

## Chapter 1

## Introduction

- 1) Lewis Structures
- 2) Representing Organic Structures
- 3) Geometry and Hybridization
- 4) Electronegativities and Dipoles
- 5) Resonance Structures
  - (a) *Drawing Them*
  - (b) *Rules for Resonance*
- 6) Aromaticity
  - (a) *Carbocycles*
  - (b) *Heterocycles*
  - (c) *Antiaromaticity*
- 7) Tautomers and Equilibrium
- 8) Acidity and Basicity
- 9) Nucleophiles and Electrophiles
  - (a) *Nucleophilicity*
  - (b) *Substrate*
  - (c) *Solvent*

Reaction mechanisms offer us insights into how reactions work / how molecules react with one another.

This understanding allows us to manipulate reactions for our benefit – higher yield, control or change stereochemistry, predict new chemistry, develop new reactions and reagents, etc.

To write correct, detailed mechanisms, we must:

- a) have a detailed knowledge of molecular structure
- b) represent these structures unambiguously.

This chapter reviews some fundamental principles of organic chemistry.

It is vitally important that we comprehend the electron distribution in a given molecule, since mechanism is *the detailed description of electron movement during a reaction process*.

The 1<sup>st</sup> two chapters are the basic tools for proposing and writing clear and correct mechanisms.

## (1) Lewis Structures

Lewis structures are fundamental to writing and comprehending organic mechanisms.

There are 2 types of Lewis structure:

a) Line = bond = 2 electrons

b) Dot = Electron

Lone pairs are often the crucial reacting parts of the molecule, so knowing if they exist or not is important.

Valence electrons can be obtained from the Periodic Table.

(Don't forget that charges add or remove electrons!)

Atoms strive for a full outer shell

So H likes to have 2 electrons.

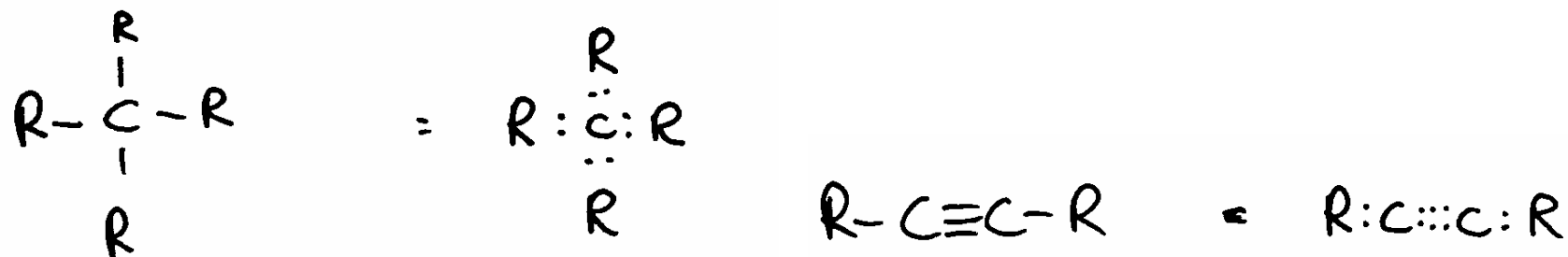
C likes to be surrounded by 8 electrons, etc.

Watch out for 3<sup>rd</sup> row elements (especially Si, P, S) that can have more than 8 electrons around them.

There are several recurring structural features that you should become **instantly familiar** with:

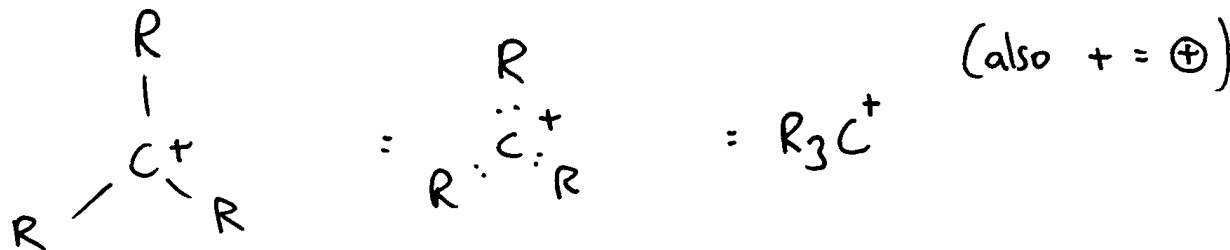
1) Hydrogen only forms one covalent bond.

2) Neutral carbon has four bonds (can be 4  $\sigma$  bonds, or combinations of  $\sigma$  and  $\pi$  bonds).

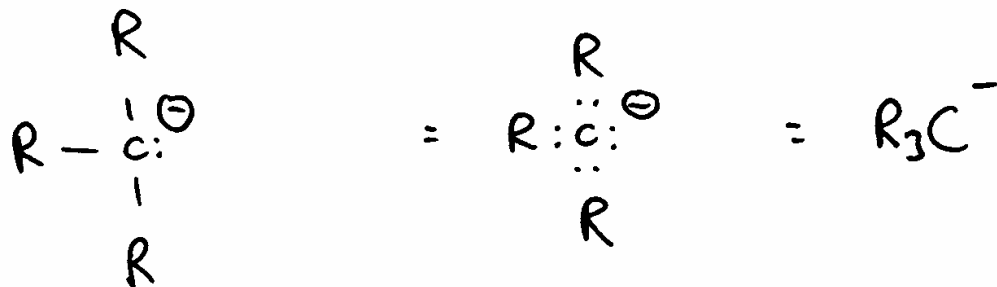


*Exceptions to 2) include CO, isonitriles and carbenes.*

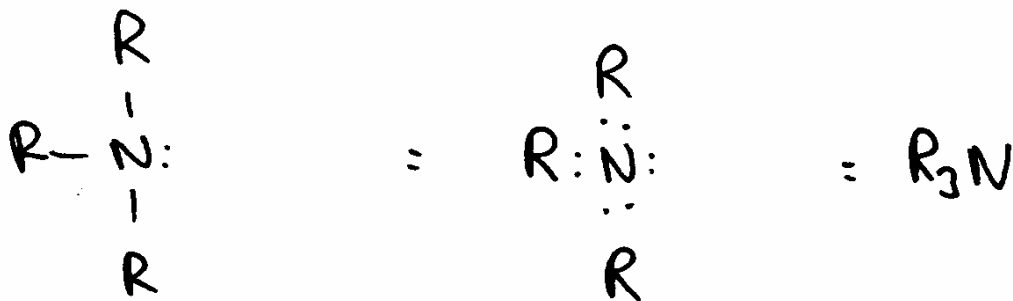
3) Positive carbon has three bonds and no lone pair:



4) Negative carbon has 3 bonds and a lone pair.

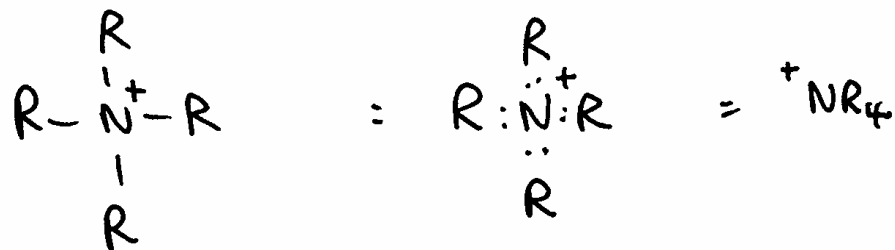


5) Neutral nitrogen has 3 bonds and a lone pair.

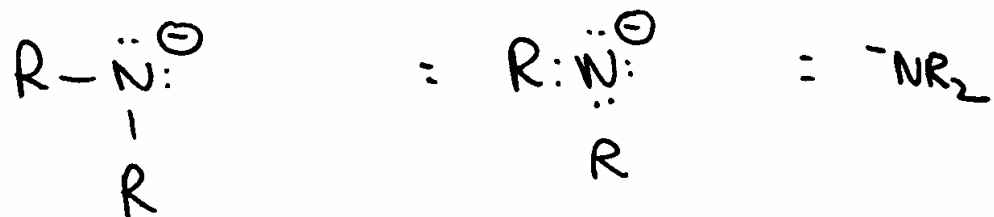


*Nitrenes are an exception to 5)*

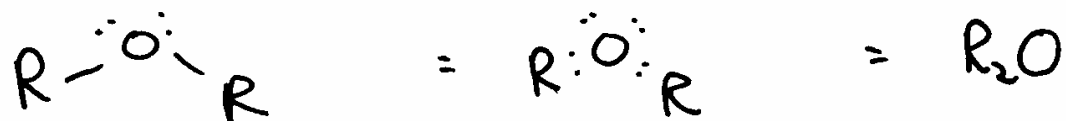
6) Positive Nitrogen has four bonds and no lone pairs.



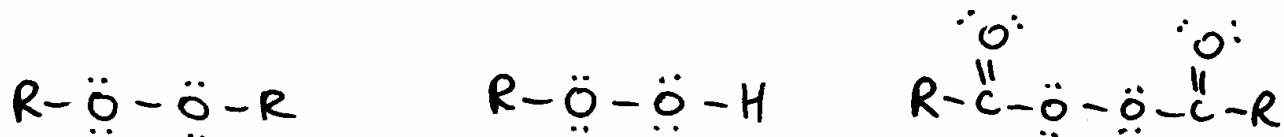
7) Negative Nitrogen has two bonds and two lone pairs.



8) Neutral Oxygen has two bonds and two lone pairs.



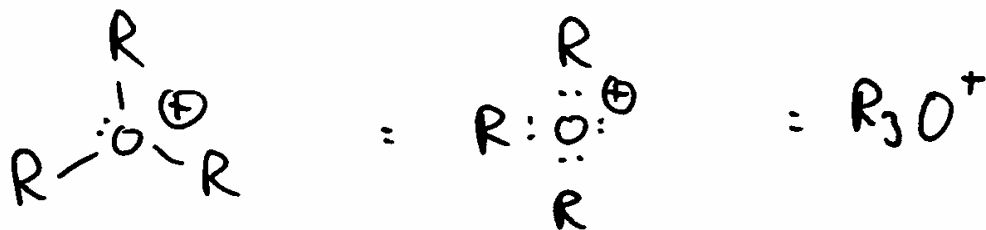
9) Oxygen-Oxygen bonds are uncommon – only in Peroxide type functionalities – unstable.



Hence  $\text{RCO}_2\text{R}$  implies ESTER.



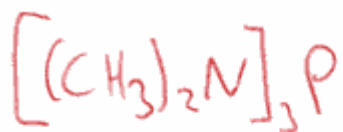
10) Positive Oxygen has three bonds and a lone pair.



*An exception to 10) are oxenium ions.*

## PROBLEMS:

Draw Lewis Structures for



= hmpa

= hexamethylphosphorous triamide

= v. polar solvent/additive.

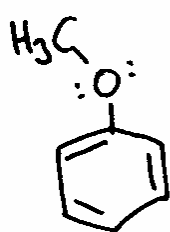
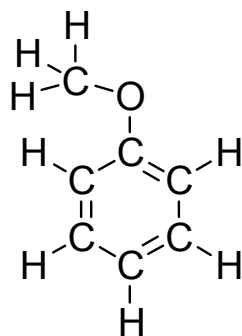
## 2) Representations of Organic Compounds

Many organic structures are implied as understood.

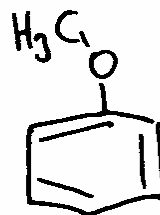
*Lone pairs and Hydrogens exist whether written or not.*

**So you must understand what is implied!!!**

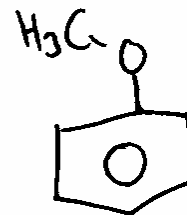
For example:



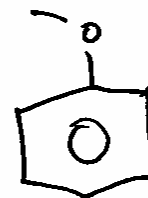
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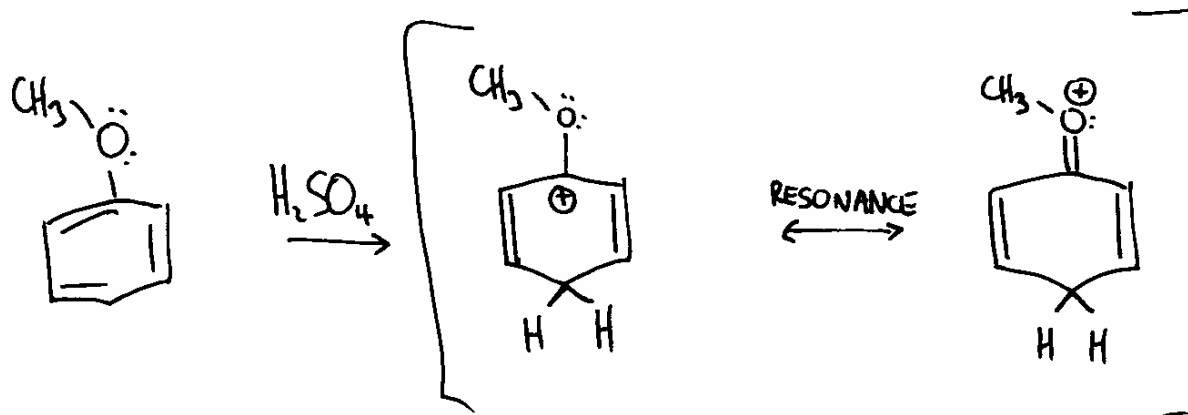
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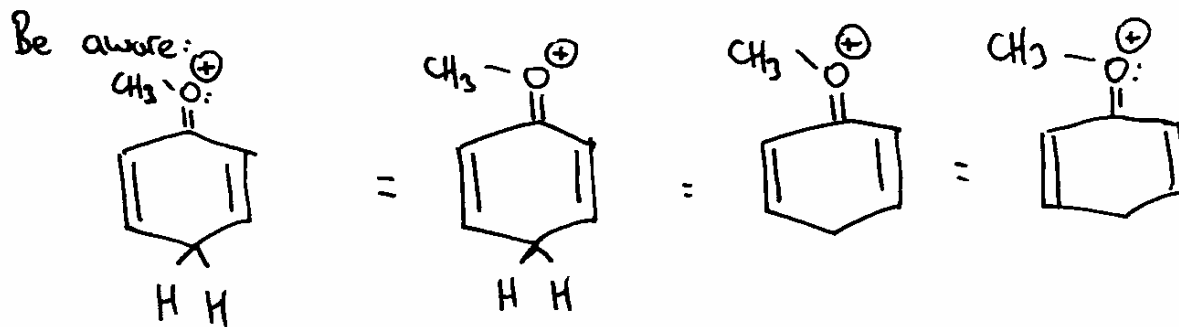
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Protonation of anisole in the *para* position.

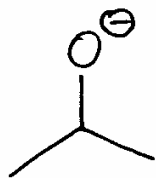


*Lone pairs and Hydrogens exist whether written or not.*



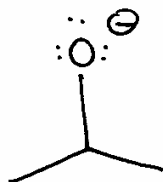
There are several ways to write anions:

E.g.



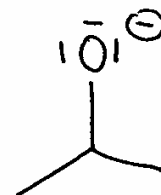
OK

=



Good

*sometimes*



Never

### (3) Geometry and Hybridization

Spatial arrangements of atoms are very important:

Isomers, including chirality

Shapes of molecules

Sterics

Can A physically react with B?

Geometry of atoms (direction of bonding regions) comes from hybridization.

#### Rules for hybridization

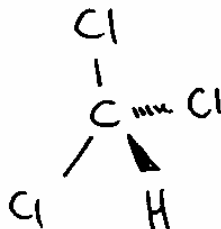
a) (# of  $\sigma$  bonds) + (# of lone pairs) = a number between 2 and 4 for C/N/O

Can be higher for 3<sup>rd</sup> row elements.

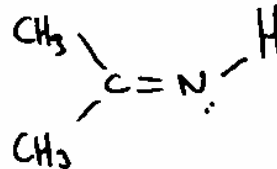
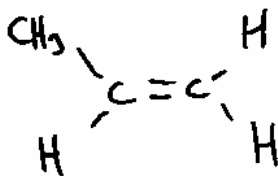
(Notice it says SIGMA bonds, and lone PAIRS)

**(# of  $\sigma$  bonds) + (# of lone pairs)**

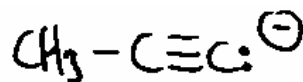
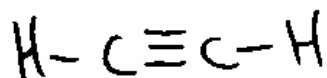
# = 4  $\rightarrow$   $sp^3$  hybridization = 4x  $sp^3$  hybrid orbitals, tetrahedron,  $109.5^\circ$  bond angles



# = 3  $\rightarrow$   $sp^2$  hybridization = 3x  $sp^2$  hybrid orbitals and 1x p orbital, trigonal planar,  $120^\circ$  bond angles, p orbital is perpendicular to the bonding plane.



# = 2  $\rightarrow$   $sp$  hybridization = 2x  $sp$  hybrid orbitals and 2x p orbitals, linear,  $180^\circ$  bond angles, p orbitals perpendicular to bonding region and each other.

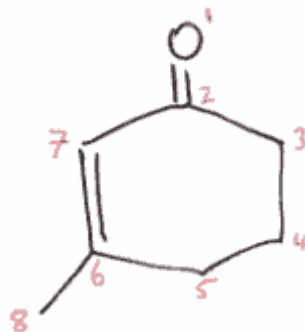


So for this molecule:

C-8, 5, 4, 3 are  $sp^3$

C-6, 7, 2 are  $sp^2$

O is  $sp^2$



This means atoms 1, 2, 3, 5, 6, 7 and 8 must lie in the same plane.

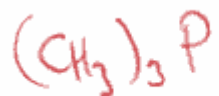
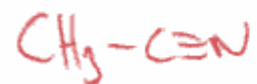
*Be aware that this is all in an effort to achieve the lowest electron arrangement for a given species.*

*Normally this is achieved by spreading out the electron pairs as far as possible to minimize e-/e- repulsions.*

*But sometimes the benefit of conjugation (esp. aromaticity) favors certain electrons being placed into unhybridized p orbitals. (e.g.  $sp^2$  oxygen in furan).*

## PROBLEMS

Predict Hybridization & Geometry for:



#### (4) Electronegativities and Dipoles

There are no gay reactions in chemistry.

Negative reacts with positive.

Nucleophile reacts with Electrophile.

Electrons react with a (partially) positive atom.

Neutral molecules can have sites of partial positive charge.

These arise from unequal sharing of electrons

= charge separation = dipoles.

Unequal sharing of electrons occurs in bonding of atoms with different electronegativities.

ELECTRONEGATIVITY = ability of an atom to bear negative charge effectively  
or = ability to pull electron density towards itself.

The higher the electronegativity, the more electron attracting the atom.

In general, electronegativity increases L to R and Down to Up in the Periodic table.

Some values from Pauling (and Sanderson).

<b>H</b>	<b>B</b>	<b>C</b>	<b>N</b>	<b>O</b>	<b>F</b>
2.1	2.0	2.5	3.0	3.5	4.0
(2.5	2.2	2.8	3.2	3.7	4.0)
	<b>Al</b>	<b>Si</b>	<b>P</b>	<b>S</b>	<b>Cl</b>
	1.5	1.8	2.1	2.5	3.0
	(1.7	2.1	2.5	3.9	3.5)
					<b>Br</b>
					2.8
					(3.2)
					<b>I</b>
					2.5
					(2.8)

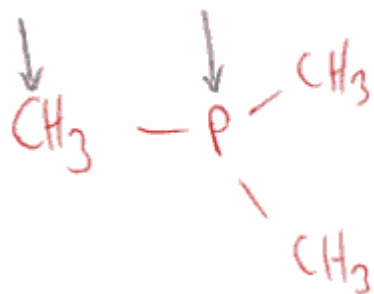
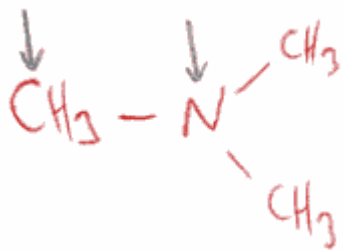
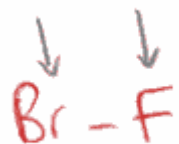
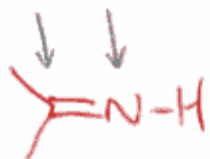
The more electronegative element takes on the partial negative charge.



More polarizable electrons are more easily attracted, hence C=O has a larger dipole than C-O.

## PROBLEMS

Predict the bond polarities of:



## (5) Resonance Structures

Lewis structures are good because they are simple, and allow electron counting.

They are however, sometimes, inaccurate in describing 'real' electron distribution.

Some species cannot be accurately represented by a single Lewis structure.

Sometimes we can use a combination of several Lewis structures to 'approximate' a species.

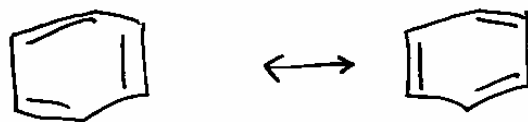
These Lewis structures can only differ in their location of electrons.

Such structures are called **RESONANCE STRUCTURES**.

They are an aid to describing 'delocalization' of electrons – which is a very common and important phenomenon in organic chemistry.

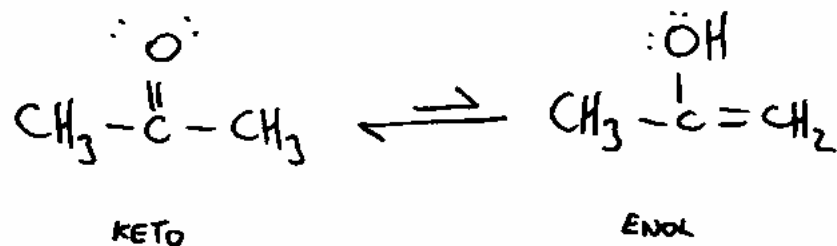
The 'real' bonding is a weighted average of the different resonance structures.

Resonance structures are indicated by a double headed arrow.



### Arrow types

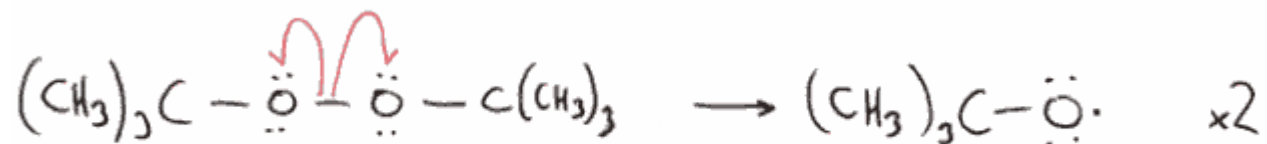
Two straight half headed arrows means EQUILIBRIUM



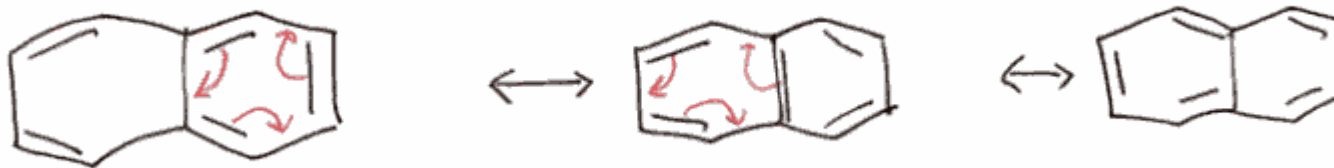
Curly (Curved) arrows means MOVEMENT OF TWO ELECTRONS.



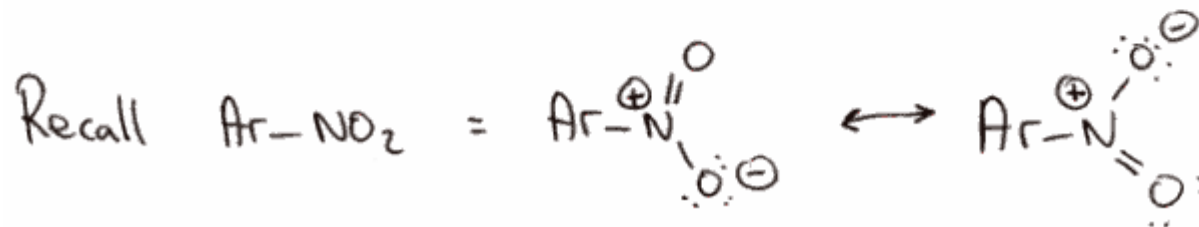
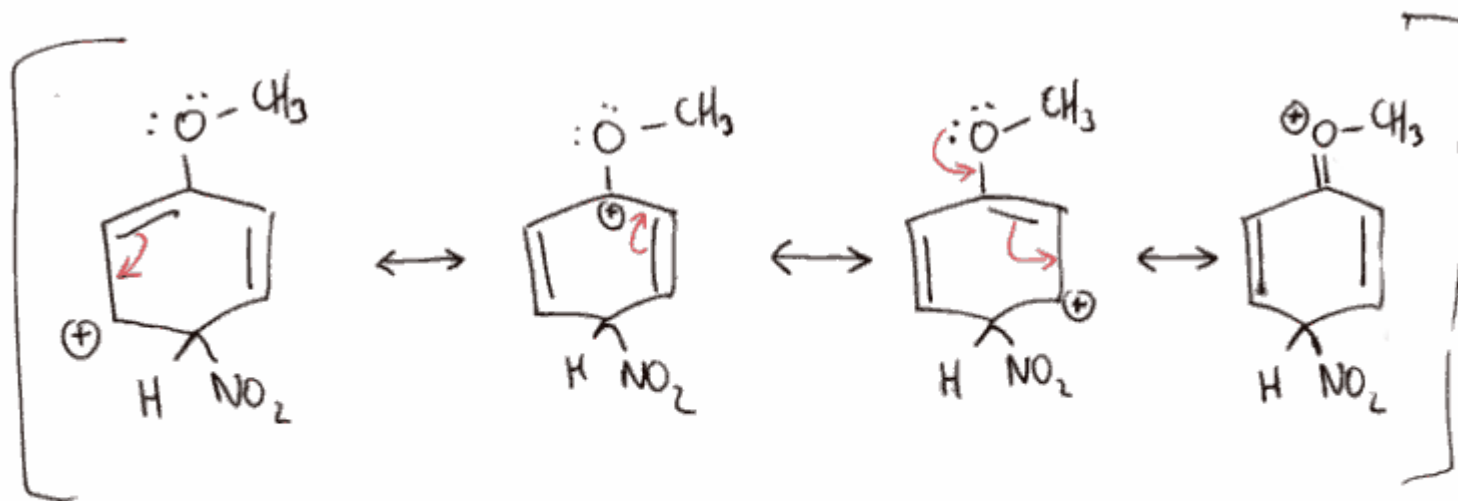
A curly (curved) half headed (single barb, fish hook) arrow means MOVEMENT OF A SINGLE ELECTRON.



For Naphthalene:

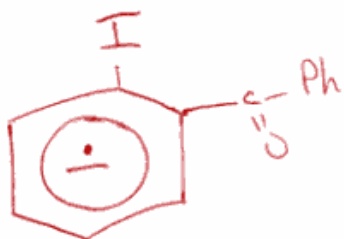
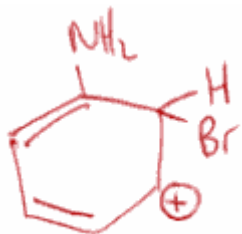
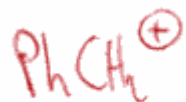
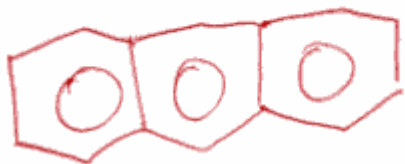


For the nitration of anisole at the para position:



# PROBLEMS

Draw resonance structures for:



## Another PROBLEM

Para-dinitrobenzene = "radical trap" used to inhibit free radical reactions.

Why is it so good at 'picking up' an electron?

## Rules For Resonance (*Species that differ only in electron distribution*)

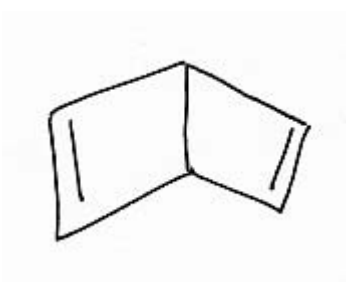
a) All the delocalization occurs with lone pairs and  $\pi$  systems.

(As with all **conjugation**, the lone pair must be put in a p orbital for delocalization).

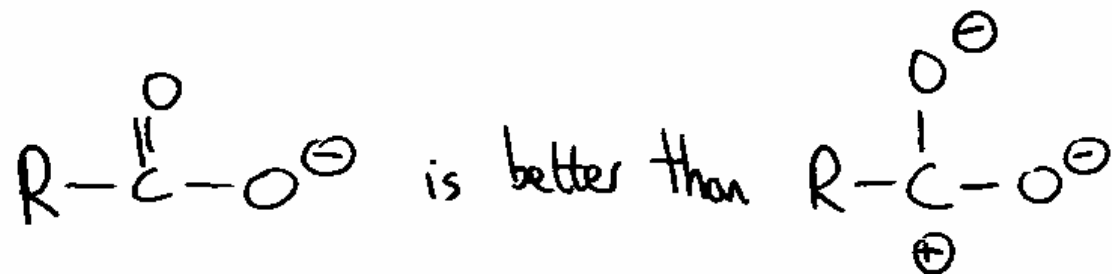
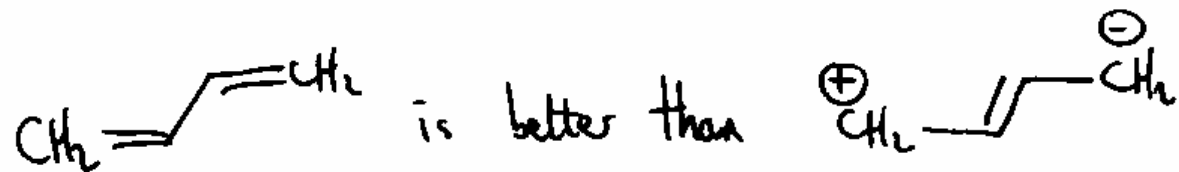
b) the total number of electrons must be the same.

c) must have identical geometries.

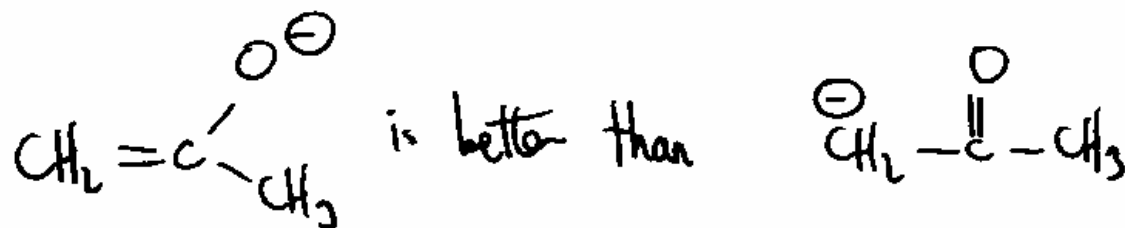
(Dewar Benzene is not a resonance structure of benzene).



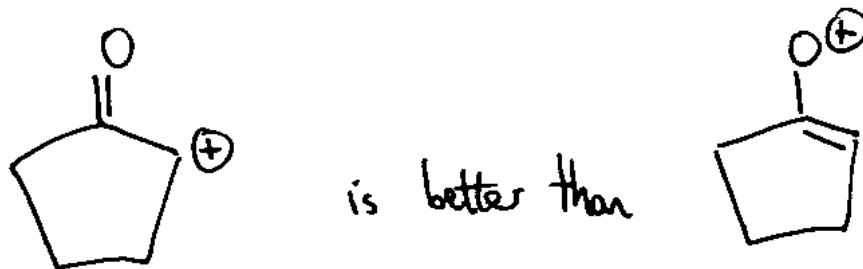
d) Charge separation → higher energy (worse / less significant contributor).



e) Negative charge on more electronegative elements is lower energy (good / more significant contributor).



And vice versa...



## PROBLEM

Write two more resonance structures for.



Which is the most stable & why?

## Another PROBLEM

What about for?



## Yet More PROBLEMS

Write good Lewis structures for the following & any significant resonance forms.



## (6) Aromaticity and Antiaromaticity

### a) Carbocycles.

Certain planar, cyclic conjugated rings show unusual enhanced stability far beyond that predicted from the benefit of conjugation.

This is AROMATICITY.

Huckel says for cyclic, planar systems that have available overlapping p orbitals at every position in the ring:

$(4N+2)$   $\pi$  electron systems are AROMATIC

$(4N)$   $\pi$  electron systems are ANTIAROMATIC.



3 membered

$2\pi e^-$



6

$6\pi$



5

$6\pi$

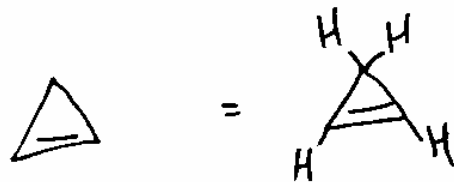


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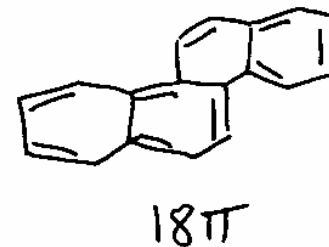
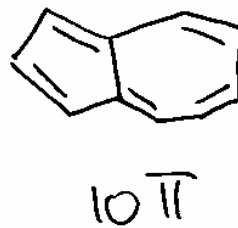
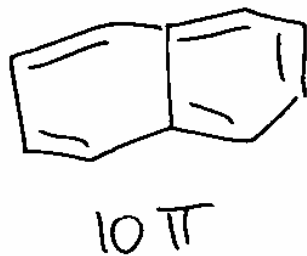
$6\pi$

Special attention should be paid with charges, and with available p orbitals at every position.

E.g. Non-Aromatic



Fused Ring Systems



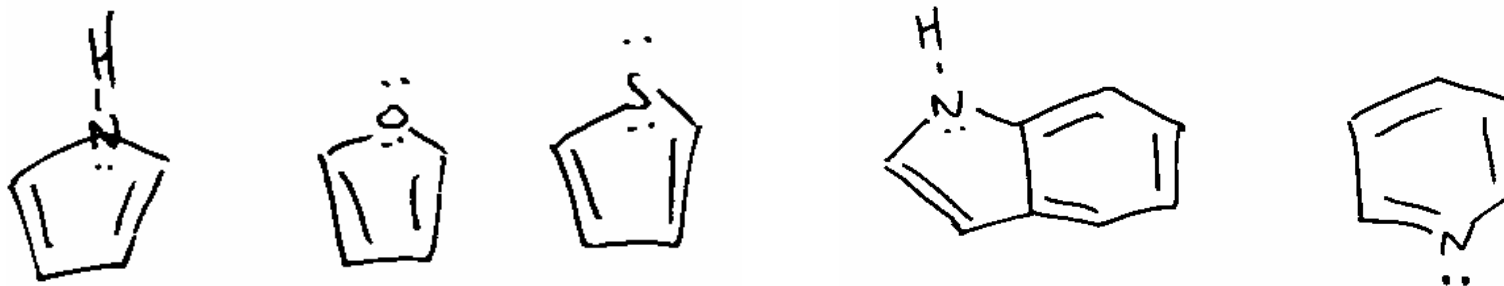
Count the 'outer'  $\pi$  electrons.

## b) Aromatic Heterocycles

Often a lone pair on a heteroatom can contribute to aromaticity.

Be aware that some systems (e.g. Py) are aromatic without the N lp being involved.

Hybridization of the heteroatom depends on the electrons supplied to the aromatic system. E.g. furan O is  $sp^2$ .



A lone pair's role in aromaticity is reflected in reactivity.

E.g. basicity of pyrrole vs pyridine.

basicity of aniline vs cyclohexamine

### c) Antiaromaticity

Antiaromatic compounds are highly unstable, and generally cannot be formed.

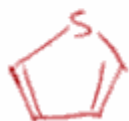


Molecules will try and avoid antiaromatic situations.



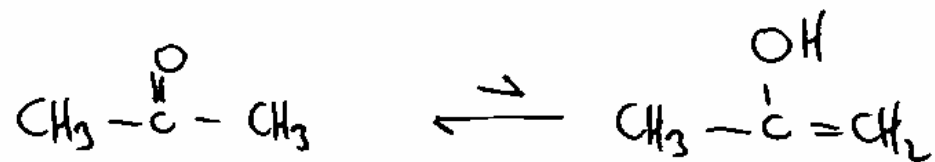
## PROBLEMS

Aromatic, antiaromatic or non-aromatic?

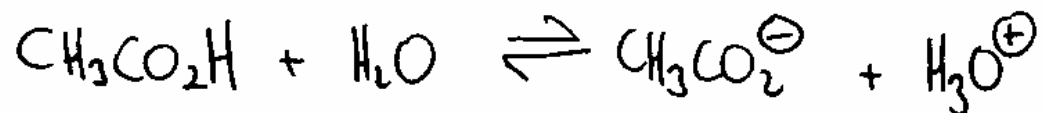


## 7) Tautomers and Equilibrium

TAUTOMERS are isomers that differ in the location of readily exchangeable atoms. (Usually an acidic hydrogen, e.g. Keto – Enol tautomerization)



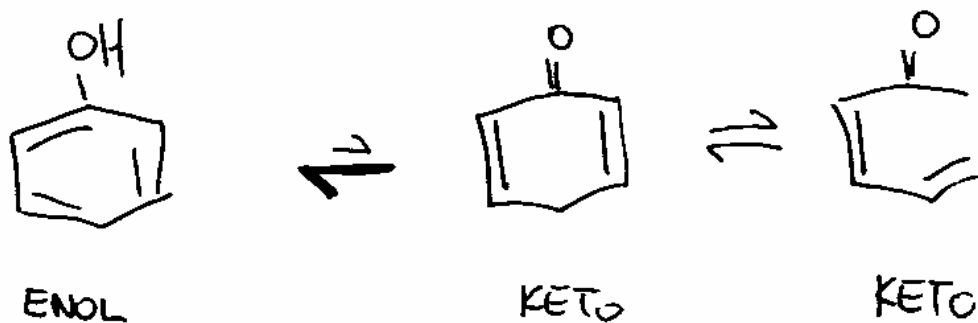
EQUILIBRIUM exists when there are equal rates for forward and reverse reactions.



The position of equilibrium (once equilibrium has been reached) is described by the equilibrium constant, K.

Equilibrium is designated by half headed arrows in both the forward and reverse reaction directions.

If equilibrium greatly favors one side, the corresponding arrow is written larger.

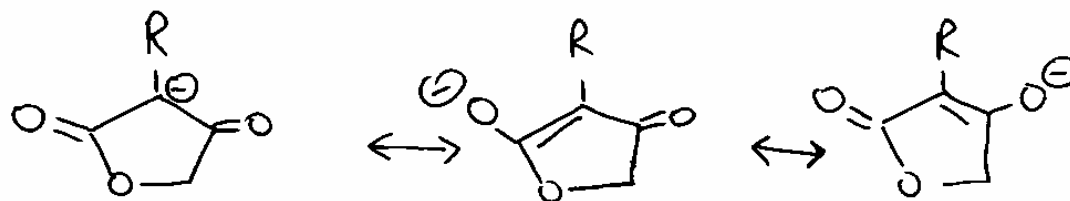
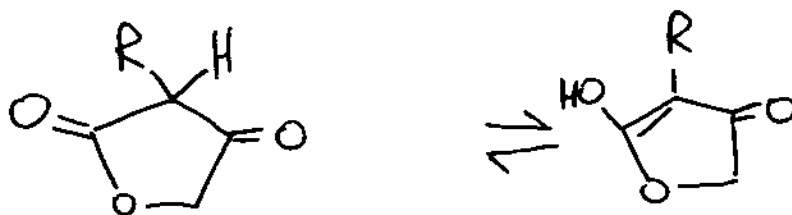


**Make sure you know the differences between:**

equilibrium and resonance

AND

resonance structures and tautomers.



## PROBLEMS

Write tautomers of the following compounds.



MORE PROBLEMS

Different, Tautomers, resonance or same?



&



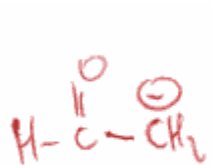
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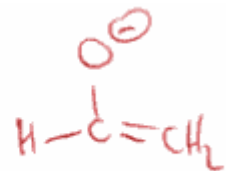
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## EVEN MORE PROBLEMS

Is this 'correct'?



If "NO", what should be changed?

## 8) Acidity and Basicity

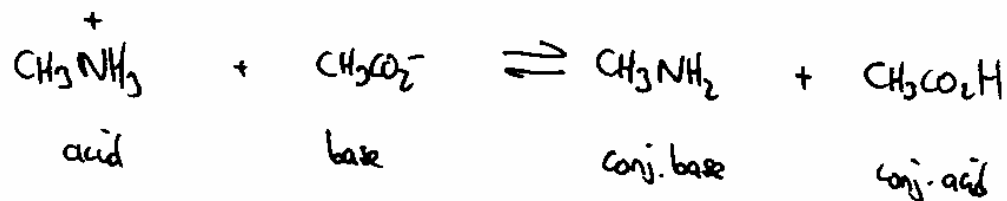
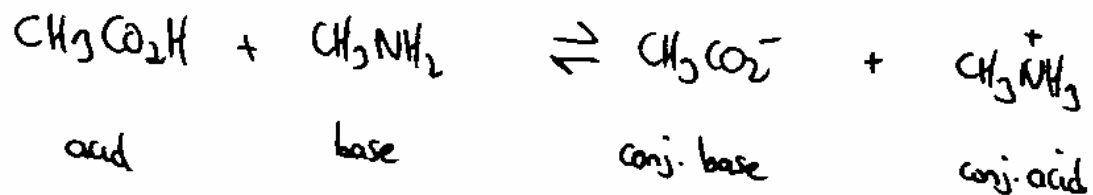
Bronsted Acid = H<sup>+</sup> donor

Bronsted Base = H<sup>+</sup> acceptor

Lewis Acid = Electron PAIR acceptor

Lewis Base = Electron Pair donor

The acidic species after acting as an acid generates a corresponding CONJUGATE Base.



A strong acid dictates a corresponding weak conjugate base.

Normally we talk of acidity in terms of  $pK_a$  values.

For general comprehension,  $pK_a$  can be thought of as (*IS !!!*) the pH of a solution where the species is 50% ionized.

The lower the  $pK_a$ , the more acidic the proton bearing species is.

There are plenty of tables out there with this kind of data.

Group	Conjugate acid <sup>a</sup>	Conjugate base <sup>a</sup>	Typical pK <sub>a</sub>
Halogen acids	HX (X=I, Br, Cl)	X <sup>-</sup>	* -10 to -8
Nitrile	$\text{R}-\overset{\ominus}{\text{C}}\equiv\text{N}-\text{H}$	$\text{RC}\equiv\text{N}$	-10
Aldehyde, ketone	$\text{R}-\overset{\ominus}{\text{C}}(\text{O}=\text{H})-\text{R}'$	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	-7
Thiol, sulfide	$\text{R}-\overset{\ominus}{\text{S}}(\text{H})-\text{R}'$	$\text{R}-\text{S}-\text{R}'$	-7 to -6
Phenol, aromatic ether	$\text{C}_6\text{H}_5-\overset{\oplus}{\text{O}}(\text{H})-\text{R}'$	$\text{C}_6\text{H}_5-\text{O}-\text{R}$	-7 to -6
Ester, acid	$\text{R}-\overset{\oplus}{\text{C}}(\text{O}=\text{H})-\text{OR}'$	$\text{R}-\overset{\oplus}{\text{C}}(\text{O}=\text{H})-\text{OR}'$	-7 to -6
Sulfonic acid <sup>b,c</sup>	$\text{R}-\overset{\oplus}{\text{S}}(\text{O})_2-\text{O}-\text{H}$	$\text{R}-\overset{\oplus}{\text{S}}(\text{O})_2-\text{O}^-$	-5 to -2
Alcohol, ether	$\text{R}-\overset{\oplus}{\text{O}}(\text{H})-\text{R}'$	$\text{R}-\text{O}-\text{R}'$	-3 to -2
H <sub>2</sub> O	$\text{H}_2\text{O}^{\oplus}-\text{H}$	$\text{H}_2\text{O}$	-1.7
Amide	$\text{R}-\overset{\oplus}{\text{C}}(\text{O}=\text{H})-\text{NR}_2$	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NR}_2$	-1
Carboxylic acid <sup>b,c</sup>	$\text{R}-\overset{\oplus}{\text{C}}(\text{O})_2-\text{O}-\text{H}$	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-$	3-5
Aromatic amine	$\text{C}_6\text{H}_5-\overset{\oplus}{\text{N}}(\text{H})-\text{R}'_2$	$\text{C}_6\text{H}_5-\text{NR}'_2$ <sup>d</sup>	4-5
Pyridine	$\text{C}_5\text{H}_5-\overset{\oplus}{\text{N}}(\text{H})$	$\text{C}_5\text{H}_5-\text{N}$ <sup>d</sup>	5
Alkylamine	$\text{R}-\overset{\oplus}{\text{N}}(\text{H})-\text{R}'_2$	$\text{R}-\text{N}-\text{R}'_2$ <sup>d</sup>	9-11
Phenol <sup>e</sup>	$\text{C}_6\text{H}_5-\overset{\oplus}{\text{O}}(\text{H})$	$\text{C}_6\text{H}_5-\text{O}^-$	9-11
Thiol <sup>e</sup>	$\text{R}-\overset{\oplus}{\text{S}}(\text{H})$	$\text{R}-\text{S}^-$	9-11

<i>Group</i>	<i>Conjugate acid<sup>a</sup></i>	<i>Conjugate base<sup>a</sup></i>	<i>Typical pK<sub>a</sub></i>
Sulfonamide <sup>c</sup>	$\begin{array}{c} \text{O} \quad \text{H} \\ \parallel \quad   \\ \text{R}-\text{S}-\text{N}-\text{H} \\ \parallel \\ \text{O} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{S}-\text{N}-\text{H} \\ \parallel \\ \text{O} \end{array}$	10
Nitro <sup>b</sup>	$\begin{array}{c} \text{H} \\   \\ \text{R}-\text{C}-\text{H}-\text{NO}_2 \end{array}$	$\text{R}-\text{C}-\text{H}-\text{NO}_2$	10
Amide	$\begin{array}{c} \text{O} \quad \text{H} \\ \parallel \quad   \\ \text{R}-\text{C}-\text{N}-\text{R} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{N}-\text{R} \end{array}$	15-17
Alcohol	$\text{R}-\text{O}-\text{H}$	$\text{R}-\text{O}^-$	* 15-19
Aldehyde, <b>ketone</b>	$\begin{array}{c} \text{H} \quad \text{O} \\   \quad \parallel \\ \text{R}-\text{C}-\text{C}-\text{R}' \\   \\ \text{R}' \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}'-\text{C}-\text{C}-\text{R}' \\   \\ \text{R} \end{array}$	17-20
Ester	$\begin{array}{c} \text{H} \quad \text{O} \\   \quad \parallel \\ \text{R}-\text{C}-\text{C}-\text{OR} \\   \\ \text{R}' \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{C}-\text{OR} \\   \\ \text{R}' \end{array}$	20-25
Nitrile	$\begin{array}{c} \text{H} \\   \\ \text{R}-\text{C}-\text{C}\equiv\text{N} \\   \\ \text{R}' \end{array}$	$\begin{array}{c} \text{R}-\text{C}-\text{C}\equiv\text{N} \\   \\ \text{R}' \end{array}$	25
Alkyne	$\text{R}-\text{C}\equiv\text{C}-\text{H}$	$\text{R}-\text{C}\equiv\text{C}^-$	25
Amine	$\text{R}_2\text{N}-\text{H}$	$\text{R}_2\text{N}^-$	35-40
Alkane	$\text{R}_3\text{C}-\text{H}$	$\text{R}_3\text{C}^-$	50-60

These  $pK_a$  values allow us to figure out what will protonate what.

Moreover, these values allow us to calculate the equilibrium constant,  $K$ , for an acid-base reaction.

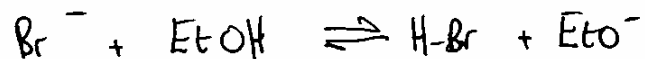
Will a reaction go at all, a little bit, a lot, or to completion?

$K_{\text{reaction}} < 1$  means more SM

$K_{\text{reaction}} > 1$  means more Pdt

$K_{\text{reaction}} = 1$  means SM = Pdt

So we can predict the result of the following reaction of **bromide** in **ethanol**:



$$K_a = \frac{[\text{HBr}][\text{EtO}^-]}{[\text{Br}^-][\text{EtOH}]}$$

$$\text{For EtOH: } K_{a_{\text{EtOH}}} = 10^{-15.9} = \frac{[\text{EtO}^-][\text{H}^+]}{[\text{EtOH}]}$$

$$\text{For H-Br: } K_{a_{\text{HBr}}} = 10^9 = \frac{[\text{Br}^-][\text{H}^+]}{[\text{H-Br}]}$$

$$\frac{K_{a_{\text{EtOH}}}}{K_{a_{\text{HBr}}}} = \frac{[\text{EtO}^-][\text{H}^+][\text{H-Br}]}{[\text{EtOH}][\text{Br}^-][\text{H}^+]} = \frac{[\text{EtO}^-][\text{H-Br}]}{[\text{EtOH}][\text{Br}^-]}$$

$$\text{So } K_a = \frac{10^{-15.9}}{10^9} = 10^{-24.9}$$

= v.v.v. small

$\Rightarrow$   $\text{Br}^-$  does NOT react with EtOH

## PROBLEM

Which is the stronger base?

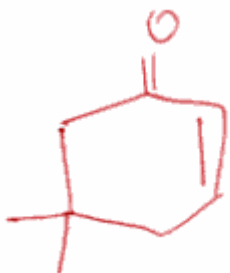


or



## More PROBLEMS

Which proton is most likely to be removed with base?



## 9) Nucleophiles and Electrophiles

A Nucleophile is a Lewis base, and it seeks out Electrophiles (Lewis Acid).

Basically electron rich reacts with electron deficient.

Reactivity in reactions usually depends on the nature of the nucleophile, the substrate and the solvent.

### a) Nucleophilicity

The nucleophilicity is the ability of a Nuc to react at an electron poor centre.

**Nucleophilicity  $\neq$  Basicity**

Nucleophilicity deals with RATES of reaction.

Nucleophilicities can be scaled using the Swain-Scott equation.

$$\log \frac{k}{k_0} = s n$$

$k$  = rate constant for reac<sup>n</sup> with the nucleophile

$k_0$  = rate constant for reac<sup>n</sup> with H<sub>2</sub>O as nuc.

$s = 1$  (for CH<sub>3</sub>-Br as substrate)

$n$  = relative nucleophilicity.

This uses the relative reactivities of Nuc and water with methyl bromide at 25°C. The larger the value of  $n$ , the greater the nucleophilicity.

Nucleophile	$n$	Nucleophile	$n$
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	6.4	pyridine	3.6
SH <sup>-</sup>	5.1	Br <sup>-</sup>	3.5
CN <sup>-</sup>	5.1	PhO <sup>-</sup>	3.5
SO <sub>3</sub> <sup>2-</sup>	5.1	CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	2.7
I <sup>-</sup>	5.0	Cl <sup>-</sup>	2.7
PhNH <sub>2</sub>	4.5	HOCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	2.5
SCN <sup>-</sup>	4.4	SO <sub>4</sub> <sup>2-</sup>	2.5
OH <sup>-</sup>	4.2	ClCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	2.2
(NH <sub>2</sub> ) <sub>2</sub> CS	4.1	F <sup>-</sup>	2.0
N <sub>3</sub> <sup>-</sup>	4.0	NO <sub>3</sub> <sup>-</sup>	1.0
HCO <sub>3</sub> <sup>-</sup>	3.8	H <sub>2</sub> O	0.0
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	3.9		

<sup>a</sup>From Wells, P. R. *Chem. Rev.* 1963, 63, 171-219.

## b) Substrate

The substrate (electrophilic species) influences the rate of reaction with a given Nuc. This is reflected in the  $s$  values.

E.g.	CH <sub>3</sub> -Br	$s = 1$	
	Cl-CH <sub>2</sub> CO <sub>2</sub> Et	$s = 1$	reacts at same rate
	I-CH <sub>2</sub> CO <sub>2</sub> Et	$s = 1.33$	reacts faster
	PhCH <sub>2</sub> -Cl	$s = 0.87$	reacts slower

## c) Solvent

Nucleophilicity is very solvent dependant.

Polar, aprotic solvents optimize nucleophilicity since they do not solvate the nucleophile making it more available attack the electrophilic centre.

Ritchie came up with an  $N_+$  value for relative nucleophilicity in different solvents.  
Higher  $N_+$  = Faster Reaction.

$$\log \frac{k_n}{k_{H_2O}} = N_+$$

$k_n$  = the rate of Nuc in a given solvent

$k_{H_2O}$  = rate of water as Nuc in water

<i>Nucleophile (solvent)</i>	$N_+$	<i>Nucleophile (solvent)</i>	$N_+$
H <sub>2</sub> O (H <sub>2</sub> O)	0.0	PhS <sup>-</sup> (CH <sub>3</sub> OH)	10.51
CH <sub>3</sub> OH (CH <sub>3</sub> OH)	1.18	PhS <sup>-</sup> [(CH <sub>3</sub> ) <sub>2</sub> SO]	12.83
CN <sup>-</sup> (H <sub>2</sub> O)	3.67	N <sub>3</sub> <sup>-</sup> (H <sub>2</sub> O)	7.6
CN <sup>-</sup> (CH <sub>3</sub> OH)	5.94	N <sub>3</sub> <sup>-</sup> (CH <sub>3</sub> OH)	8.85
CN <sup>-</sup> [(CH <sub>3</sub> ) <sub>2</sub> SO]	8.60	N <sub>3</sub> <sup>-</sup> [(CH <sub>3</sub> ) <sub>2</sub> SO]	10.07
CN <sup>-</sup> [(CH <sub>3</sub> ) <sub>2</sub> NCHO]	9.33		

<sup>a</sup>From Ritchie, C. D. *J. Am. Chem. Soc.* **1975**, *97*, 1170–1179.

## LAST PROBLEMS in CH 1

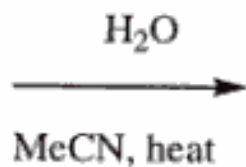
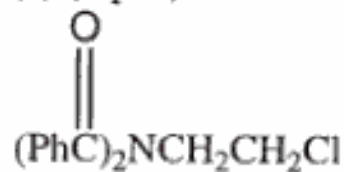
Indicate the Electrophilic & Nucleophilic sites in these reactions.



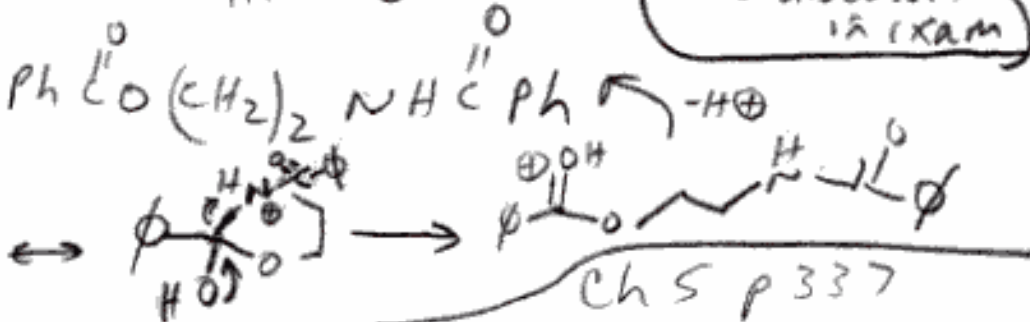
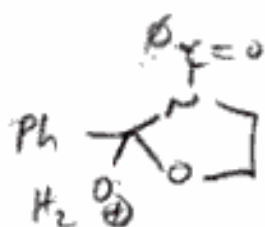
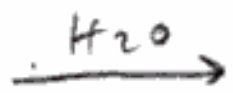
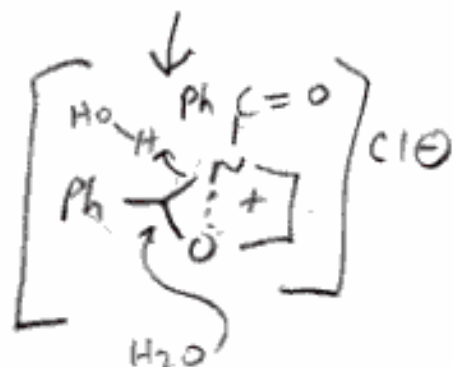
Circle all the errors on the following page of bad chemistry...

10. Draw a reasonable mechanism for the following reactions. Ch 5 p 338 prob 3k

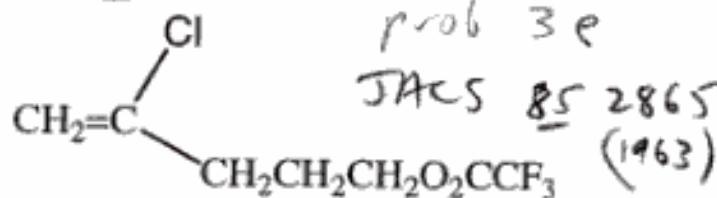
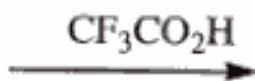
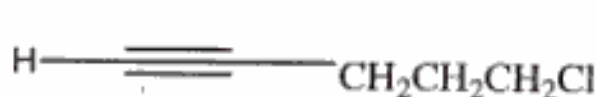
(a) (5 pts.)



J.O.C. 38 422 (1973)

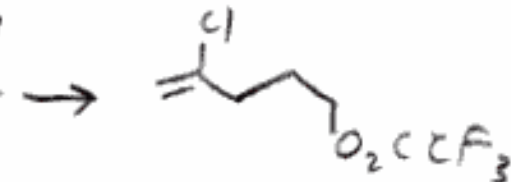
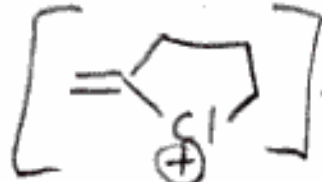
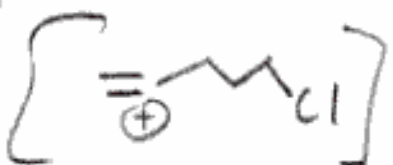
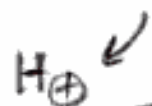


(b) (5 pts.)



Ch 5 p 337  
prob 3e

JACS 85 2865  
(1963)



11. Predict whether normal or inverse isotope effects will be observed for each reaction below. Explain. Indicate any reactions in which you would expect  $k_H/k_D > 2$ . The isotopically substituted hydrogens are marked with asterisks.