-
H
Br(e)
READY TO ELIMINATE
∴ FAST
NOW READY TO ELIM.
SINCE MINOR CONFORMER, IT'S SLOWER
Br(a)


LET'S TRY
Ha
READY TO ELIM.
KO^{t}Bu
Br a
≡
READY TO ELIM.
KO^{t}Bu
(Z)-
OTHER ONE ⇒ (E)-