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 '92 files- Chapter One

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 answers

Solomons (1978)

CHAPTER ONE

Question:

1. Draw the structure for 2-methylbutane and then label the various carbons according to class (primary, secondary, tertiary).
-

Question:

2. Label the following as ionic or covalent and then indicate if there is a permanent dipole or not: HCl, CH₄, the CH₃ of CH₃OH, HF
-

Question:

3. Draw structures (show both bonds and lone pairs) for H₂SO₄, HNO₃, CH₃OH, C₂H₆, CH₂Cl₂.
-

Question:

4. Explain the geometry of water.
-

Question:

5. A compound with the empirical formula C₁H₁ has a molecular weight of 78 g/mol. What is the molecular formula?
-

Question:

6. How many molecular orbitals are there for ethanol?
-

Question:

7. Draw and explain the Morse Potential Energy diagram for the hydrogen molecule.

Question:

8. **Question missing here.**

Question:

9. **Why doesn't He₂ exist?**

Question:

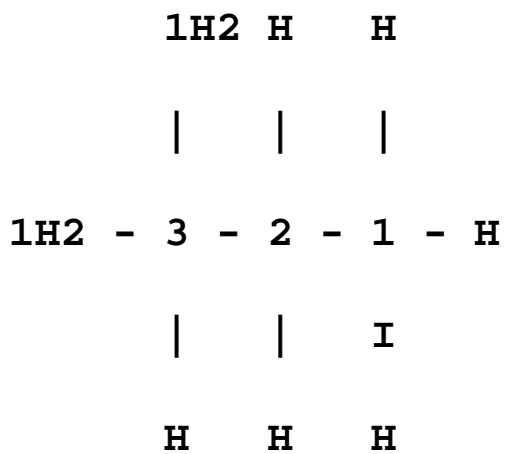
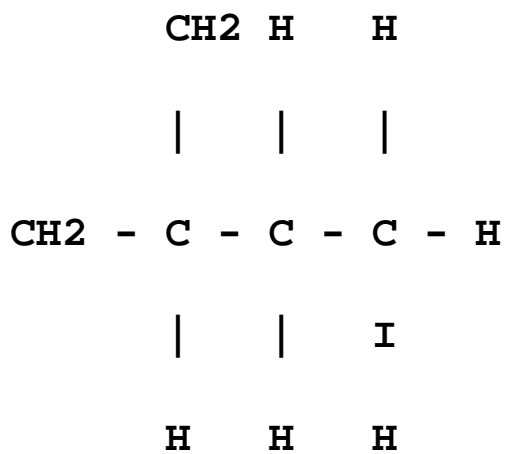
10. **Draw three canonical structures (resonance structures) for the hydrogen molecule. Rank the three canonical structures and also the actual hydrogen structure on a relative scale.**

Question:

11. **Which of the following three canonical structures is highest in energy? (HCl, H⁺Cl⁻, H⁻Cl⁺)**

Question:

12. **Are H-O-C(triple bond)N and H-N=C=O resonance structures?**

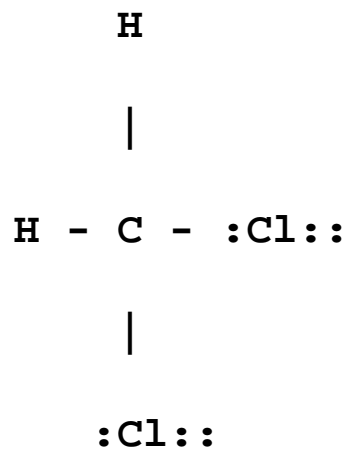
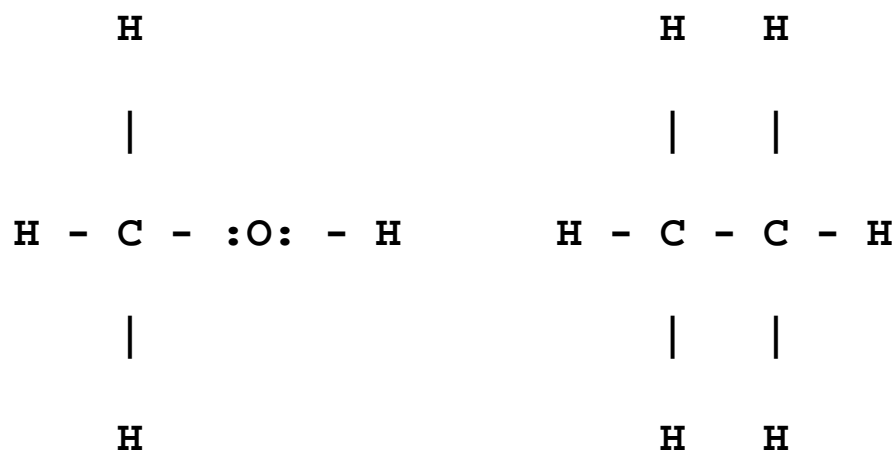
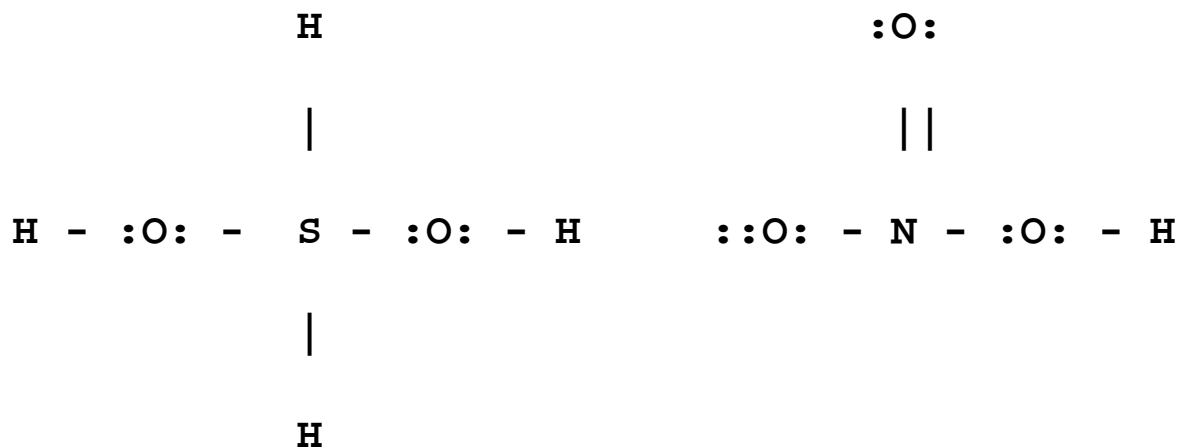


1= primary

2= primary

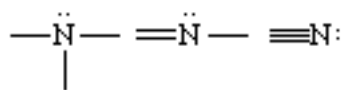
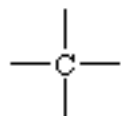
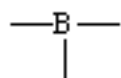
3= tertiary

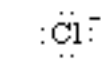
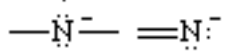
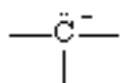
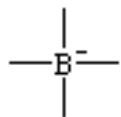
1. **HCl- ionic; permanent dipole moment**
2. **CH₄- covalent; no permanent dipole moment**
3. **CH₃- covalent; permanent dipole moment**
4. **HF- ionic; permanent dipole moment**

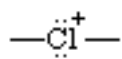
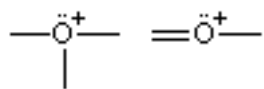
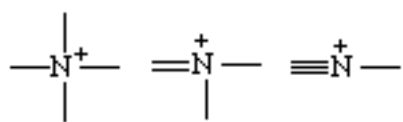
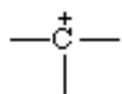


Oxygen must have two lone pairs and two bonds to have a neutral (zero)

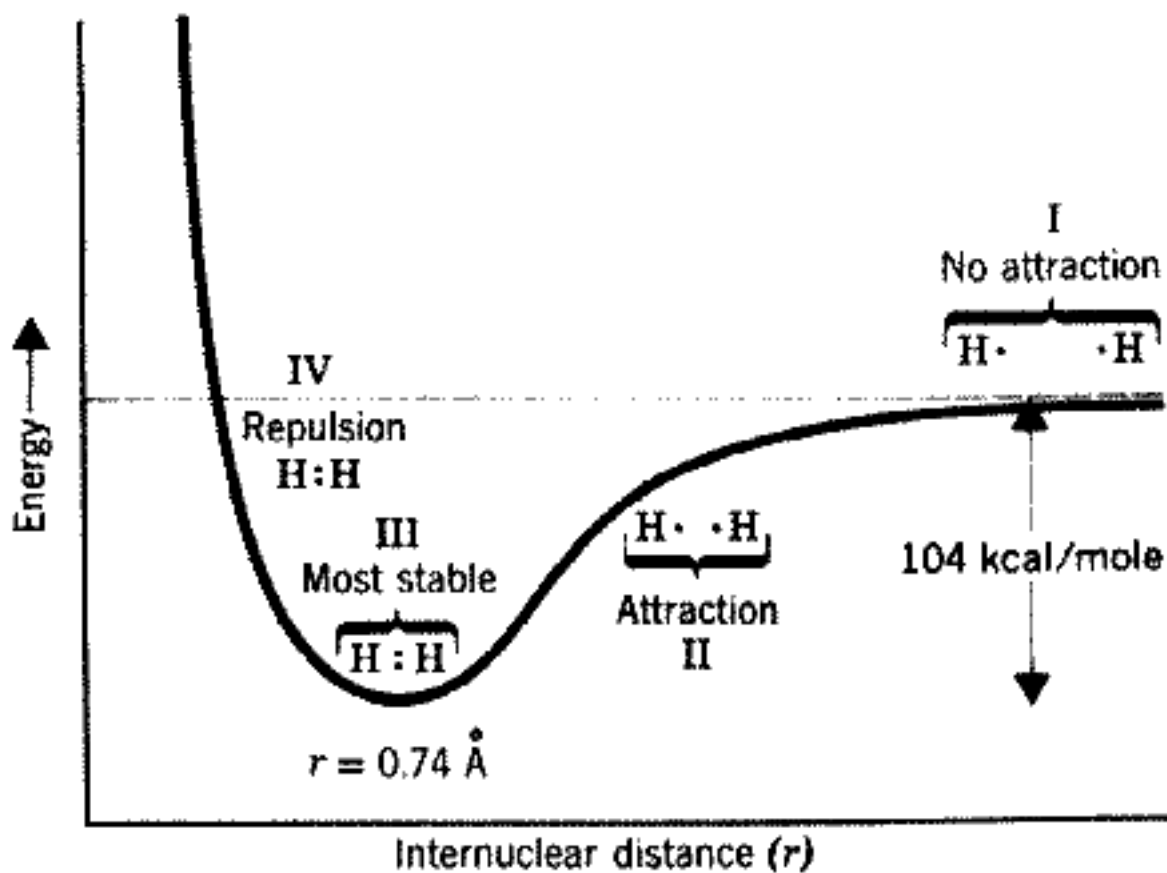
formal charge. In nitric acid, the oxygen with three lone pairs and one bond has a **-1 formal charge**, and the nitrogen with the four bonds and no lone pairs has a **+1 formal charge** because nitrogen would rather have three bonds and one lone pair.





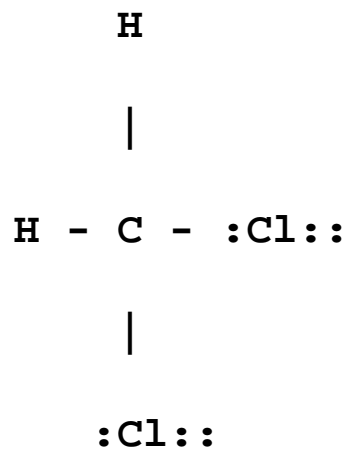
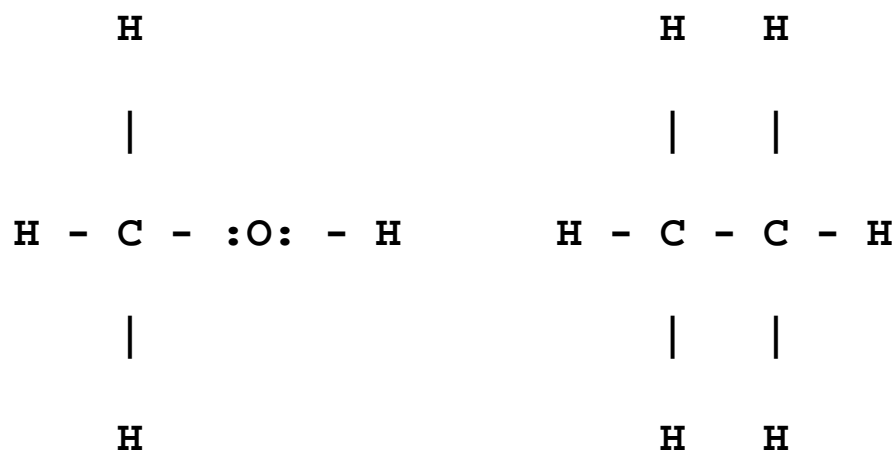
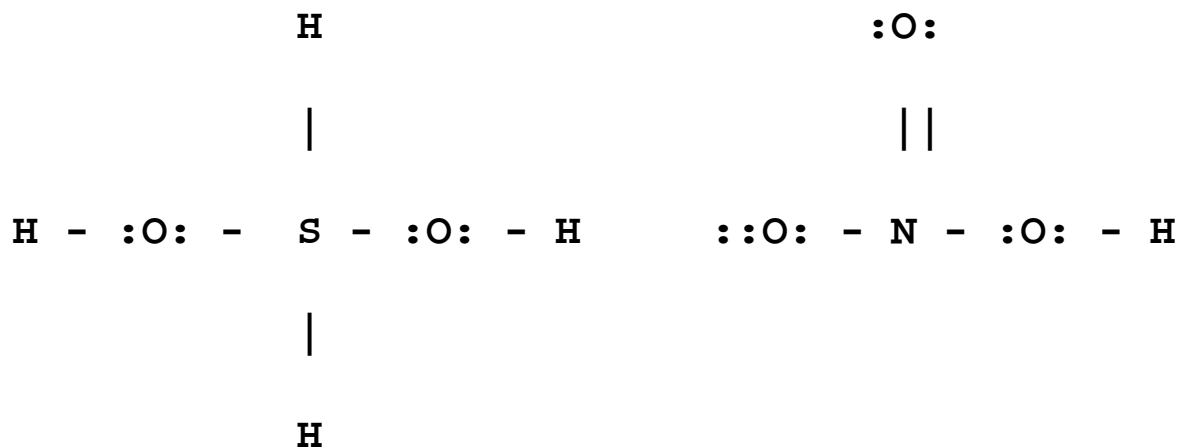


ethanol has nine atoms, and the nine atomic orbitals come together to form nine molecular orbitals (yes, there is a pattern here--a molecule with six atoms has six molecular orbitals.)



As the distance between the hydrogen nuclei approaches zero, the energy of the system approaches infinity.

The orbital into which the third and fourth electrons would go is antibonding, so the placement of two electrons in the antibonding orbital is a disadvantage that would cancel out the advantage of having two electrons in a bonding orbital, and the two atoms would fall apart.



Oxygen must have two lone pairs and two bonds to have a neutral (zero)

formal charge. In nitric acid, the oxygen with three lone pairs and one bond has a **-1 formal charge**, and the nitrogen with the four bonds and no lone pairs has a **+1 formal charge** because nitrogen would rather have three bonds and one lone pair.

1. **H(+) $\text{H}(-)$ an ionic canonical structure**
 2. **H(-) $\text{H}(+)$ an ionic canonical structure**
 3. **H - H a covalent structure**
 4. **the actual hydrogen molecule, mostly 3, but with some 1 and 2.**
-
-

Both ionic structures, 1 and 2, are of the same energy and they are the highest in energy of all the above.

The covalent structure, 3, is lower in energy than the ionic canonical structures.

But the actual structure, 4, has the lowest energy of all.

H(-)Cl(+), because the positive charge is placed on chlorine, which is a very electronegative element.

No. Resonance structures can change the number of bonds between atoms, but you can't atoms around in ways that change which atom is bonded to which atom.

If $\text{H-N}=\text{C}=\text{O}$ was the real structure, another resonance structure could be $\text{N}^+\text{-N}(\text{triple})\text{C}=\text{O}^-$, which would put a +1 formal charge on the nitrogen, and a -1 formal charge on the oxygen. This would be acceptable since the overall charge is still zero, and the negative charge is being placed on the most electronegative atom, oxygen.

Solomons (1978)

Question:

1. Show eclipsed and staggered ethane using Newman projections.
-

Question:

2. Draw trans-1,2-dichloroethene.
-

Question:

3. Show the addition of HBr to 1-propene (it follows Markovnikov addition).
-

Question:

4. Name three catalysts that promote the addition of hydrogens to an alkene.
-

Question:

5. In the addition of chlorine to a double bond choose between room temperature or lots of heat. Is light needed, is it nonconsequential, or is it something to be avoided at all costs?
-

Question:

6. What conditions and solvent are necessary for the conversion of an alkyl halide to an alkene? (this doesn't mean that only one solvent will work--pick one mentioned in your book.)
-

Question:

7. What is the result of the oxidation of 2-propanol?
-

Question:

8. **Label the following as either oxidizing or reducing:**

Ag (subscript 2) O

LiAlH (subscript 4)

NaBH (subscript 4)

Question:

9. **What is produced from an alcohol/carboxylic acid condensation reaction?**

Question:

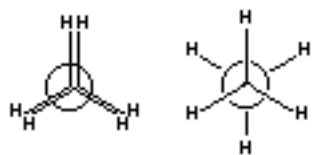
10. **How do you work backwards from ester to alcohol and carboxylic acid?**

Question:

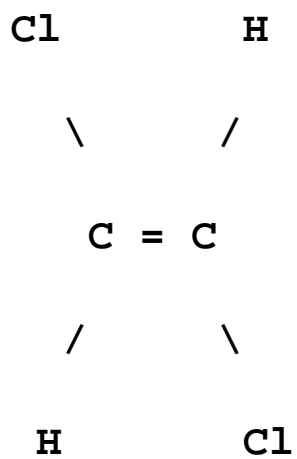
11. **Suggest a way to make an amide.**

Question:

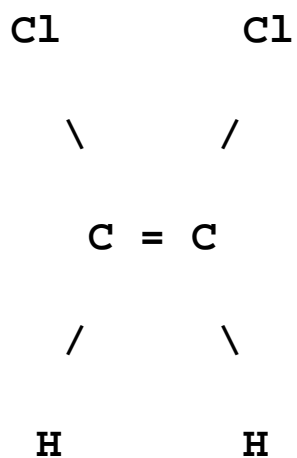
12. **Work backwards from the amide to the starting materials of the previous question.**

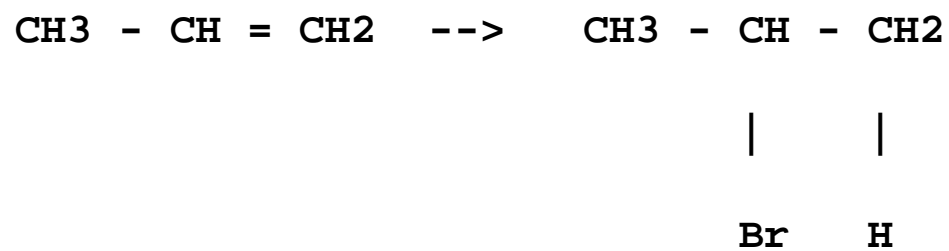


The Newman projection of ethane on the left is eclipsed, and the projection on the right is staggered.



If you had been asked for *cis*dichloroethene, you would have drawn





The bromine goes on the middle carbon, the carbon with fewer hydrogens on it to begin with.

Nickel- Ni; Platinum- Pt; Palladium- Pd

Room temperature.

Heat encourages the formation (and thereby, also the retention) of double bonds.

Light must be kept out too as it encourages substitution (light makes free radicals, which prefer substitution) and we said we wanted addition.

heat is needed;

use an alcohol for the solvent

a ketone

acetone

:O:

||

CH₃ - C - CH₃

1. **silver oxide- oxidizes**
2. **lithium aluminum hydride- reduces**
3. **sodium borohydride- reduces**

water and an ester

Use sodium hydroxide, water, and heat. This makes an alcohol and an acid salt. the addition of a mineral acid such as HCl to the acid salt converts the acid salt to a carboxylic acid with NaCl as the by-product.

add an amine to a carboxylic acid

add water and heat, followed by hydrochloric acid.

Solomons (1978) CHAPTER THREE

Question:

- Rank the following in order of decreasing acidity: ethane, ethene, ethanoic acid, ethanol, and water.
-

Question:

- What is the defining property of "Magic Acid", $\text{SbF}_5 \cdot \text{FSO}_3\text{H}$?
-

Question:

- Is boron trifluoride a lewis acid or a lewis base?
-

Question:

- Draw figures to represent sp^3 , sp^2 , and sp hybridization.
-

Question:

- Which has a lower boiling point: butane or 2- methylpropane?
-

Question:

- Heptane and water separate when placed in a beaker. Which is on the bottom? Why did they separate?
-

Question:

- Draw the potential energy diagram for butane and include Newman structures for the peaks and valleys.
-

Question:

- Discuss Van Der Waal forces in terms of separation distance and Van Der

Waal radii:

1. **separation distance exceeds the Van Der Waal radii**
 2. **separation distance is less than the Van Der Waal radii**
-

Question:

- **Draw the chair and boat conformations of cyclohexane.**
-

Question:

- **Prepare 2-methylheptane from pentyl chloride and 2- propanol.**
-

Question:

- **Prepare hexane using the Wurtz reaction.**
-

Question:

- **How do you replace the halogen of an alkyl halide with a hydrogen?**

MOST ACIDIC

- **ethanoic acid**
- **water**
- **ethanol**
- **ethene**
- **ethane**

LEAST ACIDIC

It is the strongest acid known, and it makes every other chemical behave to some degree, like a base

It makes it possible to observe some of the more stable carbocations by spectroscopy.

Lewis Acid

The term 'sp³' means the atom is connected to four other atoms using tetrahedral geometry

The term 'sp²' means the atom is connected to three other atoms

The term 'sp' means the atom is connected to two other atoms.

2-methylpropane; both have the same number of carbons but 2-methylpropane is branched.

Water is on the bottom (higher density.)

Because water is polar and heptane is nonpolar

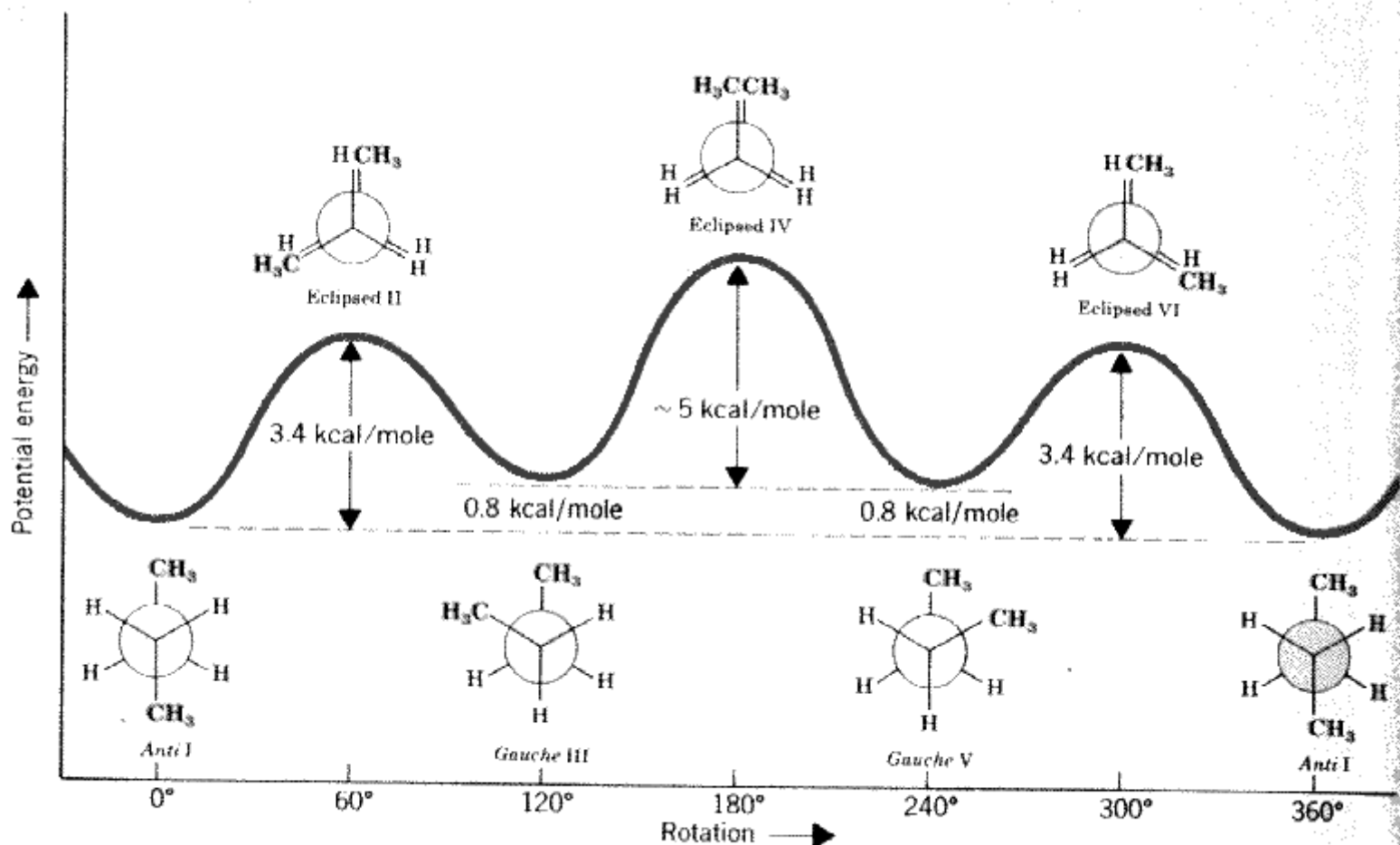


FIGURE 3.8 Energy changes that arise from rotation of the C-2—C-3 bond of butane.

1. **When the separation distance exceeds the Van der Waal radii, then the force is attractive.**
2. **When the separation distance is less than the Van der Waal radii, then the force is repulsive.**

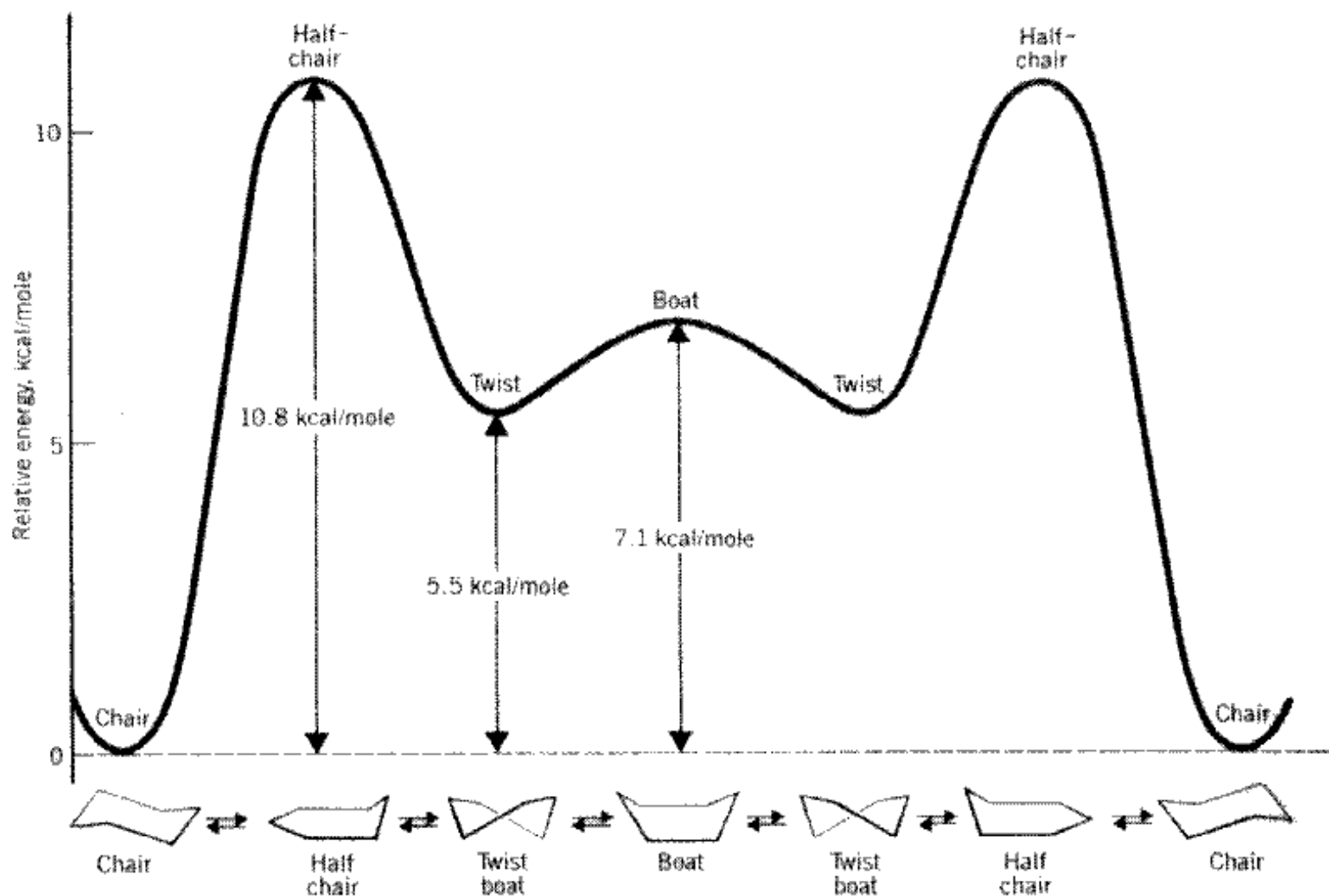


FIGURE 3.17 The relative energies of the various conformations of cyclohexane. The positions of maximum energy are conformations called half-chair conformations, in which the carbon atoms of one end of the ring have become coplanar.

Make the lithium dialkyl cuprate from 2-propanol and the alkyl halide from 1-halopentane (halo could be chloro or bromo.)

1-propyl halide plus sodium

Add acid and zinc, and be sure to use a cold temperature (heat encourages pi bond formation.)

Solomons (1978) CHAPTER FOUR

Question:

1. Distinguish between homolysis and heterolysis.
-

Question:

2. Match carbanion with acid/base and electrophile/nucleophile.
-

Question:

3. Which requires more energy, homolytic or heterolytic cleavage?
-

Question:

4. Rank methyl, primary, secondary, and tertiary radicals in terms of stability and potential energy.
-

Question:

5. Why are alkanes undesirable starting materials for synthesis ?
-

Question:

6. If one can draw several plausible mechanisms for a reaction how are incorrect mechanisms eliminated (what types of experiments are usually carried out?)
-

Question:

7. Draw the initiation, propagation, and termination steps for the free radical chlorination of methane.
-

Question:

8. **What three factors determine the rate of reaction?**

Question:

9. **Between bromine and chlorine which is more selective in it's choice of attack?**

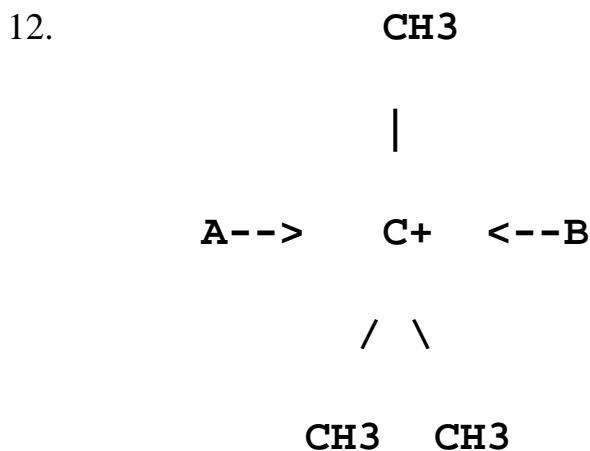
Question:

10. **What is the Hammond Postulate?**

Question:

11. **What is the geometric of a carbocation carbon (the geometry of carbon is tetrahedral...)**

Question:



In the above picture, assume the trigonal planar structure of the carbocation is in the plane of the computer screen. Attack from position A represents attack from above, and attack from position B represents attack from behind.

Homolysis- The breakage of a single bond with one electron going to each of the two atoms connected by the single bond

no charge forms

Homolysis is favored in the gas phase

Heterolysis- The breakage of a single bond with both electrons going to one of the two atoms joined by the single bond

The atom with both electrons is negatively charged and the other atom is positively charged

Heterolysis is favored by solution (I think this should be modified to read "especially if the solution is polar.")

A carbanion is usually a base and it is usually a nucleophile.

I think when Solomon's says "usually" he means that maybe sometimes its not basic enough to be called a base (like calling a pH of 7.001 basic)--I don't think he means to imply that it can sometimes be an acid (if you find something that suggests otherwise, let me know.)

heterolytic

I think this needs to be clarified, though. Heterolysis may require more energy, but in a polar solvent, the attractions between charged species and the solvent molecules provide a release of energy and the sum of the energy changes results in a net loss of Gibbs Free Energy, such that it is a preferred process. As an example the heterolytic cleavage of sodium acetate in water is favored over a homolytic cleavage.

Stability

Least Stable

1. **methyl**
2. **primary**
3. **secondary**
4. **tertiary**

Most Stable

Potential Energy

Lowest Potential Energy

1. **tertiary**
2. **secondary**
3. **primary**
4. **methyl**

Highest Potential Energy

They are very low in potential energy, and when they do react, they give multiple products which are hard to separate

Kinetics Experiments are carried out to locate the rate determining step.

Isotopic labeling may be useful; the presence of an isotope (e.g. a deuterium) on a position other the starting point may be helpful.

- **initiation-**

1. **the chlorine molecule splits into two chlorine radicals**

- **propagation-**

1. **the chlorine radical abstracts hydrogen from methane, producing HCl and a methyl radical**
2. **The methyl radical abstracts a chlorine atom from a chlorine molecule and thus creates a methyl chloride plus a new chlorine radical**

- **termination-**

1. **two chlorine radicals combine to form a chlorine molecule**
2. **two methyl radicals combine to form ethane**
3. **a methyl radical and a chlorine radical to form methyl chloride**

1. **collision factor (how often does a collision occur--this is temperature dependent)**
2. **energy factor (how vigorous is the collision--this is also temperature dependent)**
3. **collision orientation (this is not temperature dependent.)**

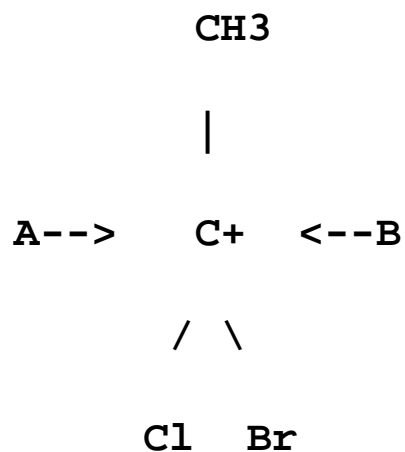
bromine

If possible, bromine will only end up on tertiary carbons. Chlorine is more indiscriminant, and will end up on secondary as well as tertiary carbons, and may even chlorinate a few primary carbons.

The transition state of an endothermic reaction is very similar to the product, and the transition state of of an exothermic reaction is very similar to the reactant.

trigonal planar

Both attacks have an equal probability of occurring. Later on you will run into the word 'racemic.'



It was an easy question, BUT, it is leading to some critical ideas. If the attacking species is anything other than CH₃, Cl, or Br, then the position of attack will determine which of two enantiomers is produced by the reaction. You will see this again...

Solomons (1978) CHAPTER FIVE

Question:

1. What catalysts are capable of facilitating the addition of hydrogen to a double bond?
-

Question:

2. Draw *N,N* Dimethylformamide (DMF). What is the significance of this solvent?
-

Question:

3. On an energy diagram which is higher, ethane or ethene?
-

Question:

4. Which is lower in energy, the cis or the trans isomer of 2-butene?
-

Question:

5. Which is lower on an energy diagram: ethene or 2-butene? why?
-

Question:

6. Are the products of elimination higher or lower in energy than the starting reactants?
-



7. How do you get from a dihalide (a.k.a vicinal or *vic* halide) to an alkene?
-



8. **How do you get an alkene from an alcohol?**



9. **How do you get an alkene from an alkyl halide?**



10. **What problem do you have to worry about if you are doing a reaction where you have a primary or secondary carbocation as an intermediate?**



11. **Solomon's tells you that the addition of hydrogen to an alkene using a metal catalyst produces syn-addition, but you've learned earlier that the barrier to single bond rotation (about 3 or 4 kcal if I remember right) is low enough that it occurs and it occurs a lot. How do you determine whether addition to a single bond is syn-addition?**

5-1

12. **Why does the ease of dehydration run 'tertiary easier than secondary easier than primary'?**



13. **Draw the mechanism for the acid catalyzed dehydration of an alcohol.**

Question:

14. **You were told when drawing resonance structures for neutral chemicals to avoid putting positive charges on electronegative elements, yet in the dehydration of an alcohol mechanism the positive charge is placed on the second most electronegative atom on the periodic table. What gives?**

Question:

15. **What property of alkyl groups aids in the stability of carbocations?**

[Question:](#)

16. **What is the rate determining step in the acid catalyzed dehydration of an alcohol?**

[Question:](#)

17. **What happens when an alcohol reacts with sodium metal?**

[Question:](#)

18. **What is special about using tert-butoxide as a solvent for the conversion of an alkyl halide to an alkene?**

[Question:](#)

19. **If a sodium alkoxide and an alkyl halide undergo a substitution reaction then what are the products?**

[Question:](#)

20. **Of what value are vic-dihalides?**

[Question:](#)

21. **How are vic-halides prepared from alkenes?**

nickel (Ni); palladium (Pd); platinum (Pt)



It is an aprotic solvent with a high "solvating" power. The term aprotic does not mean it doesn't have any hydrogens, it just means there are no hydrogens on highly electronegative atoms.

Hydrogens on highly electronegative atoms are acidic, and more likely to react with the reactants.

ethene

the trans

2-butene

2-butene could be thought of as ethene with two hydrogens replaced by methyls, and this 'higher substitution' results in more stability (and hence, lower energy.)

higher--in many cases heat is required for the reaction to occur.

acetone and zinc

note no heat is listed--perhaps the presence of the two adjacent (and very bulky) halides raises the energy of the reactant enough that the required "jump height" is low enough for the energy provided by room temperature.

Also, the zinc catalyst probably works in a manner not too unlike the way biochemical catalysis works, and all biochemical reactions in humans go at the low temperature of 37 deg C.

heat and an acid (acid protonates the alcohol), making it a better leaving group.

heat and a base (base pulls off a beta hydrogen)

It is possible that a methyl shift or a hydride shift could occur to produce a more stable carbocation before the next step of the reaction occurs.

perform the reaction on a ring structure where single bond rotation is not possible.

The difficulty of the reaction corresponds to the difficulty of creating the carbocation.

**look it up if you don't know it
(it may be placed here at a later time.)**

The species with the positive charge is not a stable species. It is lower in energy than the carbocation transition state, but higher in energy than the alcohol.

They are electron releasing

The expulsion of the leaving group, water.

The sodium replaces a hydrogen.

The bond is more ionic ($\text{Na}^+ \text{-O}^-$) than covalent (Na-O).

Because the sodium atom donates its electrons, it is considered a reducing agent.

The less substituted alkene is usually predominant.

Sodium abstracts the halide and the alkoxide hits the carbocation formed from the halide departure.

The *vic*-halide functionality can be used to protect the double bond. You convert the double bond to a *vic*-halide before carrying out a reaction that would attack the double bond, and then you carry out that other reaction, and afterwards, you can convert the *vic*-halide back to the double bond.

Bubble the diatomic halogen gas through a solution of the alkene in carbon tetrachloride at room temperature

(the author is suspicious because the opposite reaction, dihalide to alkene, is carried out at room temperature, indicating the alkene isn't much higher in energy than the dihalide. If the gap isn't much, it seems possible that in order to keep the dihalide from going back, low temperature must be maintained...{this is conjecture, but I think it's the kind of thinking you should be doing at this point})

Solomons 1978

Question:

1. Compare the strength of the pi bond to the sigma bond in a double bond.
-

Question:

2. How do acid-base and electrophile-nucleophile theory differ?
-

Question:

3. Why does Markovnikov addition occur for the addition of HX in the absence of peroxides?
-

Question:

4. Why does anti-Markovnikov addition occur when HX is added in the presence of peroxides?
-

Question:

5. If I-Cl (iodine-chlorine) is added to a double bond, which halogen adds first?
-

Question:

6. What is the technical term for reactions like these addition to double bonds where one of more than one possible possible outcomes is predominant?
-

Question:

7. Draw the mechanism for the hydration of an alkene.
-

Question:

8. What is the principle of microscopic reversibility?
-

Question:

9. What is the rate determining step for the hydration of an alkene?

Question:

10. **What reagents are used for Oxymercuration/ Demercuration? What is the regioselectivity?**

Question:

11. **How can this mercuric acetate chemistry be used to obtain an ether?**

Question:

12. **When is mercuric trifluoroacetate necessary?**

Question:

13. **How does one obtain anti-Markovnikov regioselectivity for the hydration of a double bond?**

Question:

14. **What is the safety problem of diboranes and alkylboranes?**

Question:

15. **Hydroboration is probably the first concerted reaction you've seen (two or more things happening at once in tandem). What is unique about the transition state?**

Question:

16. **Is Hydroboration-Oxidation addition *syn* or *anti*?**

Question:

17. **What is the classical test to distinguish between alkanes and alkenes (the question assumes you know it has to be one or the other)?**

Question:

18. **What is a peracid?**

Question:

19. **What is the result of the acid catalyzed hydrolysis of an epoxide?**

[Question:](#)

20. **What is the regioselectivity of the oxidation of an alkene using cold potassium permanganate (KMnO₄) with base?**

[Question:](#)

21. **Cold temperatures are required when oxidizing an alkene to a diol. Why?**

[Question:](#)

22. **In general, what is the value of diglyme?**

The pi bond is weaker because it experiences less orbital overlap.

Acid-base theory is concerned with equilibrium.

Electrophilicity and nucleophilicity deal with kinetics.

To some extent this can be a problem if you think too much about it because at some point you were told "faster reactions go farther" and this statement ties equilibrium to kinetics, yet there are times you are expected to treat them separately.

The H is the first to add since the double bond is going to attract an electrophile, and that hydrogen is placed in a way to make a more stable carbocation--this leads to Markovnikov addition.

The peroxides create halide radicals (X.) which add first, and thus they add to the site the protons would add to if there were no peroxides.

the iodide

it's lower electronegativity means it will have a partial positive charge.

Regiospecific (since the question was rather vague, 'unsymmetrical addition' probably should get full credit too.)

look it up in the book (someday it may be place here.)

The term 'microscopic reversibility' applies to reactions where the reverse reaction follows a mechanism that is exactly opposite to the that of the forward reaction.

This ties back to that concept of the transition state and the mountain pass.

Formation of a carbocation.

Oxymercuration- water, mercury acetate ($\text{Hg}(\text{O}_2\text{CCH}_3)_2$)

Demercuration- sodium borohydride (NaBH_4)

Markovnikov

Switch the water with an alcohol containing the desired alkyl group.

When a tertiary alcohol is to be used for the ether synthesis.

Hydroboration-Oxidation

Add diborane, $(\text{BH}_3)_2$ to place an H and a BH_2 and then add base and hydrogen peroxides.

They are "air sensitive", meaning they can explode if exposed to oxygen.

It is a four center transition state; the pi bond of the alkene and one of the sigma bonds of the borane split into four partial bonds.

syn

Add a solution of bromine in carbon tetrachloride to your product in the dark

:O:

||

R - C - :O: - :O: - H

a diol

syn

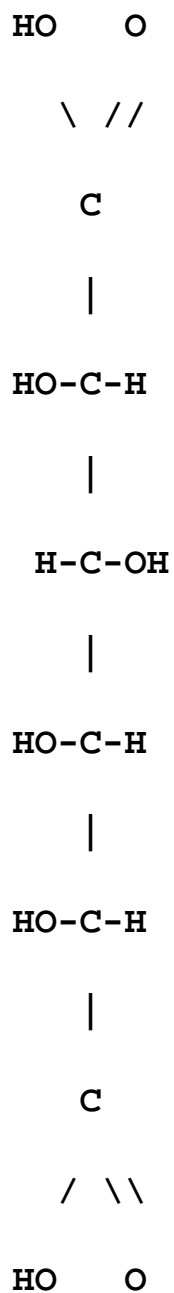
KMnO₄ is a very strong oxidizer, even stronger than potassium dichromate (K₂CrO₇), and if it goes too far it will rip the double bond in two, forming carboxylic end groups.

No acidic protons, but a high boiling point. Usually high boiling solvents have acidic hydrogens (their high boiling point is a consequence of the hydrogen bonding that the acidic hydrogens undergo.) Triglyme boils even higher, and higher still is tetraglyme (a new product from Aldrich.)

Solomons 1978

Question:

1. Chirality problem from Hell- Below is sigma-D-(+)-glucose:



Identify the four chiral centers as either R or S according Cahn, Ingold, Prelog.

Question:

2. **Why does a racemic mixture fail to rotate plane polarized light?**
-

Question:

3. **True or False: The Kleinman Correlation Rules relate the R,S configuration to the direction of rotation for plane polarized light.**
-

Question:

4. **In a reaction involving a -Br attached to a chiral carbon, the Br is expelled, forming a carbocation, and then a nucleophile comes in and takes its place. Will there be retention of configuration, or will a racemic mixture form?**
-

2-R

3-S

4-S

5-S

Because it is a 50:50 mixture, and the sum of all the rotations encountered adds up to zero.

false- there is no such correlation.

A racemic mixture will be formed, since both sides of the carbocation are equally available for attack.

There is an assumption here that the carbocation forms before there is any interaction with the nucleophile. If some "push" from the nucleophile is required before the carbocation will form, it may be easier for the attack to come from one side than the other, and one enantiomer may be preferred over another.

(I'm going to check and make sure the book agrees with me on this. Hey, better yet, ask your professor in class what s/he thinks so that you'll put the "correct" answer down on the test.

Solomons 1978

I couldn't find anything for chapter eight in my files.

Solomons 1978

Question:

1. Rank alcohol, alkane, alkene, alkyne, and amine in decreasing acidity.

Question:

2. Compare the C to C bond lengths for ethane, ethene, and ethyne.

Question:

3. How does one regioselectively reduce an alkyne to an alkene with trans-hydrogens?

Question:

4. How does one regioselectively reduce an alkyne to an alkene with cis hydrogens?

Question:

5. What reagents are used to hydrate an alkyne?

Question:

6. How do you make an aldehyde out of a terminal alkyne?

Question:

7. How do you displace the hydrogen of an alkyne with a sodium?

Question:

8. How can you convert a terminal alkyne into a longer non-terminal alkyne?

Question:

9. How does one locate the position of an alkyne in if it is unknown?
-

TIME OUT! I'm not going to ask questions about all those tests for functional groups in that one table. Here's what you do--make nine flash cards and on one side right the functional group and on the other write the applicable tests and their results.

Question:

10. Why does the halogenation of an alkene under high temperature result in substitution rather than addition?
-

Question:

11. Add the allyl carbocation to the stability list {primary, secondary, and tertiary}.
-

Question:

12. Describe the addition of HCl to 1,3-Butadiene.
-

Question:

13. In the addition of HBr to 1,3 butadiene which product is kinetically controlled and which product is thermodynamically controlled?
-

Question:

14. Draw the potential energy vs reaction coordinate diagram which compares the 1,3 butadiene radical to the 1,2 and the 1,4 product.
-

Question:

15. What happens in a Diels Alder Adduct formation reaction?
-

TIME OUT! The next natural question would concern the stereoselective character of the adduct formation.

There is a highly simplified MO explanation that twists the pi lobes of the HOMO for a heat reaction or the LUMO for a light reaction (the light kicks an electron up into the LUMO making the term 'unoccupied' inappropriate for as long as that light source is on.)

Lowest Acidity

1. **alkane**
2. **alkene**
3. **amine**
4. **alkyne**
5. **alcohol**

Highest Acidity

Shortest

1. **ethyne**
2. **ethene**
3. **ethane**

Longest

Use Li metal in liquid ammonia

When they say liquid ammonia, it's their way of saying the pure stuff, as opposed to the aqueous ammonia you used in Freshman lab. Ammonia picks up water from the atmosphere, so this would probably require working with some type of system that keeps out water.

Use hydrogen gas and the Lindlar catalyst.

It was a cruel trick question. Yes you can try to put an -OH group on an alkyne to make an 'alkene-ol', but the moment it is made it is going to 'keto-enol tautomerize" to make a ketone. I'm sure this 'trick' will be on the test in some form.

(very carefully!) add sodium metal and liquid ammonia.

need to look this up--previous listed answer did not answer the question.

need to look this one up.

KMnO₄, alcohol, and room temperature, according to Solomons.

I like Morrison and Boyd's KIO₄ (potassium hypoiodite) because I believe it is a stronger oxidant.

It is sometimes explained using the LeChatlier's Principle. Addition is an exothermic process, meaning that heat is given off, and if the temperature is high enough, this just isn't going to happen. You must work in a cool surrounds so that the heat will disappate.

Lowest Stability

1. **primary**
2. **secondary**
3. **allyl**
4. **tertiary**

Highest Stability

The electron density which comprises one of the pi bonds (C1 and C2) is kicked off the butadiene in the direction of the proton, and it forms a single bond between C1 and the proton.

Bond formation is favored because the process lowers the overall energy of the molecule.

The electron density of the second double bond (C3 and C4) [this sentence needs to be completed!]

The placement of the positive charge on C2 was better than leaving it on the proton.

1,2 is kinetic. Kinetic control requires low temperature, and that -80 deg C is the result of placing chunks of "dry ice" (solid carbon dioxide) in acetone to make a cold bath.

1,4 is thermo

answer key just lists Fig. 10.7

A diene and a dienophile use pi electron density to form sigma bonds, thus joining two molecules together in a ring structure.

Solomons 1978

I can't find anything for Chapter 10.

CHAPTER ELEVEN was just Special Topics

Solomons 1978

Question:

1. Which of the three general class of reactions are aromatic rings likely to undergo? (addition, elimination, substitution)

Question:

2. (This challenge problem can be answered from what you learned in the section discussing the molecular orbitals of benzene.) Structures with pi bond systems can be treated with calculations that look only at the pi bonds. In these cases drawing showing the pi lobes (often with colors as well as the +/- notation) are used. Below are the six MO wavefunctions for 1,3,5 hexatriene. Rank them in order of increasing energy:

- a ++++++
- b +---+-
- c +---+-
- d ---+++
- e +---+-
- f ---+--

(How to read the structures) When you see ++++++ you know to draw six pi orbitals side by side, each with the '+' lobe sticking up. Similarly, when you see the ---+++ you should see the first three of the six lobes as having the '-' sign up and the last three as having the '+' sign up.

Question:

3. Which numbers in the following sequence are Huckel numbers (5,7,6,4,3,2,11,10,17)?

Question:

4. Are any of the following statements is not true:?
1. Aromatic rings are capable of sustaining an induced current
 2. An aromatic ring has a planar structure
 3. An aromatic ring follows the $4n + 2$ Huckle rule
 4. All C to C bonds in an aromatic ring are of equal length
 5. An aromatic ring is lower in energy than what we would calculate using extrapolations from non-aromatic systems
 6. An aromatic ring shows a signal higher up on the NMR (for benzene it is 7.3 ppm)
-

Question:

5. How does Nature make cyclopentadiene aromatic?
-

Question:

6. Does naphthalene have two aromatic rings?
-

Question:

7. Unfortunately you should know some trivial names for substituted benzenes. What are the substituents on the following?
- toluene
 - phenol
 - aniline
 - benzoic acid
 - acetophenone

Question:

8. **Draw pyridine. Is it aromatic?**
-

Question:

9. **Draw pyrrole. Is it aromatic?**

substitution

Lowest Energy

1. ++++++

2. ----+++

3. --+++--

4. +---++-

5. +-+++++

6. +-+++-

Highest Energy

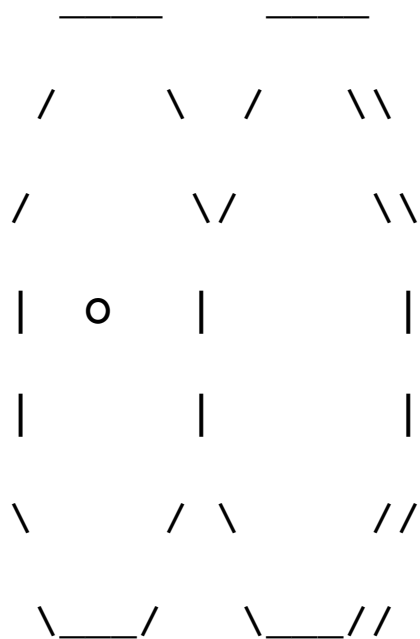
The more nodes there are in a system, the higher the energy of that system; alternately long stretches of matching lobes is energetically favored.

6, 2, 10

h) is not a characteristic of aromatic annulenes; all others are characteristics. a) and f) tie together; e) and g) tie together; b) is a requirement for resonance and d) results from resonance--do you see things coming together? a) and f) are things you haven't covered yet.

A proton can be removed from the sp^3 carbon and since the H leaves as proton there are two electrons left behind which can now contribute to aromaticity. Note that we are saying here that the cyclopentadiene anion is aromatic, not the neutral cyclopentadiene molecule.

No. One ring is aromatic, and the other isn't. The nonaromatic ring shows its nonaromatic character by its ability to undergo addition reactions.



- **toulene has a methyl**
- **phenol has an -OH**
- **aniline has an - NH₂**
- **benzoic acid has a carboxylic acid group**
- **acetophenone has a carbonyl on one side and a methyl on the other**

yes; you should see the electron pair, the single bond, and the double bond as trigonal planer, and you should remember that the pi bonds leading to aromaticity are perpendicular to the plane of the ring.

yes; notice the structure is NOT sp^3 . Usually a lone pair and three bonds (for a total of four entities) meant sp^3 . Up till now it was convenient for structures with four entities to take a tetrahedral geometry to minimize steric repulsions, but now there is a new factor in the game--aromaticity. (What those atoms won't do to get it!) Notice that the O in furan and the S in thiophene are also sp^2 and there it comes down to basically one pair is "in" (in the aromaticity) and the other is "out".

You could ask, 'How does the molecule decide which goes where since they're symmetrically equivalent?'

I'll speculate. Aromaticity is caused by perturbation. I've never seen this written anywhere. Perturbation occurs during any reaction. Attacking molecules carry electrons, right?, and moving charges produce magnetic fields which in turn stimulate more electronic movement (current). It also occurs during any type of spectroscopic study. We can't isolate one pyrrole molecule from perturbation so we'll never see evidence of the perfect 'unperturbed pyrrole'.

Danger. If you think about this any further you could go crazy.

Solomons 1978

Question:

1. How do you substitute a halogen for a hydrogen on a benzene ring?
-

Question:

2. How do you nitrate a benzene ring?
-

Question:

3. How do you add an SO₃H group?
-

Question:

4. What is Friedel-Crafts alkylation?
-

Question:

5. What is Friedel-Crafts acylation?
-

Question:

6. Draw the three resonance structures which characterize the benzene intermediate in electrophilic substitution.
-

Question:

7. Draw a general potential energy diagram for electrophilic substitution.
-

Question:

8. The formation of a complex between a halogen gas (such as bromine) and a Lewis acid (such as iron tribromide) runs against what you've been told so far in that the result puts a positive charge on the most

electronegative element and to add insult to injury, it puts a negative charge on an electropositive metal. Metals are supposed to be electropositive!

Question:

9. **Draw the mechanism for the aromatic halogenation of a benzene ring. Use MX_3 as your lewis acid (M as in metal).**
-

Question:

10. **Show the reaction for the addition of sulfuric acid to nitric acid (the two together are called "aqua regia", and this combination was used in the James Bond movie 'Octopussy'.)**
-

Question:

11. **How do you remove a sulfonic acid group?**
-

Question:

12. **Name some groups whose presence on a benzene ring will prevent Friedel Crafts substitution.**
-

Question:

13. **What is the product of the reaction of acetic anhydride with benzene in the presence of aluminum trichloride at 80 C?**
-

Question:

14. **Show what happens when aluminum trichloride is mixed with an acyl chloride.**
-

Question:

15. **What are the two resonant structures for the acylium ion?**
-

Question:

16. Describe the Clemmenson Reduction.
-

Question:

17. Show th reaction of succinic anhydride with benzene in the presence of aluminum trichloride at 90 C. Succinic anyhydride is a five membered ring: -CH₂-CH₂-carbonyl-O- carbonyl-.
-

TIME OUT! Probably the easiest way to remember meta vs. ortho para and activating vs. deactivating is that a) the halogens are odd in that they deactivate but direct ortho para; b) all metas are deactivating and include cyanide and anything with a double bond to an oxygen (CHO, COR, COOH, COOR, SO₃H, NO₂) except that amides are ortho para activating; everything else is ortho para activating. But I see you are told to know relative strengths--so make six index cards 'cause its memorization time... (this applied to Karen at NMSU in '92--I don't know if it applies to UMR Organic students in '94 or beyond)

Question:

18. Which makes it easier to carry out aromatic electrophilic substitution:
1. electron releasing groups
 2. electron withdrawing groups?
-

Question:

19. Draw the four resonance structures for the benzyl radical.
-

Question:

20. How can you prepare benzoic acid from toluene?

Bubble the halogen gas through the benzene solution with FeX_3 (X is a halogen; could be chlorine or bromine) present.

Add nitric acid and sulfuric acid and do some mild heating (~50 C)

Add sulfuric acid at room temperature. H₂SO₄ is really SO₃ hydrated by water molecules (SO₃ + H₂O yields H₂SO₄ algebraically.)

I guess when they say fuming sulfuric they mean there is an excess of SO₃ present. The presence of excess SO₃ would make the solution hygroscopic (it would take water out of the air for stabilization purposes.)

Addition of an alkyl group to a benzene ring by adding the appropriate alkyl halide to a benzene solution with aluminum trichloride, AlCl_3 , a Lewis acid. The aluminum trichloride accepts the halide off the alkyl halide and this makes the alkyl group a more reactive species.

Addition of an acyl group to a benzene ring by adding the appropriate acyl chloride to a solution of benzene in the presence of aluminum trichloride. Some heating is required (80 C.)

The electrophile hits a carbon forming an sp^3 hybridization. In each canonical structure there are two double bonds and the remaining carbon (which doesn't have a double bond) carries a positive charge.

look it up in the book (later on it may be put here.) Be sure to note the difference between transition state and intermediate.

At this point the "octet rule" people gleefully come in and point out that every atom as an octet. I don't like this because back when you were drawing resonance structures for things like sulfuric acid, you were encouraged to put the negative charges on the oxygens when you were going to place charges.

You were told to only put positive charges on electronegative elements (such as O and N) when drawing transition states; indeed, it made sense that such entities would lie at the peaks of the potential energy diagrams because you had to pay an energy price for such a (necessary) violation in order to get to the other side.

Now it seems it will be necessary to keep a list of cases where the simple rules taught earlier fall apart. In complex formation we must conclude that the energy gained from forming a bond (bond energy) is more than enough to compromise the "electronegativity" of the involved molecules.

look it up. It may be placed here later.

The interesting thing here is a stronger acid treating another strong acid (the second is relatively weaker) as a base. I would argue that the dissociation is favored to a large extent by the presence of that positive charge on the oxygen. It also helps that the dissociation produces an extremely stable water species.

Add dilute sulfuric acid and pass steam through the reaction mixture.

Powerful electron withdrawing groups like NO₂, NR₃⁺, and CF₃.

Acetophenone

The aluminum forms an adduct with the chlorine in the acyl chloride; the bond between the chlorine and the carbonyl breaks, forming an acylium ion.

a) R-C=O with a (+) charge on the C;

b) R-C(triple bond)O with a (+) on the O;

The octet rule people (I'm not be derisive here, am I?) would point out that the latter has the advantage that every atom has an octet. Since this is a transition state species, the positive oxygen becomes a convenient "low point of the mountain pass."

A zinc and mercury amalgam with HCl are combined in a reflux (reflux means a setup where the solution boils and the vapor condenses above and drips back down the side walls into the container so you don't boil off your solvent and waste it.)

the carbonyl is reduced down to a carbon with two hydrogens, and thus the ketone substituent becomes an alkyl substituent. This could be useful because maybe you want the position of your alkyl group to direct meta; by putting a ketone there it will direct meta, and when that is done, the ketone can be reduced to the alkyl group.

The bond between the ether linkage (the lone oxygen) and a carbonyl is broken.

electron releasing groups

look it up in the book

oxidation by KMnO_4

Question:

1. **How many different types of chemically equivalent hydrogens are there in butane? 2-chlorobutane? 1- chlorobutane?**
-

Question:

2. **Which is further downfield, a hydrogen on a benzene ring, or a hydrogen on a carbon with two chlorines and another carbon?**

Two; Four; Four

The introduction of the chlorine to the very symmetric butane reduces the symmetry of the molecule. Symmetry will be talked about in P-Chem.

The benzene ring. Even the presence of the two chlorines on the carbon shifts the peak a long distance, it cannot shift the peak as far as the aromaticity shift for aromatic protons.

ANSWERS>



1. **Electron releasing group, such as methyl: remember how tertiary carbocations were especially stable because the methyls released electron density to lower the positive charge [note: a minus charge coming in is mathematically equivalent to a positive charge spreading out.]**
2. **Look it up.**
3. **Oxidize it with potassium permanganate, base, and heat. This will produce a carbonyl-O with a negative charge because of the base. Add acids to put a proton on the negative O to make a carboxylic acid.**

I'M NOT SURE WHAT HAPPENED HERE...



1. **How many different types of chemically equivalent hydrogens are there in butane? 2-chlorobutane? 1-chlorobutane?**
2. **Which is further downfield, a hydrogen on a benzene ring, or a hydrogen on a carbon with two chlorines and another carbon?**
3. **Two; Four; Four. You should notice that the introduction of a chlorine to the very symmetric butane has reduced the symmetry of the molecule. Symmetry will be talked about in P-Chem.**
4. **The benzene ring. Even though the presence of two chlorines on the same carbon shifts the peak a long distance, it can't quite compete with the aromaticity of the benzene ring. ANSWERS**



1. **substitution**

- a) ++++++ < d ----++ < f ---+-- < b +----+ < c +-+--+ < e +-+--+** The punchline here is that as the more nodes there are in a system, the higher the energy of that system; alternately long stretches of matching lobes is energetically favored.
- 6, 2, 10**
- h) is not a characteristic of aromatic annulenes; all others are characteristics. a) and f) tie together; e) and g) tie together; b) is a requirement for resonance and d) results from resonance--do you see things coming together? Granted, a) and f) are things you haven't covered yet.**
- Kick off a proton from the sp³ carbon and since the H leaves as proton there are two electrons left behind which can now contribute to aromaticity.**
- (A glimpse of what you'll see in the future, just to show you that chemistry can be interesting...) Here's where it gets really weird. Advanced texts will speak of naphthalene as having one aromatic ring and a second ring with two double bonds as the reaction chemistry suggests. In Inorganic you will talk about perturbation. All by itself, the naphthalene's two rings are equivalent, but when you bring something in, the electromagnetic interaction (a.k.a field effects) are going to perturb that molecule, and one ring is going to go aromatic and the other will be more receptive to addition--but hey, you don't have to worry about this now.**
- Here's what you have to see. The bromine comes in and adds to one double bond. The other ring is still aromatic and therefore the second bromine will add to the other double bond which is a far easier target due to its higher energy. You will end up with a brominated cycloalkyl chain attached a benzene. Half of the molecules will have the deuterium on the benzene ring, and the other half will have it on the brominated aliphatic chain.**
punchlines 1) one aromatic ring, resistant to all the bromine in the world at room temperature and 1 atm; 2) at the very onset before

the first reaction occurred, both rings were equal.

8. Toulene has a methyl, phenol has an -OH, aniline has an -NH₂, benzoic acid has a carboxylic acid group, and acetophenone has a carbonyl followed by a methyl (think of it as methyl benzyl ketone).
9. yes; you should see the electron pair, the single bond, and the double bond as trigonal planer, and you should remember that the pi bonds leading to aromaticity are perpendicular to the plane of the ring.
10. yes; notice the structure is NOT sp³. Usually a lone pair and three bonds (for a total of four entities) meant sp³. Up till now it was convenient for structures with four entities to take a tetrahedral geometry to minimize steric repulsions, but now there is a new factor in the game--aromaticity. (What those atoms won't do to get it!) Notice that the O in furan and the S in thiophene are also sp² and there it comes down to basically one pair is "in" (in the aromaticity) and the other is "out". A sarcastic student will ask, 'How does the molecule decide which goes where since they're symmetrically equivalent?' I'm about to go out on an academic limb here. Aromaticity is caused by perturbation. I've never seen this written anywhere. Perturbation occurs during any reaction. Attacking molecules carry electrons, right?, and moving charges produce magnetic fields which in turn stimulate more electronic movement (current). It also occurs during any type of spectroscopic study. We can't isolate one pyrrole molecule from perturbation so we'll never see the perfect 'unperturbed pyrrole'. ENOUGH!
11. Bubble the halogen gas through the benzene solution with FeX₃ present.
12. Add nitric acid and sulfuric acid and do some mild heating (50 C)

13. **Add sulfuric acid at room temperature. H_2SO_4 is really SO_3 hydrated by water molecules ($\text{SO}_3 + \text{H}_2\text{O}$ yields H_2SO_4 algebraically). I guess when they say fuming sulfuric they mean there is an excess of SO_3 present. I believe the presence of excess SO_3 would make the solution hygroscopic (it would take water out of the for stabilization purposes).**
14. **Addition of of an alkyl group to a benzene ring by adding the appropriate alkyl halide to a benzene solution with aluminum trichloride (a Lewis acid) present. The aluminum trichloride accepts the halide off the alkyl halide and this makes the alkyl group a more reactive species.**
15. **Addition of an acyl group to a benzene ring by adding the appropriate acyl chloride to a solution of benzene in the presence of aluminum trichloride. Some heating is required (80 C).**
16. **The electrophile hits a carbon forming an sp^3 hybridization. In each canonical structure there are two double bonds and the remaining carbon (which doesn't have a double bond) carries a positive charge**
17. **Look it up in the book. Be sure to note the difference between transition state and intermediate.**
18. **At this point the "octet rule" people gleefully come in (in M&B) and point out that every atom as an octet. I don't like this because back when you were drawing resonance structures for things like sulfuric acid, you were encouraged to put the negative charges on the oxygens when you were going to place charges. You were told to only put positive charges on electronegative elements (such as O and N) when drawing transition states; indeed, it made sense that such entities would lie at the peaks of the potential energy diagrams because you had to pay an energy price for such a (necessary) violation in order to get to the other side. only when dealing with transition states Now it seems it will be necessary to keep a list of cases where the simple rules taught**

- earlier fall apart. In complex formation we must conclude that the energy gained from forming a bond (bond energy) is more than enough to compromise the "electointegraty" of the involved molecules.
19. Look it up.
20. The interesting thing here is A stronger acid treating another strong acid (the second is relatively weaker) as a base. I would argue that the dissociation is favored to a large extent by the presence of that positive chare on the oxygen. It also helps that the dissociation produces an extremely stable water species.
21. Add dilute sulfuric acid and pass steam through the reaction mixture.
22. Powerful electron withdrawing groups like NO₂, NR₃⁺, and CF₃. I don't know why they listed some activating groups. I think that is a mistake.
23. Acetphenone
24. The aluminum forms an adduct with the chlorine on the acyl chloride; the bond between the chlorine and the carbonyl breaks, forming an acylium ion.
25. a) R-C=O with + on the C; b) R-C(triple bond)O with a + on the O; the octet people would point out that the latter has the advantage that every atom has an octet. Since this is a transition state species, the positive oxygen becomes a convenient "low point of the mountain pass".
26. A zinc and mercury amalgum with HCl are combined in a reflux (reflux means a setup where the solution boils and the vapor condenses above and drips back down the side walls into the container so you don't boil off your solvent and waste it). The carbonyl is reduced down to a carbon with two hydrogens and

thus the ketone substituent becomes an alkyl substituent. This could be useful because maybe you want to position of your alkyl group to direct meta; by putting a ketone there it will direct meta, and when that is done the ketone can be reduced to the alkyl group.

- 27. The bond between the ether linkage (the lone oxygen) and a carbonyl is broken (by the aluminum trichloride probably- I would assume this is similar to the Friedel crafts acylation mechanism only the $AlCl_3$ remains on the tail end of the open chain until the H liberated from the benzene ring comes along and pops it off taking its place--parenthesis my speculation.)**

Prelab Information

1. [Organic Lab I](#)

[One .gif after another](#)

[Comparative Melting Points](#)

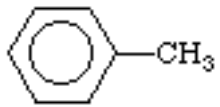
[Recrystallization](#)

- [1. Separation of the Components of a Solution by Distillation](#)
- [2. Separation of Two Liquids by Distillation](#)
- [3. Thin Layer Chromatography](#)
- [4. Semi-Microscale Recrystallization](#)
- [5. Microscale Recrystallization](#)
- [6. Addition of Br₂ to Cholesterol and Zn-assisted Debromination](#)
- [7. Acid-catalyzed Dehydration of Alcohols: Cyclohexene from Cyclohexanol](#)
- [8. Diels-Alder Reaction of Cyclopentadiene with Maleic Anhydride](#)
- [9. Extraction-Separation of a Mixture of Acid, Base and a Neutral Compound](#)

[toluene](#)

[p-xylene](#)

Toluene- CAS REGISTRY [108-88-3]



F.W. 92.14 g/mol

m.p. -93 deg C

b.p. 111 deg C

n (20 over D) 1.4960

d 0.867 g/ml

p-xylene- CAS REGISTRY [106-42-3]

A benzene ring with two methyl groups at opposite ends of the ring.



F.W. 44.10 g/mol

m.p. -188 deg C

b.p. -42 deg C

n (20 over D) not available

d not available

Fp (flashpoint) not available

comments: Flammable gas!

[2-Butanone](#)

[Cyclohexane](#)

[Ethyl Acetate](#)

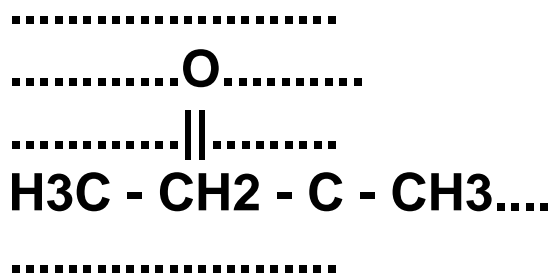
[Toluene](#)

[o-Xylene](#)

[m-Xylene](#)

[p-Xylene](#)

2-butanone- CAS REGISTRY [78-93-3]



F.W. 72.11 g/mol

m.p. -87 deg C

b.p. 80 deg C

n (20 over D) 1.3790

d 0.805 g/ml

Fp (flashpoint) -3 deg C

comments: Flammable liquid!

m-Xylene- CAS REGISTRY [108-38-3]

F.W. 106.17 g/mol

m.p. -47.4 deg C

b.p. 138-139 deg C

n (20 over D) 1.4970

d 0.868 g/ml

Fp (flashpoint) 25 deg C

comments: insoluble in water; miscible with alcohol, ether, and many other organic solvents.

Hints for the TLC lab

Acetaminophen

Acetic Acid

Acetosalicyclic Acid

Ammonium Hydroxide

Butanol

Caffeine

Ethanol

Ethyl Acetate

Ibuprofen

In progress.

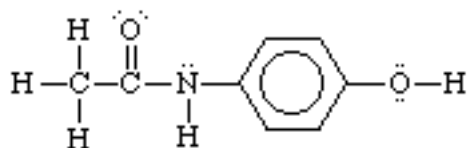
Click on [this](#) to return to the index.

Acetaminophen- CAS REGISTRY [103-90-2]
also known as 4-Acetamidophenol
and also known as 4'-hydroxyacetanilide

```

.....
.....O.....
.....| |.....
H3C - C - N - (p)benzene - O - H..
.....|.....
.....H.....
.....

```



more information is available on disubstituted [benzene](#), which is shown above.

F.W. 151.16 g/mol

m.p. 169-170 deg C

b.p. decomposes before boiling

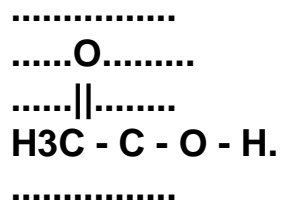
n (20 over D) not applicable

d 1.293 g/ml

comments: white

properties from Aldrich and comments from Merck

Acetic Acid- CAS REGISTRY [64-19-7]



F.W. 60.05 g/mol

m.p. 16 deg C

b.p. 116- 118 deg C

n (20 over D) 1.3720

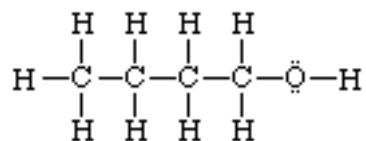
d 1.049 g/ml

comments: clear liquid; pungent odor!

properties from Aldrich and comments from Merck

1-butanol- CAS REGISTRY [71-36-3]

.....
H3C - CH2 - CH2 - CH2 - O - H..
.....



F.W. 74.12 g/mol

m.p. -90 deg C

b.p. 118 deg C

n (20 over D) 1.3990

d 0.810 g/ml

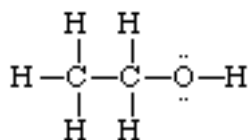
Fp (flashpoint) 35 deg C

comments: Flammable liquid!

Click on [this](#) to return to the index.

ethanol- CAS REGISTRY [64-17-5]

.....
H3C - CH2 - O - H.....



F.W. 46.07 g/mol

m.p. -130 deg C

b.p. 78 deg C

n (20 over D) 1.3600

d 0.785 g/ml

Fp (flashpoint) 8 deg C

[Activated Carbon](#)

[Benzilic Acid](#)

[Benzoic Acid](#)

[Ethanol](#)

[4-Nitrophenylacetic Acid](#)

Click on [this](#) to return to the index.

Activated Carbon (charcoal)- CAS REGISTRY [7440-44-0]

.....
....structure not applicable.....
.....

F.W. not applicable

m.p. not applicable

b.p. not applicable

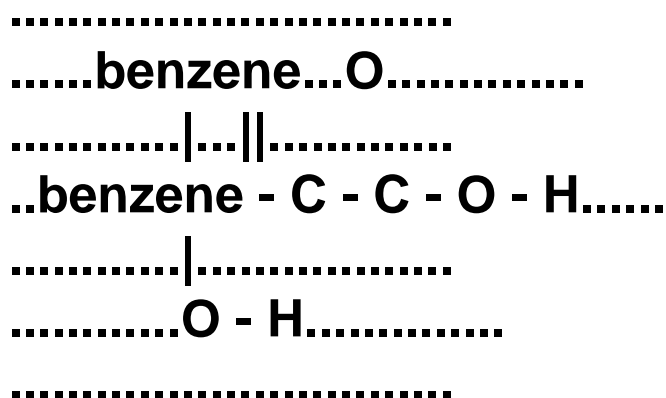
n (20 over D) not applicable

d not available

Fp not available

Click on [this](#) to return to the index.

benzilic acid- CAS REGISTRY [76-93-7]



F.W. 228.25 g/mol

m.p. 150 deg C

b.p. decomposes first

n (20 over D) not applicable

d not available

Fp not available

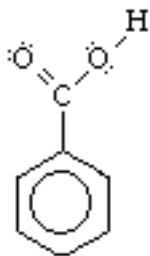
Click on [this](#) to return to the index.

Benzoic Acid- CAS REGISTRY [65-85-0]

O

||

It's a benzene ring with a - C - O - H substituent.



F.W. 122.12 g/mol

m.p. 122-123 deg C

b.p. 249 deg C

n (20 over D) not applicable

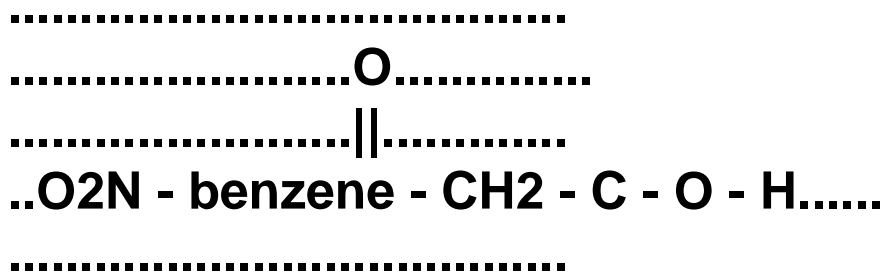
d not given

Fp (flashpoint) 121 deg C -- hey, if this number is right, then this stuff can go !BOOM! one degree before it melts...

comments: Hygroscopic!

Click on [this](#) to return to the index.

4-Nitrophenylacetic Acid- CAS REGISTRY [104-03-0]



F.W. 181.15 g/mol

m.p. 154 deg C

b.p. decomposes first

n (20 over D) not applicable

d not available

Fp not available

Click on [this](#) to return to the index.

[Benzoin](#)

[Ethanol](#)

[Click here to return to the index](#)

[Hints for the 6th lab](#)

[Cholesterol Lab Handout](#)

[Acetic Acid](#)

[Bromine](#)

[Cholesterol](#)

[Diethyl Ether](#)

[Ethanol](#)

[Methanol](#)

[Sodium Acetate](#)

[Sodium Chloride](#)

[Sodium Hydroxide](#)

[Zinc](#)

[Click here to return to the index](#)

You will want to dissolve the cholesterol in 1 ml of water, rather than 0.5 ml, because otherwise the ether will evaporate off before the cholesterol completely dissolves. Later on in the lab it will most likely be necessary for you to add more ether to replace ether which has evaporated from the system.

Add 15 drops of the ether/sodium acetate solution.

For the two washings with 30% ether/70% acetic acid (I have down, use 0.5 ml for each washing, but) you want to minimize the amount of washing solution used because it dissolves the brominated cholesterol.

When transferring the brominated cholesterol solid, be sure to place a piece of weighing paper under the vial you transfer the solid into, so that if some spills over, you can still transfer it.

A water rinsing is used to get most of the acid out before the addition of the base; this is a standard protocol, the benefit of which is more apparent when you scale up your operation to a level where the violence between the reaction of an acid with a base can be a technical problem.

Be sure to use a microspatula when transferring the sodium sulfate to dry the ether layer to minimize the amount of sodium sulfate used.

Cholesterol Lab Handout

The bromination of a double bond is an important and well-understood reaction. In the present experiment, it is employed for the very practical purpose of purifying crude cholesterol through the process of bromination, crystallization, and then zinc dust debromination.

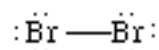
The reaction involves nucleophilic attack by the alkene on bromine with the formation of a tertiary carbocation that probably has some brominium ion character resulting from the sharing of the nonbonding electrons on bromine with the electron-deficient C-5 carbon. This ion is attacked from the backside by the bromide ion to form dibromocholesterol with the bromine atoms in the *trans* and diaxial configuration, the usual result when brominating a cyclohexene.

Cholesterol isolated from natural sources contains small amounts (0.1 to 0.3%) of *3beta*-cholesterol, 7-cholesten-*3beta*-ol, and 5,7-cholestadien-*3beta*-ol. These are so very similar to cholesterol in solubility that their removal by crystallization is not feasible. However, complete purification can be accomplished through the sparingly soluble dibromo derivative *5alpha, 5beta*-

Bromine- CAS REGISTRY [7726-95-6]

Two bromines are bonded with a single bond, and each bromine is surrounded with six nonbonding electrons, often referred to as three "lone electron pairs."

.....
Br - BR.....



F.W. 159.82 g/mol

m.p. -7.25

b.p. 59.5 C

n (20 over D) not given

d 3.102 g/ml

Fp none

CAUTIONS:

Highly Toxic!!!!!!!!!!!!!!!

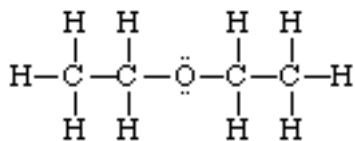
Oxidizer!!!!!!!!!!!!!!!

Basically, if you stick your finger in pure bromine, you'll pull out a bone.

Click on [this](#) to return to the index.

Diethyl Ether- CAS REGISTRY [60-29-7]

.....
..H3C - CH2 - O - CH2 - CH3..
.....



F.W. 74.12 g/mol

m.p. -116 deg C

b.p. 34.6 deg C

n (20 over D) 1.3530

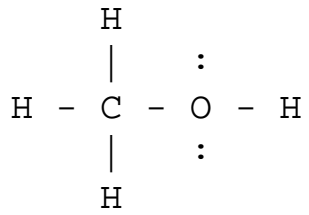
d 0.708 g/ml

comments: Flammable!!!!!!!!!!!!
It only takes one spark...

[Click here to return to the index](#)

Methanol

CAS REGISTRY [67-56-1]



F.W. 32.04 g/mol

m.p. -98 deg C

b.p. 64.6 deg C

n (20 over D) 1.3290

d 0.791 g/ml

comments: Flammable!!!!!!!!!!!!
poisonous--blindness and death...

Sodium Acetate- CAS REGISTRY [127x09x3]

.....
.....O.....
.....||..-+....
..H3C - C - O.Na...
.....



F.W. 82.02 g/mol

m.p. decomposes before melting

b.p. decomposes before boiling

n (20 over D) not applicable

d not available

[Click here to return to the index](#)

Sodium Chloride - CAS REGISTRY [7647-14-5]

.....

...+..-...

..Na..Cl..

.....



F.W. 58.44 g/mol

m.p. 804 deg C

b.p. volatizes slightly above melting temperature

1e- + Na+(l) -> Na(0)(g)

Cl-(l) -> Cl(0)(g) + e-

n (20 over D) not applicable

d 2.17 g/ml

1 g dissolves in 2.18 ml (25 deg C)

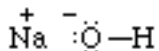
aqueous solution is neutral

[Click here to return to the index](#)

Sodium Hydroxide- CAS REGISTRY [1310-73-2]

Information taken from Merck

.....
...+..-.....
..Na..O - H..
.....



F.W. 40.01 g/mol

m.p. 318 deg C

n (20 over D) not applicable

d 2.13 g/ml

1 g dissolves in 0.9 ml (25 deg C)

aqueous solution 0.05% w/w NaOH/H₂O is p=12; a little bit makes a LOT of "basicity."

Anhydrous (completely dry) sodium hydroxide picks up water rapidly out of the air, and it looks like the pellets are "sweating."

NaOH generates considerable heat while dissolving

Interesting note: sodium hydroxide is used to "dehorn" calves.

[Click here to return to the index](#)

Acid-catalyzed Dehydration of Alcohols: cyclohexene from cyclohexanol

[Bromine](#)

[Carbon Tetrachloride](#)

[Cyclohexanol](#)

[Cyclohexene](#)

[Ethylene glycol dimethyl ether](#)
(a.k.a. 1,2-dimethoxyethane)

[Phosphoric Acid](#)

[Potassium Permanganate](#)

[Sodium Chloride](#)

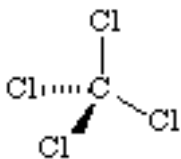
[Sodium Sulfate](#)

[Sulfuric Acid](#)

[Click here to return to the index](#)

Carbon Tetrachloride [CAS REGISTRY 56-23-5]

Carbon tetrachloride is similar to methane, except that each hydrogen is replaced with a chlorine. Each chlorine is singly bonded to the carbon, and contains three pairs of lone electrons. Carbon tetrachloride has tetrahedral geometry.



FW = 153.82 g/mol

mp = -23 deg C

bp = 77 deg C

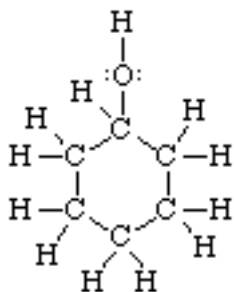
n (20 over D) = 1.4595

density = 1.594 g/ml

Flashpoint (none)

cyclohexanol- CAS REGISTRY [108-93-0]

It's a six membered oxygen ring with an alcohol group (-OH) on one of the carbons.



F.W. 100.16 g/mol

m.p. 20-22 deg C

b.p. 160-161 deg C

n (20 over D) 1.4650

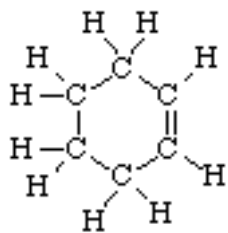
d 0.963 g/ml

Fp (flashpoint) 67 deg C

comments: Hygroscopic!

Click on [this](#) to return to the index.

Cyclohexene is a six carbon ring with five single bonds and one double bond, and the appropriate number of hydrogens on each carbon.



FW 82.15 g/mol

mp -104 deg C

bp 83 deg C

n (20 over D) 1.4460

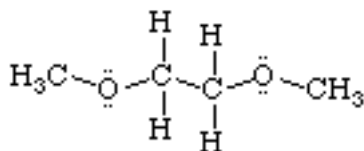
d 0.811 g/ml

F.p. -12 deg C

Cautions: Flammable liquid

1,2 Dimethoxyethane [CAS REGISTRY 110-71-4]
also known as Ethylene glycol dimethyl ether

A methoxy group is -O-CH₃
CH₃ - O - CH₂ - CH₂ - O - CH₃



F.W. 90.12 g/mol

m.p. -58 deg C

b.p. 85 deg C

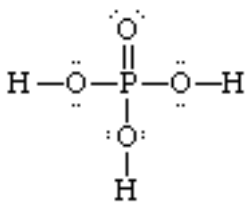
n(20 over D) 1.3791

d 0.867

flashpoint 0 deg C

Phosphoric Acid [CAS REGISTRY 7664-38-2]

A P in the center with three -OH groups and one "phosphonyl" P=O group.



oops, the .gif image has one too many -OH groups

F.W. 98.00 g/mol

m.p. 41-44 deg C

b.p. 158 deg C

n(20 over D) not given

d not given

flashpoint none

Caution: flammable liquid!

Potassium Permanganate [CAS REGISTRY 7722-64-7] There is a manganese at the center, and it is surrounded by four oxygens, three of which are doubly bonded to the manganese ("manganyls") and the fourth oxygen is singly bonded, and you know oxygen doesn't like to have only one bond, so it thus carries a minus one formal charge, and this is counterbalanced by the presence of the potassium ion. As always, the oxygens with their two bonds have two lone pairs of electrons.

.....

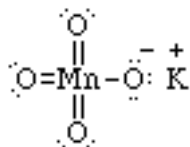
.....O.....

.....||..-...+....

.....O = Mn - O K....

.....||.....

.....O.....



FW 158.04

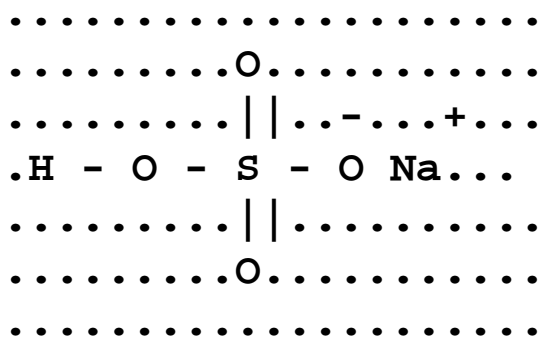
b.p. not listed

d. 2.703 g/ml

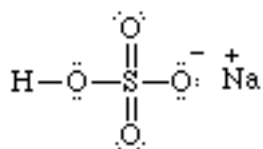
n (20 over D) not applicable

no flash point

Cautions: OXIDIZER FROM HELL! THE QUEEN OF CORROSION!

Sodium Sulfate [CAS REGISTRY 7757-82-6]

Each of the two doubly bonded oxygens (the "sulfonyls") has two pairs of lone electrons, the -OH oxygen also has two lone pairs, but the oxygen with only one bond has three lone pairs, and thus carries a formal charge of negative one, and thus attracts the sodium cation.



F.W. 142.04

m.p. 884 deg C

b.p. not available

n(20 over D) not applicable

d. 2.680 g/ml

flashpoint none

Sulfuric Acid [CAS REGISTRY 7664x93x9]

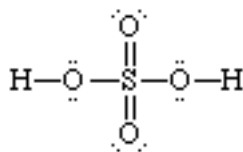
Sulfur is bonded to four oxygens: two of the oxygens have double bonds with the sulfur, and the other two oxygens have single bonds. At this point you know that oxygen likes to have two bonds, so it makes sense that the single bonded oxygens are bonded to hydrogens, with one hydrogen for each singly bonded oxygen.

```

.....
.....O.....
.....| |.....
.H - O - S - O - H...
.....| |.....
.....O.....
.....

```

Each oxygen has two pairs of lone electrons.



F.W. 98.08

m.p. not given

b.p. not available

n(20 over D) not applicable

d. 1.84 g/ml

flashpoint none

cautions: HIGHLY TOXIC! OXIDIZER

The Diels- Alder Reaction of Cyclopentadiene with Maleic Anhydride

[*cis*-5-endo-2,3-Dicarboxylic anhydride](#)

[Dicyclopentadiene](#)

[Ethyl Acetate](#)

[Ligroin](#)

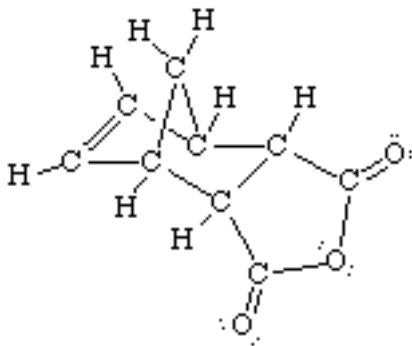
[Maleic Anhydride](#)

[Petroleum Ether](#)

[Click here to return to the index](#)

cis-5-endo-2,3-dicarboxylic anhydride [Cas Registry 129-64-6

To complicated to draw with alpha numerics



F.W. 164.16 g/mol

m.p. 165-167 deg C

b.p decomposes first

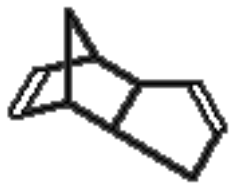
density not reported

n(20 over D) not applicable

flashpoint none

When a manufacturer prepares cyclopentadiene, the product undergoes a second process to form a dimer of cyclopentadiene, which is dicyclopentadiene.

Impossible to draw with alphanumeric.



F.W. 98.06 g/mol

d 1.48 g/ml

m.p. 53 deg C

b.p. 202 deg C

Ligroin and Petroleum Ether [CAS REGISTRY 8032-32-4]

No structure appropriate. Both ligroin and petroleum ether are fractions of a petroleum product extracted from the ground called "naptha."

Aldrich lists ligroin as boiling at 60 to 80 deg C, with a refractive index (20 over D) of 1.3760, a density of 0.656, and a flashpoint of -26 deg C. I'm just a little more than a little bit suspicious, because I don't think any two shipments of ligroin are identical, hence the lack of precision in defining the boiling point. How the heck, then, can they precisely know the refractive index, the density, and the flashpoint? Just my two cents.

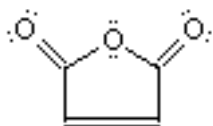
Cautions: Flammable Liquid

Aldrich lists petroleum ether as boiling from 35 to 60 deg C, with a refractive index (20 over D) of 1.3630, a density of 0.640, and a flashpoint of -49 deg C. Megadittos on the suspicion.

Maleic Anhydride [CAS Registry 108-31-6]

```
.....====.....  
.....|...|.....  
.....//\./\.....  
.....O...O...O.....
```

Maleic anhydride a five membered ring with a double bond, and an oxygen on the point of the pentagon opposite of the double bond. Two carbonyl groups (C=O) are positioned on both sides of this oxygen.



F.W. 98.06 g/mol

m.p. 54 to 56 deg C

b.p. 200 deg C

density not given

n(20 over D) not applicable

Flash Point 103 deg C

Acid-catalyzed Dehydration of Alcohols: cyclohexene from cyclohexanol

[Benzoic Acid](#)

[Ethyl p-Aminobenzoate](#)

[Hydrochloric Acid](#)

[Magnesium Sulfate](#)

[Methylene Chloride](#)

(a.k.a. 1,2-dimethoxyethane)

[Naphthalene](#)

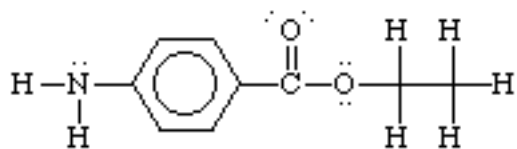
[Sodium Hydroxide](#)

Ethyl 4-aminobenzoate- CAS REGISTRY [94-09-7]

O

||

H₂N - C₆H₄ - C - O - CH₂ - CH₃



F.W. 165.19 g/mol

m.p. 88-90 deg C

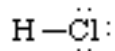
b.p. it decomposes first

n (20 over D) not applicable

d not given

Hydrochloric Acid- CAS REGISTRY [7647-01-0]

H-Cl



F.W. 36.46 g/mol

m.p. not applicable

b.p. not applicable--since the "stuff" you will be working with is aqueous (it pulls water vapor out of the air until only 37% of the mass is acid), you can say it boils a 100 deg C.

n (20 over D) not reported--I'm sure it is a constant--you probably don't want to be putting acids on the refractometer, though, because acids might attack the glass structure (I don't know off hand if quartz is acid resistance or not.)

d not given

comments: Corrosive

[Click here to return to the index](#)

Magnesium Sulfate - CAS REGISTRY [7487-88-9]

+ -

Mg SO

4



F.W. 120.37 g/mol

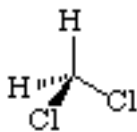
m.p. not available --perhaps the sulfate decomposes first

b.p. not applicable
n (20 over D) not applicable

d not applicable

Dichloromethane- CAS REGISTRY [75-09-2]

It's a methane with two chlorines replacing two hydrogens



F.W. 84.93 g/mol

m.p. -97 deg C

b.p. 40 deg C

n (20 over D) 1.4240

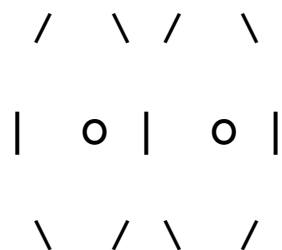
d 1.325

Fp (flashpoint) none

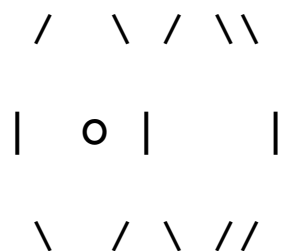
Click on [this](#) to return to the index.

Naphthalene [CAS # 91-20-3]

Kind of crazy--it's drawn as two aromatic rings, fused together,



But actually, the chemistry that naphthalene undergoes indicates that one ring is aromatic, and the other acts as a conjugated diene, but its ability to undergo addition reactions.

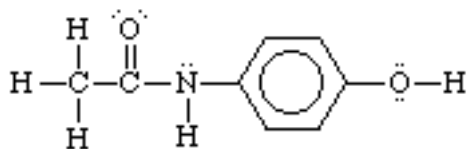


F.W. 128.17

m.p. 80-82 deg C

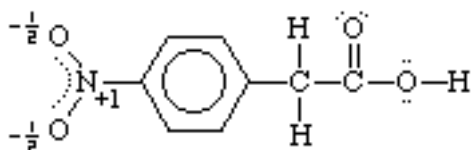
b.p. 218 deg C

Flashpoint 78 deg C



103-90-2

Acetaminophen



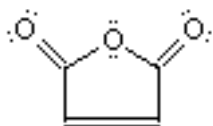
104-03-0

4-Nitrophenylacetic Acid



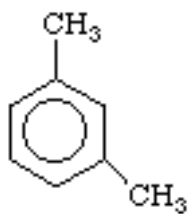
106-42-3

p-Xylene



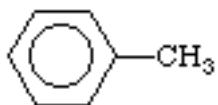
108-31-6

Maleic Anhydride



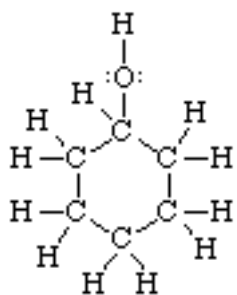
108-38-3

m-Xylene



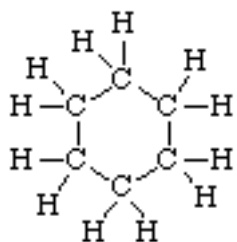
108-88-3

Toluene



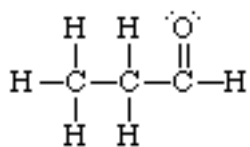
108-93-0

Cyclohexanol



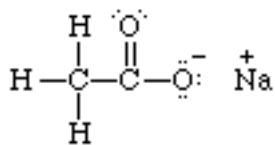
110-82-7

Cyclohexane



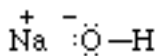
123-38-6

Propionaldehyde



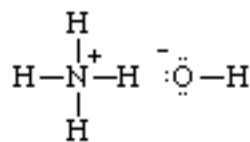
127-09-3

Sodium Acetate



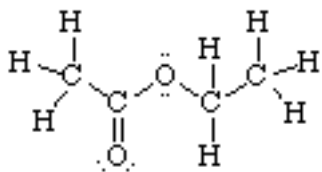
1310-73-2

Sodium Hydroxide



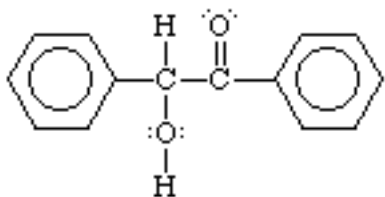
1336-21-6

Ammonium Hydroxide



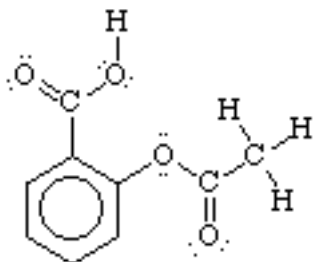
141-78-6

Ethyl Acetate



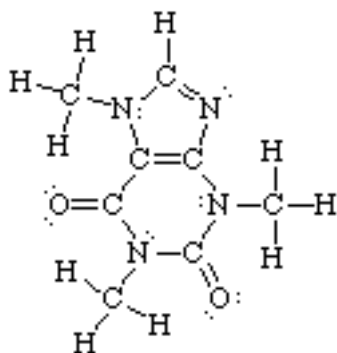
579-44-2

Benzoin



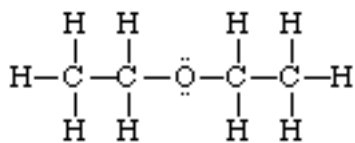
50-78-2

Acetylsalicylic Acid



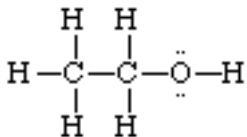
58-08-2

Caffeine



60-29-7

Diethyl Ether

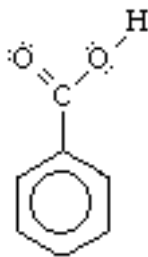


64-17-5

Ethanol

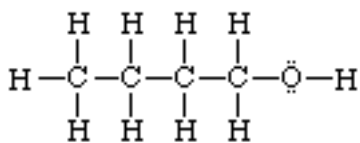
64-19-7

Acetic Acid (is wrong: it goes methyl, carbonyl, OH)



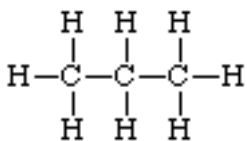
65-85-0

Benzoic Acid



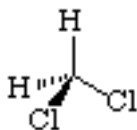
71-36-3

Butanol



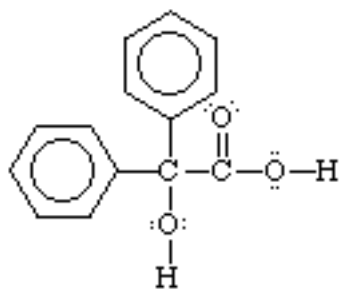
74-98-6

Propane



75-09-2

Dichloromethane

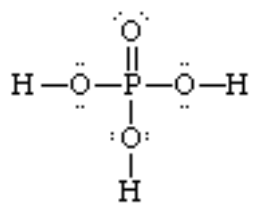


76-93-7



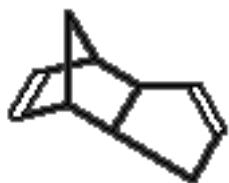
7647-01-0

Hydrochloric Acid



7664-38-2

Phosphoric Acid



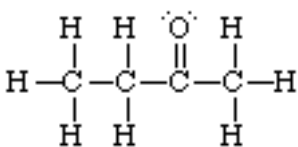
77-73-6

Dicyclopentadiene



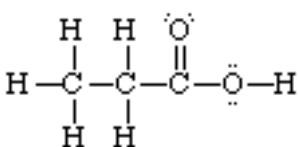
7726-95-6

Bromine



78-93-3

2-Butanone



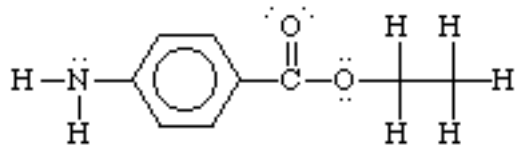
79-09-4

Propionic Acid



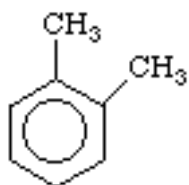
91-20-3

Naphthalene



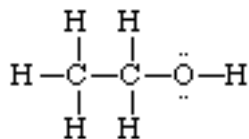
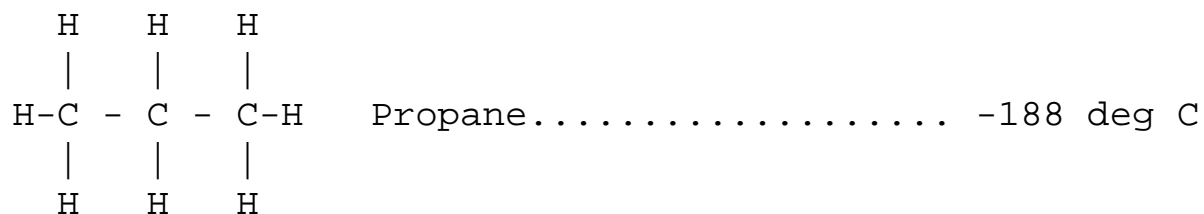
94-09-7

Ethyl 4-Aminobenzoate

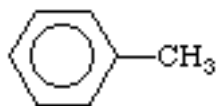
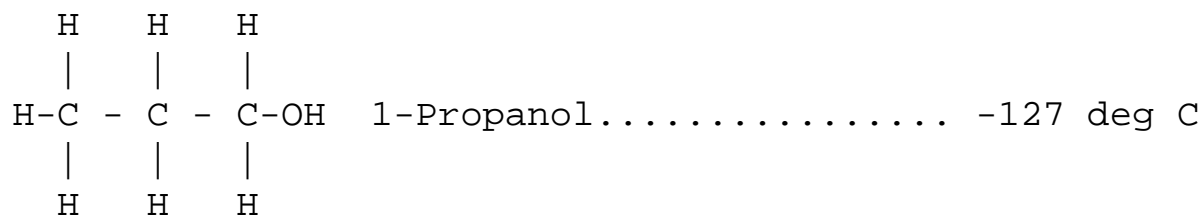


95-47-6

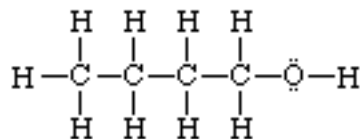
o-Xylene



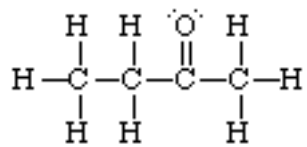
[Ethanol..... -130 deg C](#)



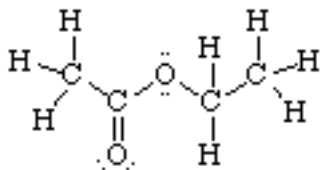
[Toluene..... -93 deg C](#)



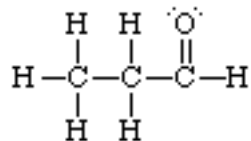
[1-Butanol..... -90 deg C](#)



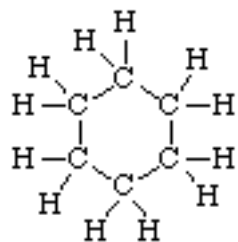
2-Butanone..... -87 deg C



Ethyl Acetate..... -84 deg C



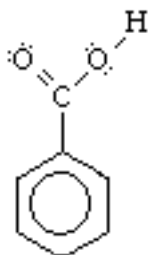
1-Propionaldehyde..... -81 deg C



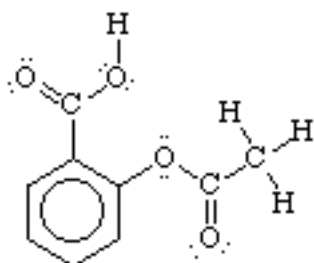
Cyclohexane..... 7 deg C



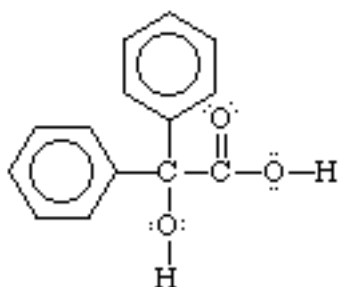
[Ammonium Hydroxide..... 16 deg C](#)



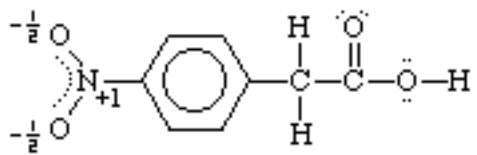
[Benzoic Acid..... 122 deg C](#)



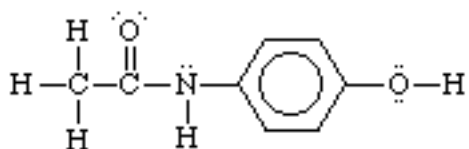
[Acetosalicic Acid..... 138 deg C](#)



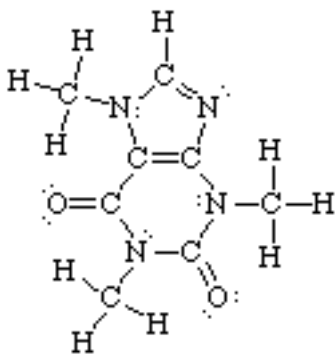
[Benzilic Acid..... 140 deg C](#)



[4-Nitrophenylacetic Acid . 154 deg C](#)

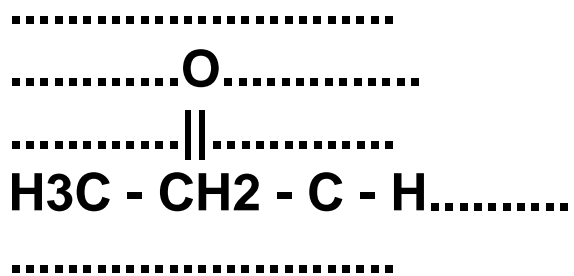


[Acetaminophen..... 169 deg C](#)



[Caffeine..... 234 deg C](#)

1-propionaldehyde- CAS REGISTRY [123-38-6]



F.W. 58.08 g/mol

m.p. -81 deg C

b.p. 46 to 50 deg C

n (20 over D) 1.3650

d 0.805 g/ml

Fp (flashpoint) -26 deg C

comments: Flammable liquid!

Click on [this](#) to return to the index.

Recrystallization often is a two part process, with one part keeping the desired compound in a precipitant form while impurities stay dissolved and wash away (that would be the aspiration step, or the second half of last weeks lab), and the other being to keep impurities in the solid form (or bound to something like charcoal), and to have the desired compound stay dissolved and wash through the filter paper (that would be the first filtration through the large glass funnel.)

A lot of times water is used for recrystallization of organic chemicals because they DON'T want to dissolve in such an extremely polar liquid (and it's so cool that water is so cheap!) but at 100 deg C, the temperature weakens the intermolecular attractions, forcing the organic to fall apart. And of course at room temp, the organic chemical precipitates almost completely out of solution.

So what you probably end up doing is taking 50 mls of distilled deionized water (as pure as you can get it), heat it to a boil, and then carefully start "dumping" the impure chemical into the water and keep doing that until no more will dissolve. You will notice that the temperature drops somewhat as you add the room temperature organic. You then let the system heat back to a boil, and then add just enough water (if it is necessary to add a little more) until the organic completely dissolves, and then pour the liquid into a large watch glass, and watch it crystallize back a powder with a purer white than before (most organics reflect all the wavelengths in the visible spectrum (400 nm to 700 nm) and this explains the typical white appearance.

Why the need to recrystallize in water? Odds are the organic was prepared in some organic (nonpolar) solution, possibly using inorganic catalysts, and those inorganic catalysts were not "comfortable" in the hostile organic environment of that nonpolar solvent, so they took refuge next to the polar character of the organic (the carboxyl groups are a great place for an inorganic to hide from a hostile nonpolar solvent) and the organic chemical crystallized around the inorganic.

Once in water, the inorganic can dissolve, and it bids farewell to the organic, and the organic crystallizes with another organic molecule, which is what it would have preferred to do all along, anyway.

Now if you contaminate is a side reaction chemical (in your Organic text you probably have already encountered instances where a reaction can produce "competing products") then things are a little (to a lot) more difficult because side reactants have the same function groups and similar physical properties (e.g. solubility in a given solvent, etc.)

Organic Reactions

[Construction Alert]

This file does not work for a text-reader.

[Acid Chloride](#)

[Alcohol](#)

[Aldehyde](#)

[Amide](#)

[Anhydride](#)

[Carboxylic Acid](#)

[Ketone](#)

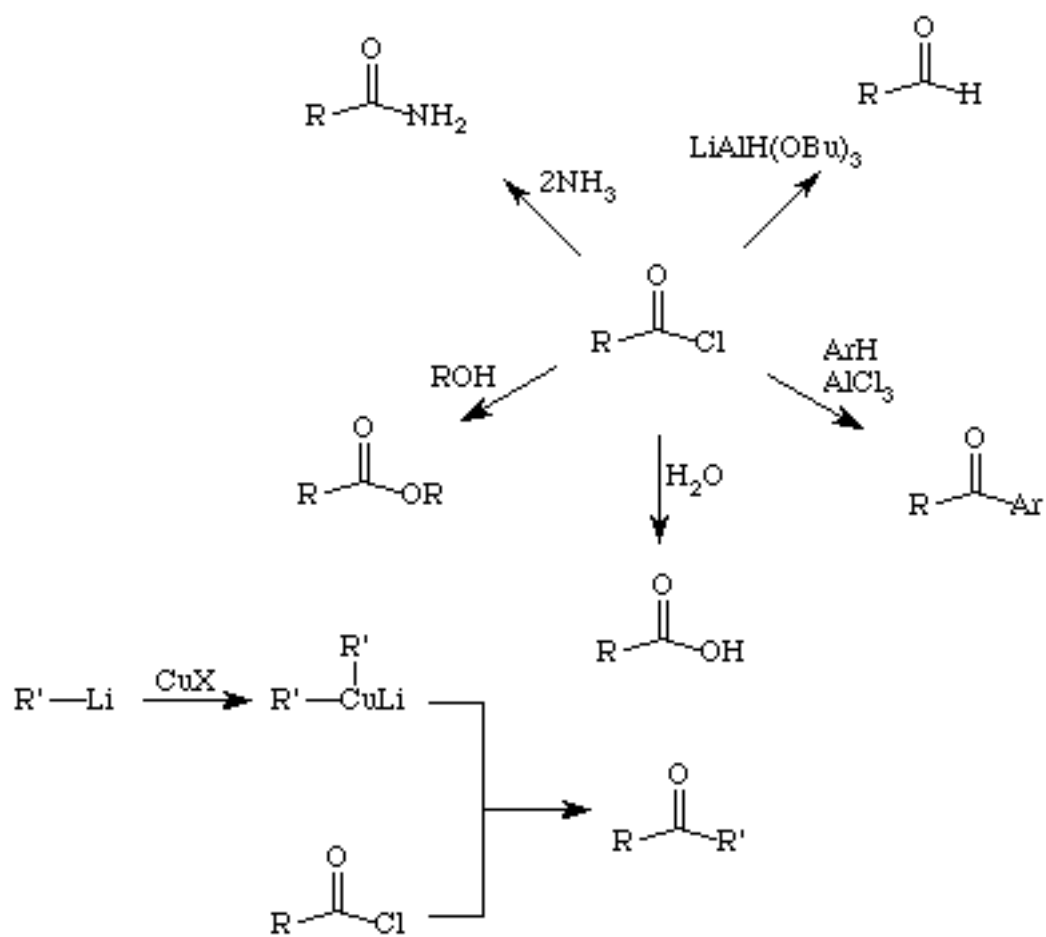
[Nitrate](#)

[Nitrile](#)

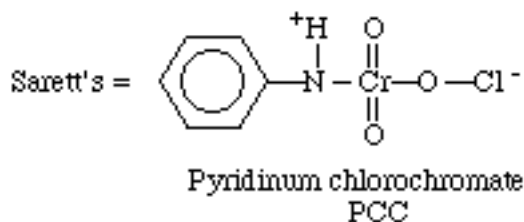
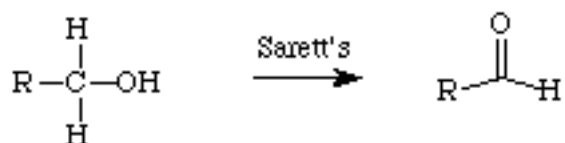
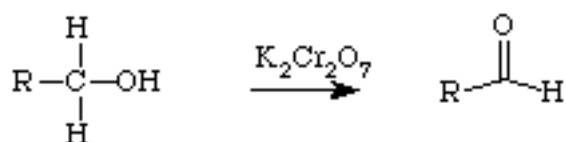
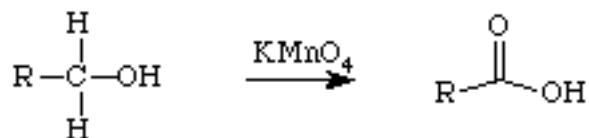
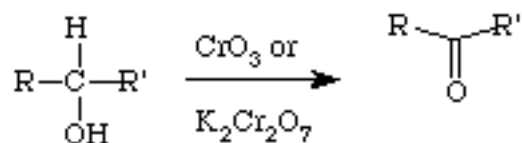
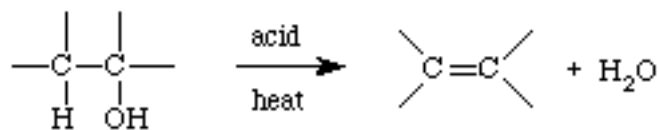
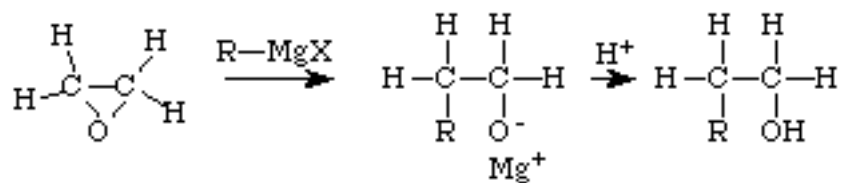
[One after the other](#)

Last Update- January 8, 1995- wld

Acid Chlorides

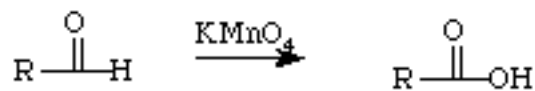
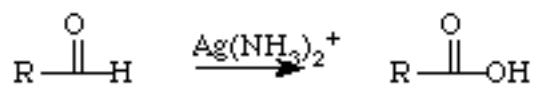
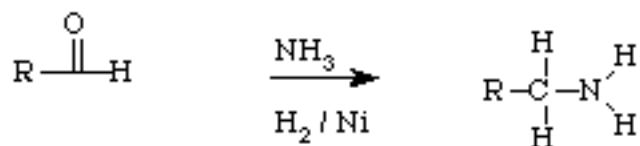
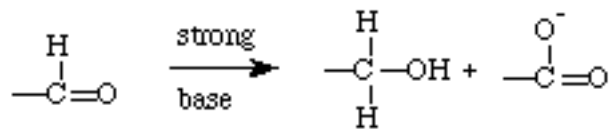
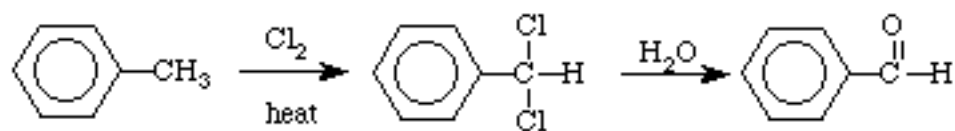


Alcohols

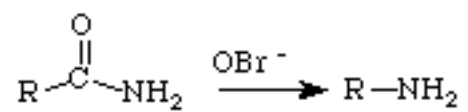


You should understand how this beast got its name

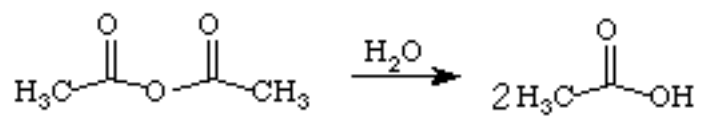
Aldehydes



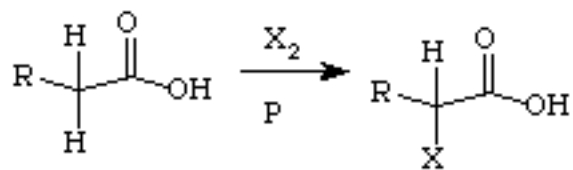
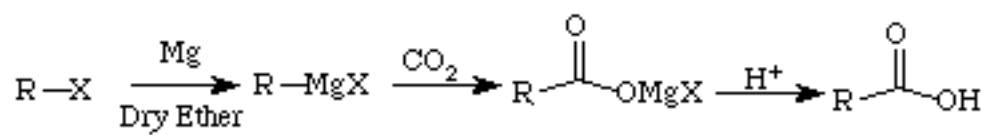
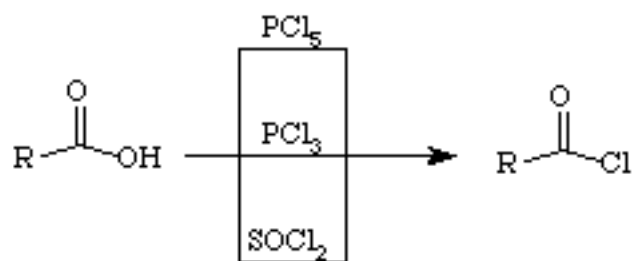
Amides



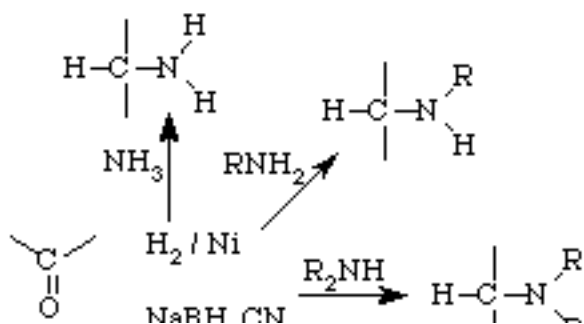
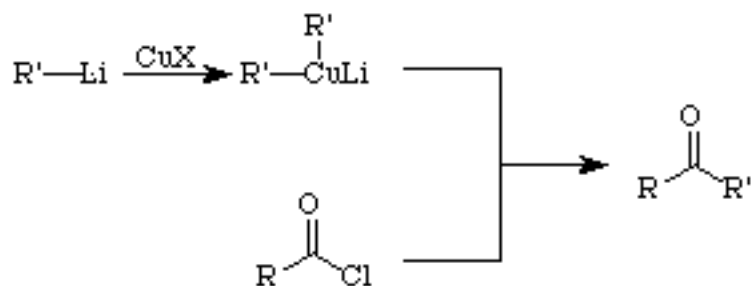
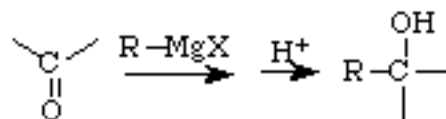
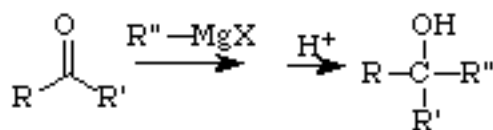
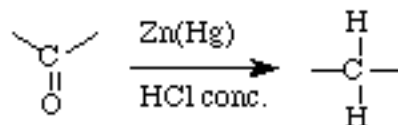
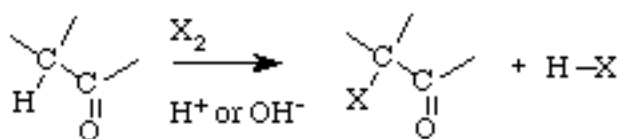
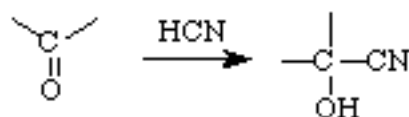
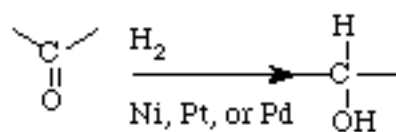
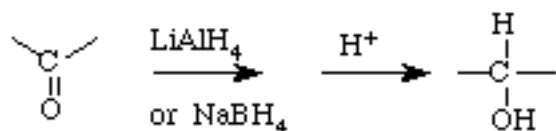
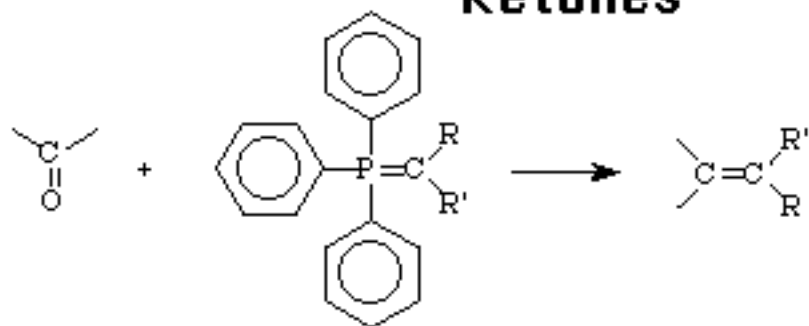
Anhydrides



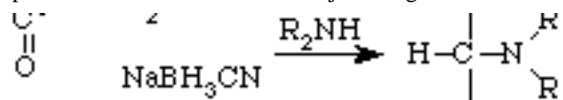
Carboxylic Acids



Ketones

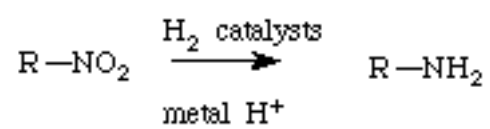


I believe the use of R for each alkyl group does NOT imply they all have to be the same.

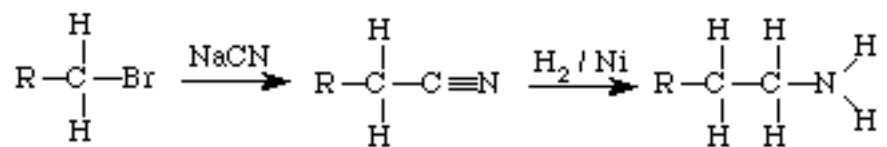
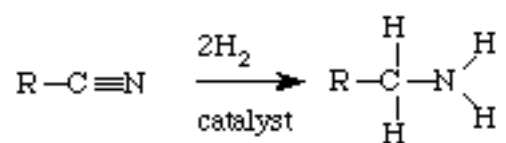


I believe the use of R for each alkyl group does NOT imply they all have to be the same.

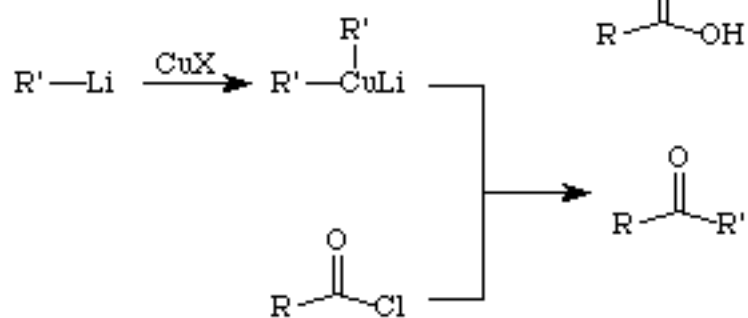
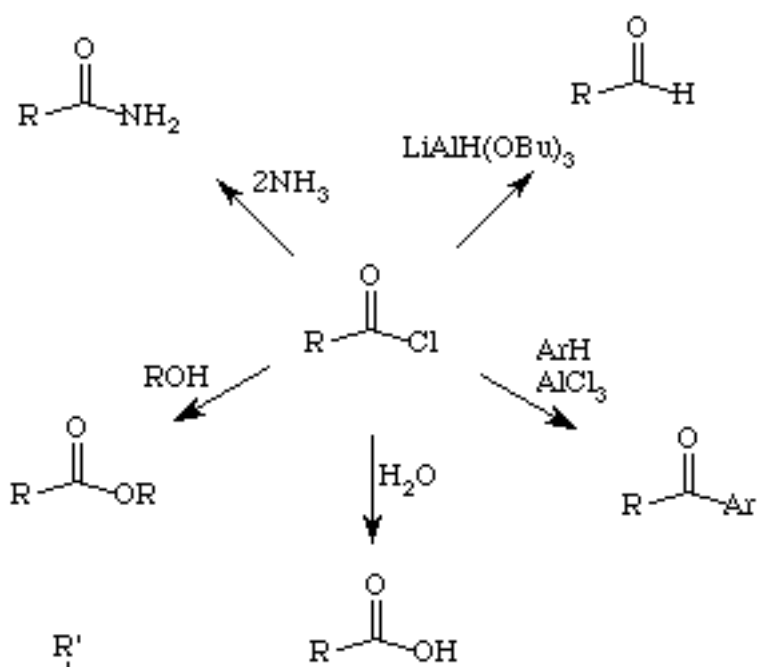
"Nitrates?"



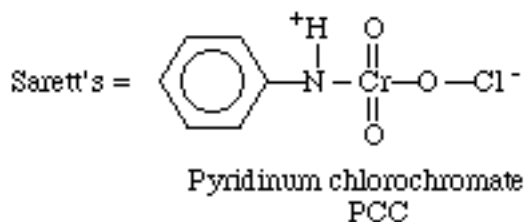
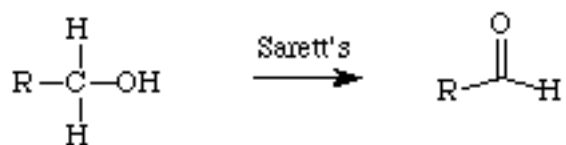
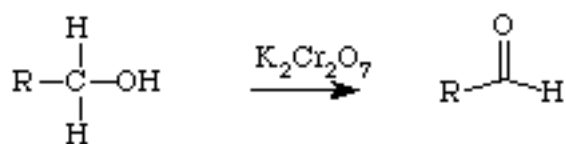
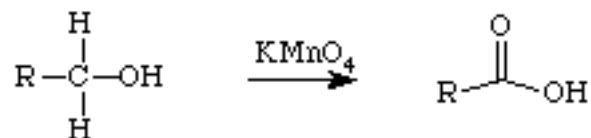
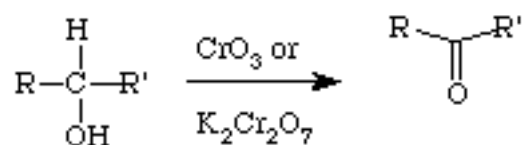
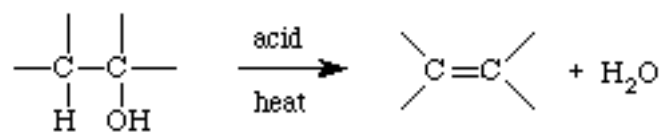
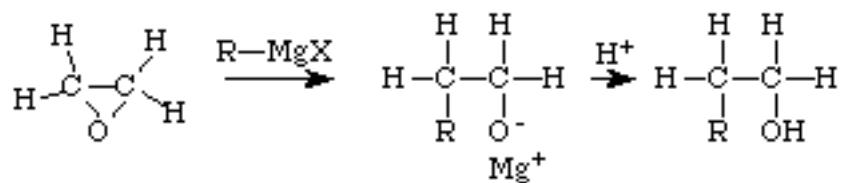
Nitriles



Acid Chlorides

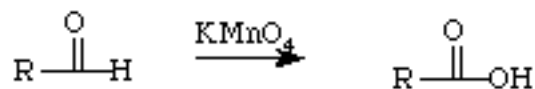
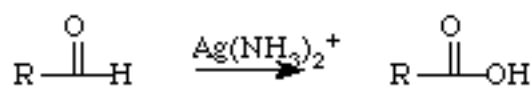
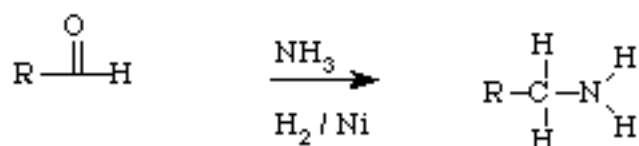
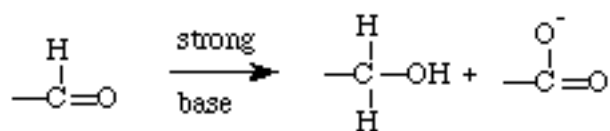
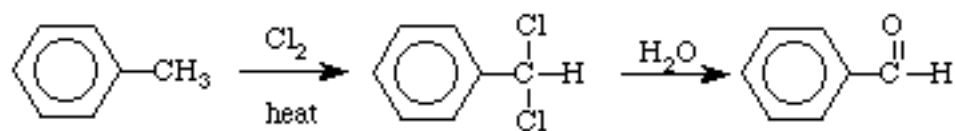


Alcohols

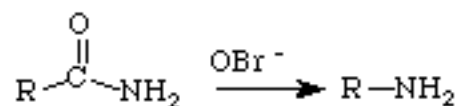


You should understand how this beast got its name

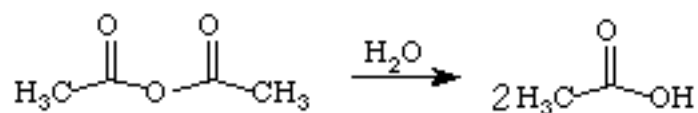
Aldehydes



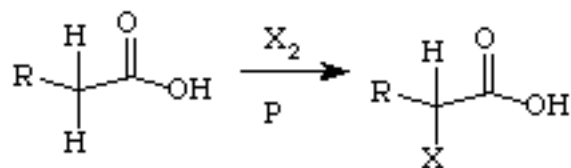
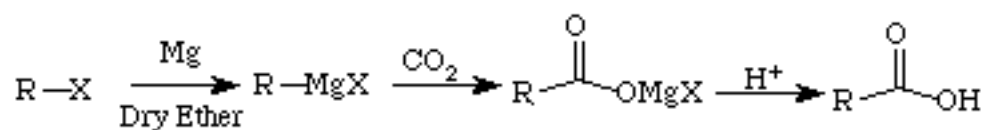
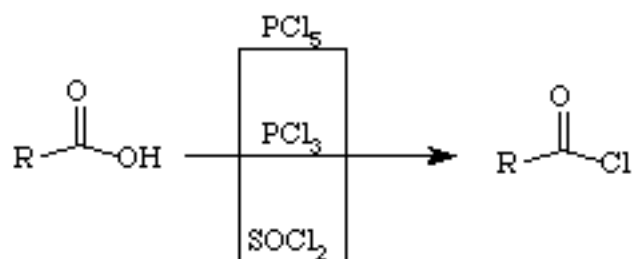
Amides



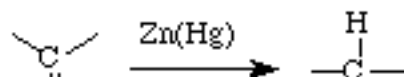
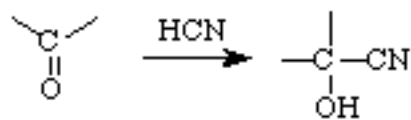
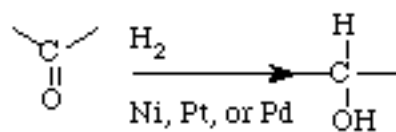
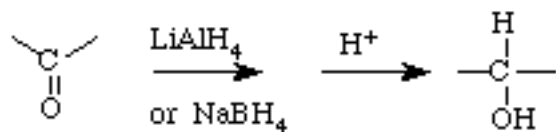
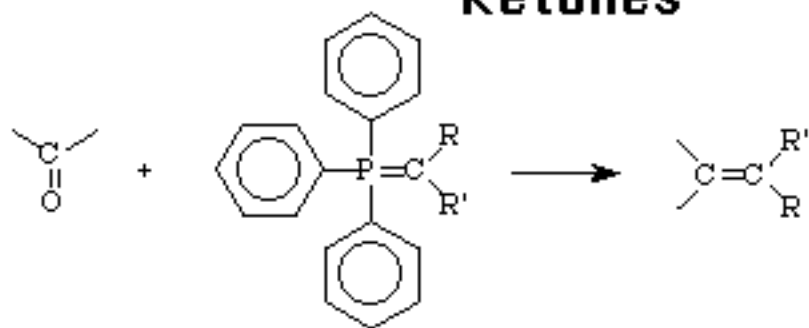
Anhydrides

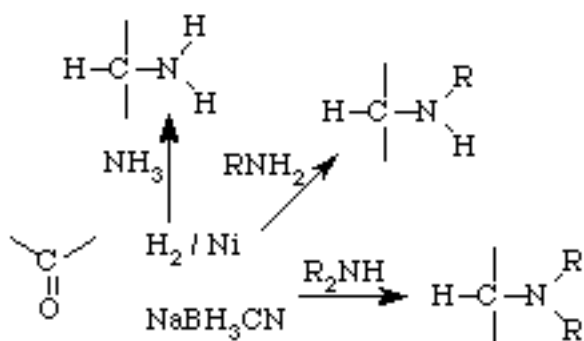
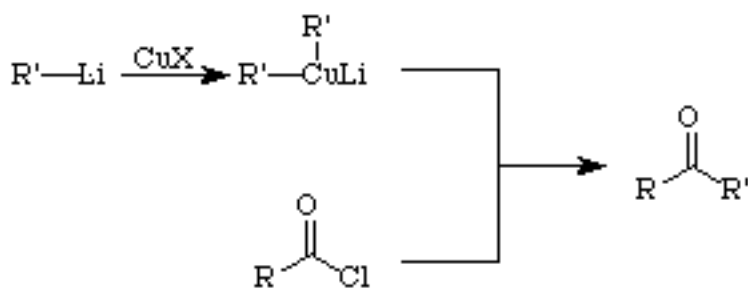
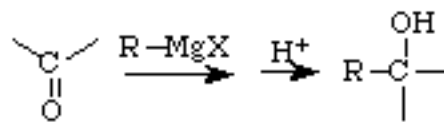
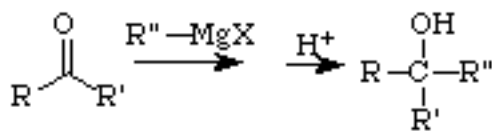
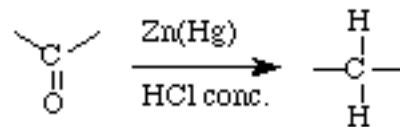
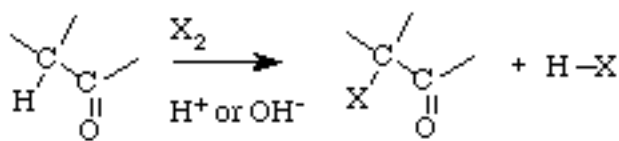


Carboxylic Acids



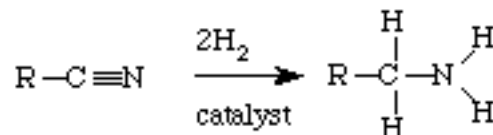
Ketones





I believe the use of R for each alkyl group does NOT imply they all have to be the same.

Nitriles



"Nitrates?"

