REVIEW

OUTLINE

1. Reactions

2. Spectroscopy and Stereochemistry

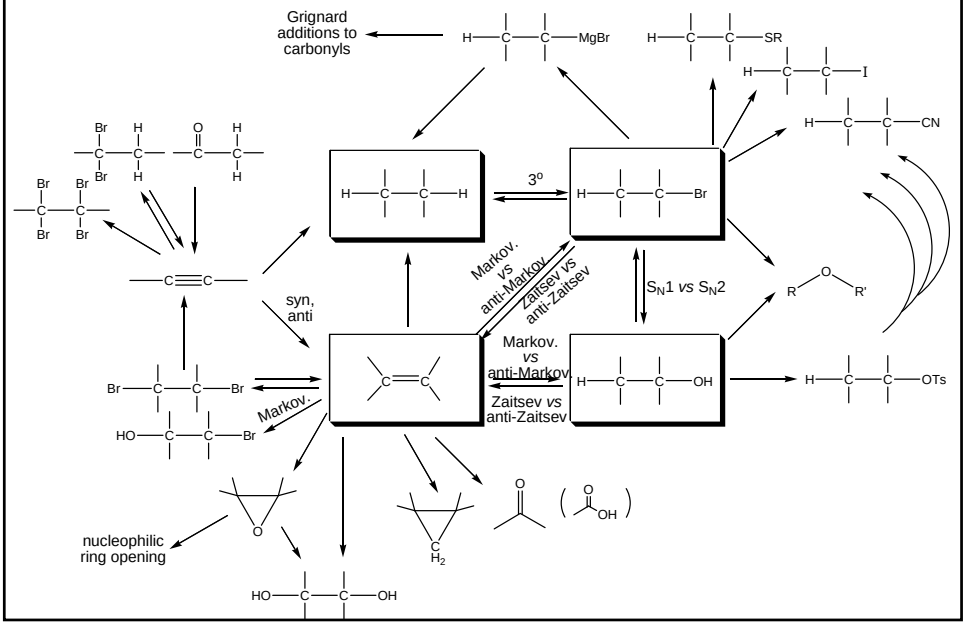
3. Preview of Final

REVIEW OF REACTIONS

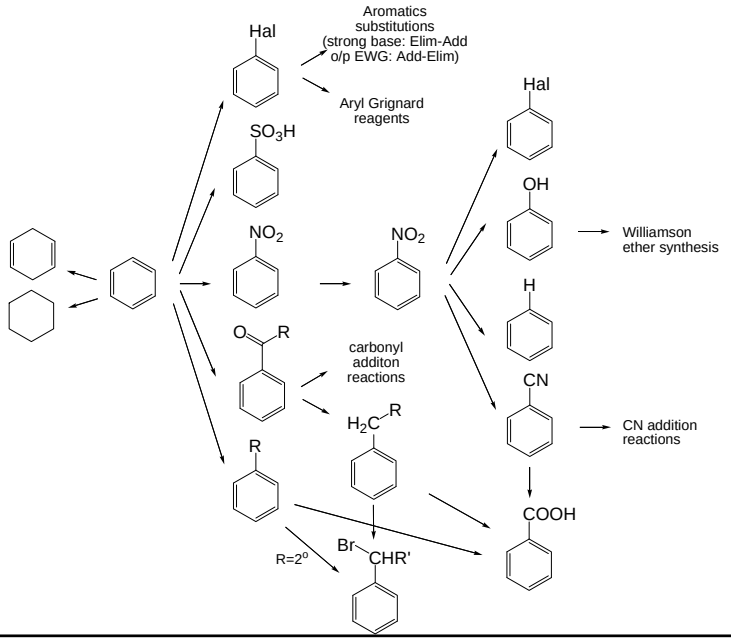
While the following schemes group reactions by type of functional group, recognize that functional groups often undergo a certain type of reaction (e.g., substitution, addition, elimination), and react by a certain type of mechanism, based on their nucleophilicity or electrophilicity.

REACTIONS FROM ORGANIC-I

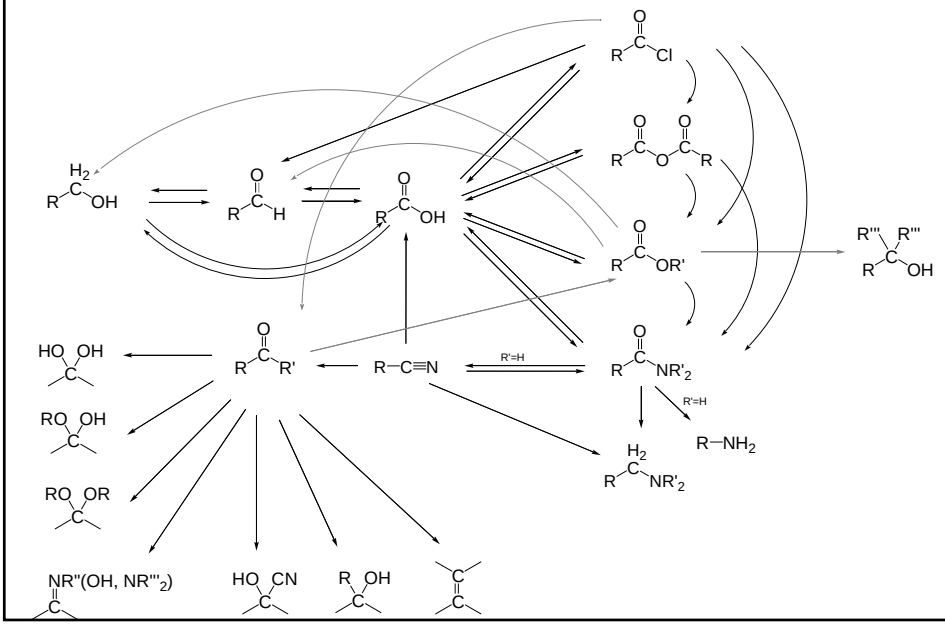
Substitutions (S_N), Additions (C=C,C≡C), Eliminations



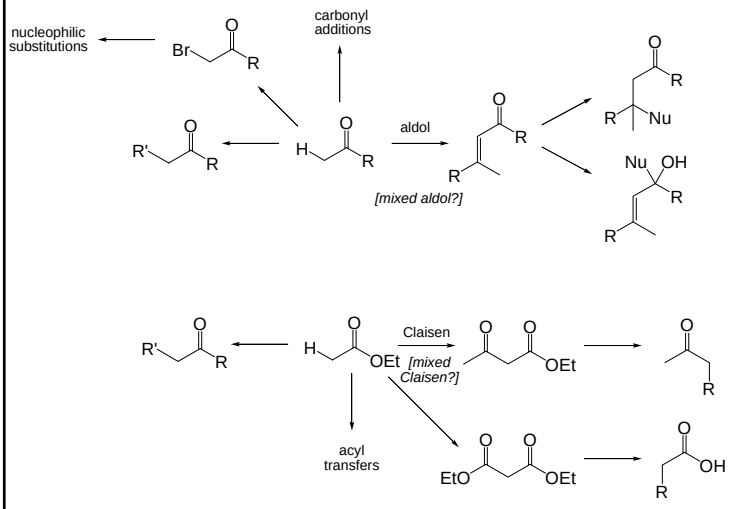
REACTIONS OF AROMATIC COMPOUNDS



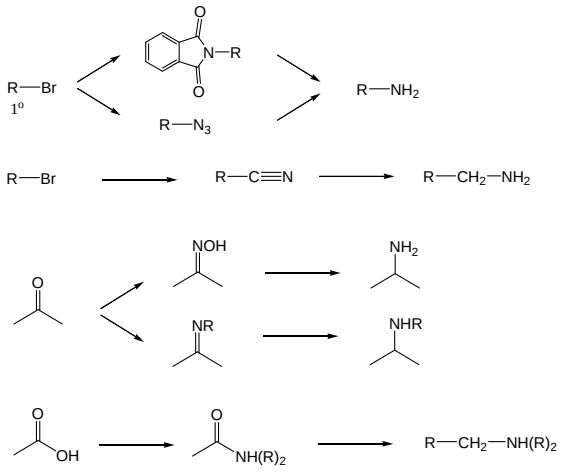
REACTIONS OF CARBONYL COMPOUNDS AND ACID DERIVATIVES



REACTIONS OF ENOLATES

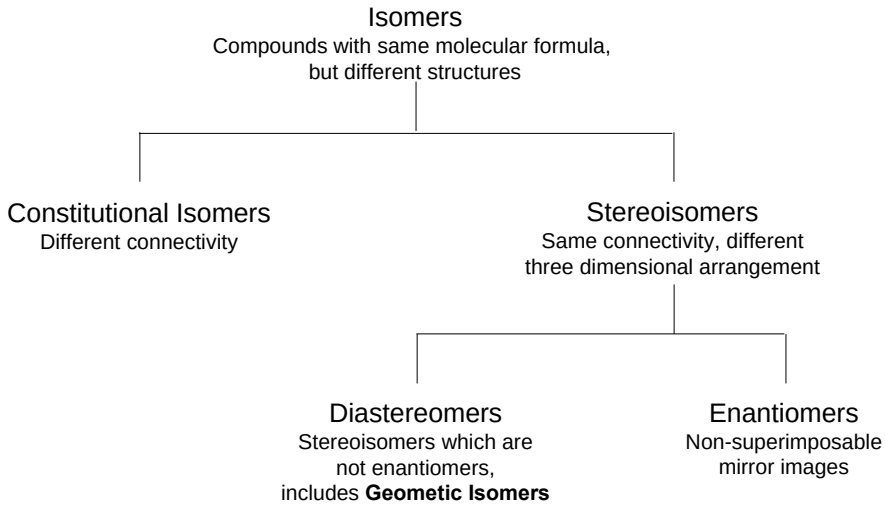


SYNTHESIS OF AMINES



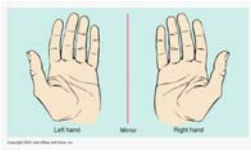
REVIEW OF STEREOCHEMISTRY AND SPECTROSCOPY

RECOGNIZING ISOMERS



CHIRALITY: ENANTIOMERS

S:5.1-5
Prob 5.30,31,33, 35a,b,f

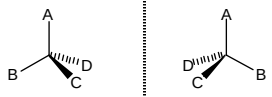


An object which has a non-superimposable mirror image is chiral (the opposite of chiral is "achiral"). Another test for chirality is to assess whether the object itself has a mirror plane of symmetry or point of symmetry (point of inversion).

Molecules can be *chiral*. Pairs of molecules which are non-superimposable mirror images of one another are called *enantiomers*. Enantiomers are examples of *stereoisomers*: molecules which differ only in the spatial arrangement of atoms.

Molecules with a single carbon atom bearing *four different* substituents can exist as a pair of enantiomers which differ in the arrangement ("configuration") of these substituents.

The carbon is *stereogenic*
The carbon is a *stereocenter*



You must be able to recognize when pairs of molecules are identical (superimposable) or entiomers (non-superimposable mirror images)

Designating Configuration

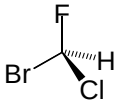
Stereocenters are designated as having either *R*- or *S*-configurations….

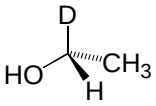
- Assign priorities to the substituents using the Cahn-Ingold-Prelog system (briefly, atoms are ranked in order of atomic number; if two atoms are identical, the next set of attached atoms is considered).
- View the molecule with the lowest priority (4) substituent pointing away from you.
- Trace from highest priority (1) to second priority (2), to third (3)….

Clockwise = *R*

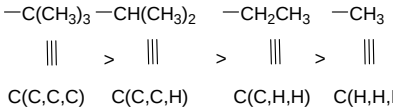
Counterclockwise = *S*

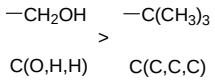
e.g.,

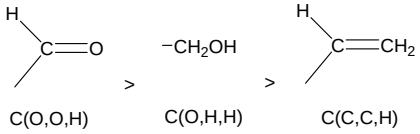




D = deuterium = ^{2}H;
D > H







Optical Rotation

The observed rotation is α

The observed specific rotataion is $[\alpha] = \alpha / c \cdot l$

where c = concentration in g/mL and l = pathlength in dm
(1 dm = 10 cm = 10^{-1} m)

The observed rotation, α or $[\alpha]$ depends on solvent, temperature and wavelength of the polarized light. Generally the sodium D line is used for the light sorce and the experiment is done at room temperature, 25 °C.

The specific rotation is then noted as $[\alpha]_D^{25}$ (conc./solvent)

The specific rotation of an optical pure chiral compound is a "property" like melting point or boiling point

The specific rotation of a given sample depends on it "optical purity"

Optical Purity

Problem: The [α] of the *R*-isomer of compound **A** is +100.
What is the [α] of the *S*-isomer? What is the [α] of a equal mixture of the *R*- and *S*-isomers (racemic mixture)?

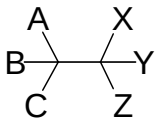
The % excess amount of one enanatiomer over the other is called the *enantiomeric excess* (ee). *e.g.*, 100 % one enantiomer, ee = 100 %;
50% one enantiomer, 50% other enantiomer, ee = 0 %.

Problem: The [α] of the *R*-isomer of compound **A** is +100.
The [α] of a certain mixture of *R*- and *S*-isomers of compound **A** is -50 °.
What is the ee of this mixture? What is the % *R*-isomer in this mixture?

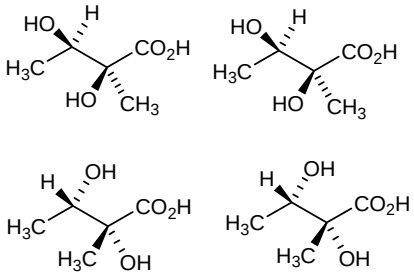
STEREOISOMERS WITH MORE THAN ONE STEREOCENTER

S:5.11-12
Prob:5.33,34,
35c-e,41

Diastereomers



There are four stereoisomers

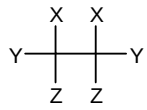


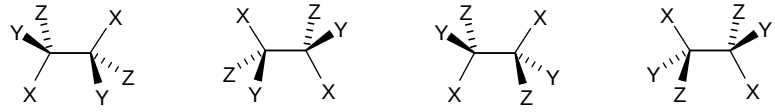
For a molecule with *n* stereocenters, there are a maximum of 2^n stereoisomers.

Stereoisomers which are not mirror images of each other are called *diastereomers*.

Meso Compounds

If the sets of substituents on stereogenic centers are identical there will be fewer than 2^n stereoisomers.



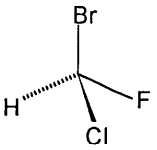


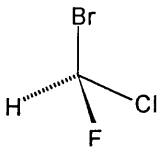
Compounds with stereogenic centers which are *not* chiral are called *meso compounds.*

Meso compounds possess a point or plane of symmetry

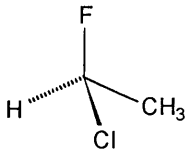
For the following sets of structures, which pairs are enantiomers?

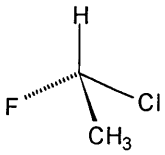
I.



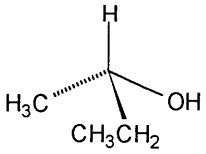


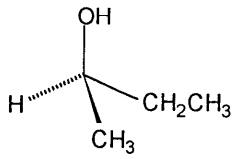
II.





III.



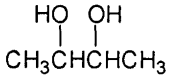


a) I, II b) I, III c) II, III d) none

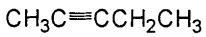
Trans-2-pentene was reacted with bromine in carbon tetrachloride to give two 2,3-dibromopentanes. What are the configurations of the two compounds?

a) 2R, 3R and 2S, 3S
b) 2S, 3S and 2R, 3S
c) 2S, 3R and 2R, 3S
d) 2R, 3S and 2S, 3S

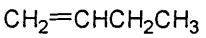
Which of the following molecules can have diastereomers but not enantiomers?



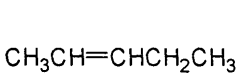
I



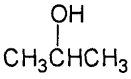
II



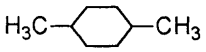
III



IV



V



VI

a) I, III b) III, IV c) II, V d) IV,VI

IDENTIFICATION OF ORGANIC COMPOUNDS

1. COMBUSTION ANALYSIS ⇒ EMPIRICAL FORMULA

Measure mass of CO_2 and H_2O formed by combustion of a known mass of compound; data cited as mass % of each element present.

2. MASS SPECTRUM ⇒ MOLECULAR WEIGHT

3. EMPIRICAL FORMULA, MOLECULAR WEIGHT ⇒ MOLECULAR FORMULA

Molecular formula is an integral number of times the empirical formula

4. MOLECULAR FORMULAS; DETERMINATION OF "SODAR"

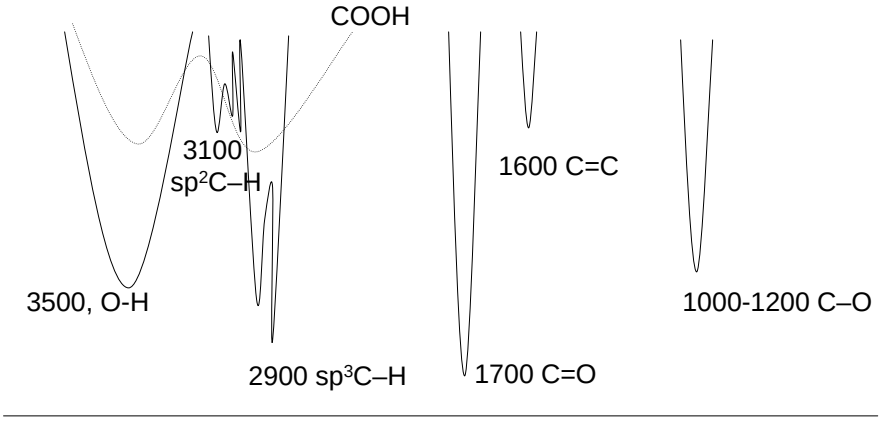
Sum of double bonds or rings ("SODAR")

For C,H,O,N,Hal: "SODAR" = (2#C + 2– #H – #Hal + #N) / 2

If SODAR calculated from empirical formula is not a positive integral (or 0), this cannot be the molecular formula.

5. INFRARED SPECTROSCOPY

Bonds vibrate at characteristic frequencies – absorb irrad\ation in IR region of the electromagnetic spectrum

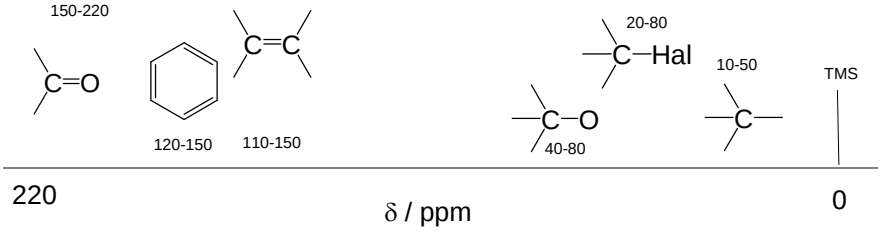


5. ^{13}C NMR SPECTROSCOPY

For ^{13}C nuclear magnetic resonance spectra:

(a) the number of peaks ⇒ number of different types of carbon

(b) the chemical shift ⇒ proximity to functional groups



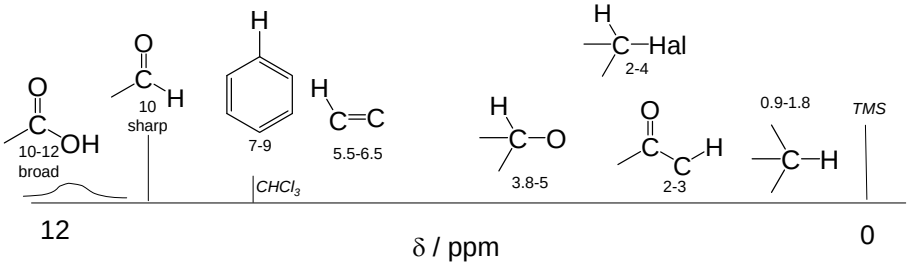
6. ^{1}H NMR SPECTROSCOPY

For a ^{1}H nuclear magnetic resonance spectrum:

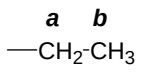
(a) number of signals ⇒ number of different types of proton

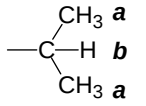
(b) integral ⇒ relative number of each type of proton

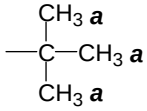
(c) chemical shift ⇒ proximity to functional groups

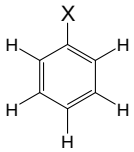


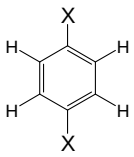
(d) coupling ⇒ the number of *adjacent* protons

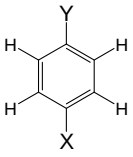


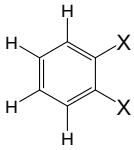








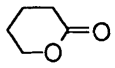




What is the most likely structure for a compound that has the molecular formula, $C_5H_8O_2$, and the following proton NMR spectral data?

singlet	δ	2.2	(3H)
singlet	δ	3.7	(3H)
singlet	δ	5.5	(1H)
singlet	δ	6.0	(1H)

a) $CH_2{=}CHCO_2CH_2CH_3$

b) 

c) $CH_2{=}C(CH_3)CO_2CH_3$

d) $CH_2{=}C(CH_3)COCOCH_3$

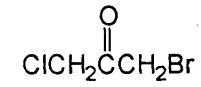
What kind of compound has a very broad IR band in the region of 3300 cm^{-1}?

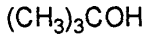
a) hydrocarbon b) aromatic c) alcohol d) halide

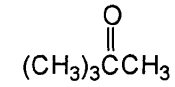
Which of the following compounds has a sharp IR absorption band at 1710 cm^{-1} and a broad band at 3300 cm^{-1}?

a) acetic acid b) ethanol c) acetone d) diethyl ether

Which of the following has a proton NMR consisting of two singlets of equal intensity and an IR spectrum having a strong band in the 1700 cm^{-1} region?

a) 

b) 

c) 

d) 

NEXT LECTURE…..

THE FINAL – WHAT TO EXPECT….

- ACS standardized final
- 70 multiple choice questions
- The final is *REQUIRED!*
- Your grade on the final exam will be the *higher* of:
  - your raw score (# x 1.5) (max. = 105!)
  - your national %ile
- Course grade (out of 700 points):

$$\underbrace{\text{E1-E5} + \text{HW/HWeb/PRS}}_{\text{(drop lowest)}} + (\textbf{final exam})$$

≥87.5% = A; ≥72.5% = B; ≥65% = C; ≥55% = D.

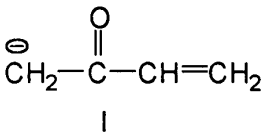
MULTIPLE CHOICE QUESTIONS!

Which of the following molecules have bond angles of about 109.5 degrees?

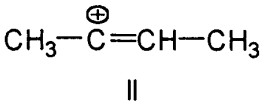
CS_2	BCl_3	$AlCl_4^-$	NH_2^-	NH_4^+
I	II	III	IV	V

a) I, II, IV b) III, IV, V c) II, III, IV d) I, III, V

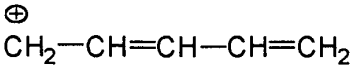
Which of the following ions are stabilized by resonance?



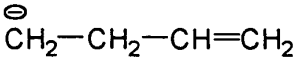
I



II



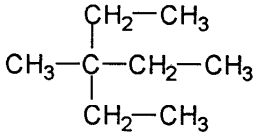
III



IV

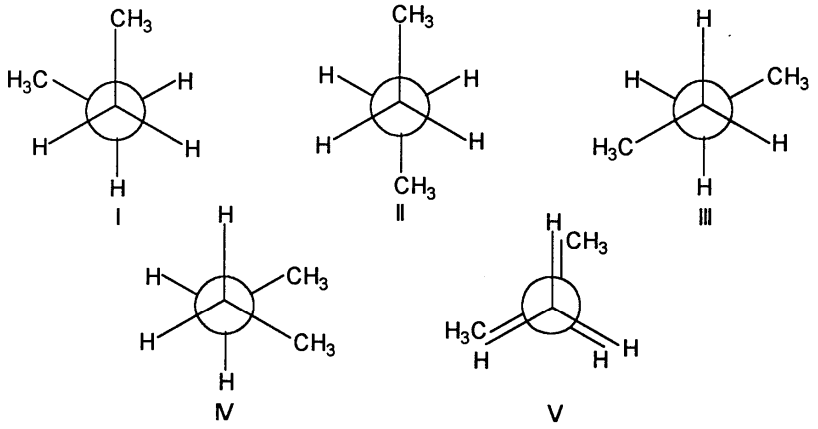
a) I, II b) I, III c) II, IV d) III, IV

What is the IUPAC name for the compound having the following structure?



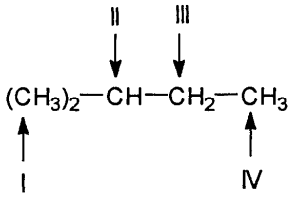
a) 2,2-diethylbutane
b) 2,2,2-triethylethane
c) 3-methyl-3-ethylpentane
d) 3-ethyl-3-methylpentane

Which of the following are anti forms?



a) I and IV b) II and III c) II and IV d) III and V

When 2-methylbutane and bromine react with light, what is the order of increasing amounts of products having bromine in the indicated positions (least first)?



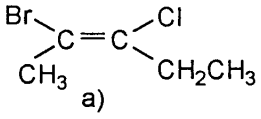
a) I,II,III,IV b) IV, II, III, I c) I, IV, III, II d) IV, I, III, II

What is the correct description for the hybridized bonds (C-C, C-H) in ethylene?

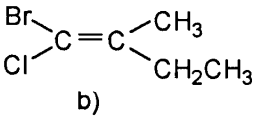
a) sp-sp, sp-s b) sp^2-sp^2, sp^2-s c) sp^2-sp^2, sp^3-s d) Π, s

---

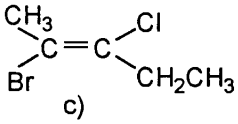
What is the correct structure for Z-2-bromo-3-chloro-2-pentene?



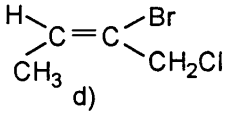
a)



b)



c)



d)

Which of the following substituents can stabilize a carbocation?

I. CH_3 II. C_2H_5 III. H IV. Cl V. $(CH_3)_3C$

a) I, II, V b) III, IV c) I, II, III d) I, II

Which of the following are examples of syn addition to alkenes?

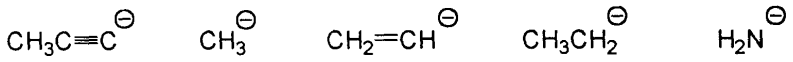
I. catalytic hydrogenation
II. addition of HBr
III. hydration
IV. hydroboration

a) I, II b) II, III c) III, IV d) I, IV

Compound A has the molecular formula, $C_{12}H_{18}$, and undergoes catalytic hydrogenation to give $C_{12}H_{24}$. What is the correct combination of rings and double bonds for compound A?

	rings	double bonds
a)	0	4
b)	3	1
c)	1	3
d)	4	0

What is the order of decreasing basicity (strongest first) for the following ions?



I II III IV V

a) I, III, IV, II, V b) IV, II, III, V, I c) II, IV, III, I, V d) V, I, III, IV, II

What is the best method for converting acetylene to trans-3-hexene?

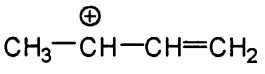
a) $NaNH_2$ → $2\ C_2H_5Br$ → $2\ Na / NH_3(l)$ →

b) $2\ Na / NH_3(l)$ → $NaNH_2$ → $2\ C_2H_5Br$ →

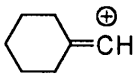
c) $NaNH_2$ → $2\ C_2H_5Br$ → $\xrightarrow[Pt]{H_2}$

d) $NaNH_2$ → C_2H_5I → $CH_3(CH_2)_3\ \overset{\ominus}{}\ \overset{\oplus}{Li}$ → CH_3Br → $Na / NH_3(l)$ →

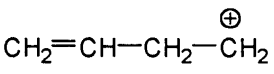
Which of the following are examples of allylic carbocations?



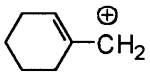
I



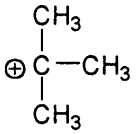
II



III



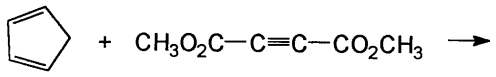
IV

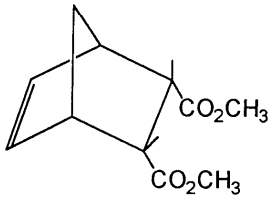


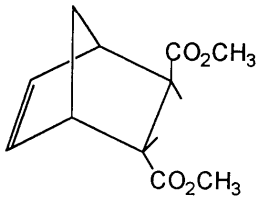
V

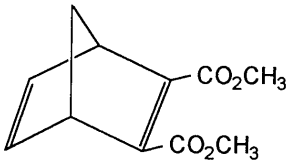
a) II, V b) II, IV c) I, III, IV d) I, IV

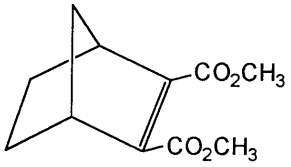
What is the major product from the following Diels-Alder reaction?



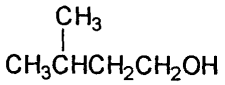
a) 

b) 

c) 

d) 

Which of the following structures have the correct IUPAC name?



3-methyl-butanol

I

2,4-butanediol

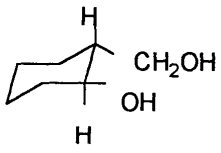
II

2-chloroethanol

III

2-chloroethyl-1-propyl alcohol

IV



trans-2-(hydroxymethyl) cyclohexanol

V

a) III, IV, V b) I, IV, V c) I, III, V d) I, II, IV

Which of the following reaction sequences is best for converting 1-propanol to 2-propanol?

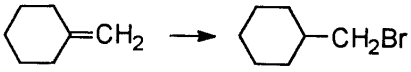
a) $\xrightarrow[\text{EtOH, heat}]{\text{NaOEt}} \xrightarrow{\text{dil } H_2SO_4}$

b) $\xrightarrow[\text{heat}]{H_2SO_4} \xrightarrow{B_2H_6} \xrightarrow[\text{NaOH}]{H_2O_2}$

c) $\xrightarrow[\text{heat}]{H_2SO_4} \xrightarrow{Hg(OAc)_2} \xrightarrow{NaBH_4}$

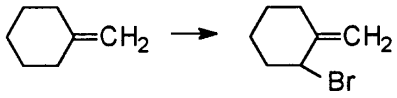
d) $\xrightarrow[\text{EtOH, heat}]{\text{NaOEt}} \xrightarrow{KMnO_4}$

What are the best conditions for preparing the following halide?



a) Br_2 in CCl_4 b) HBr and peroxides c) HBr d) NBS and light

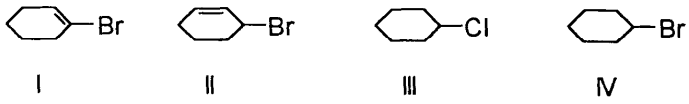
What are the best conditions for preparing the following halide?



a) Br_2 in CCl_4 b) HBr and peroxides c) HBr d) NBS and light

---

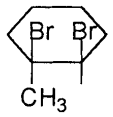
Place the following alkyl halides in the order of increasing reactivity in an S_N2 reaction (least first).

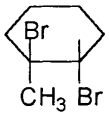


I II III IV

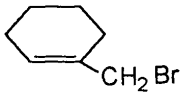
a) I, III, IV, II b) IV, III, II, I c) II, IV, III, I d) II, I, IV, III

Which of the following compounds can be prepared by reacting 1-methylcyclohexanol with aqueous sulfuric acid, and treating the product with bromine in carbon tetrachloride?

a) 

b) 

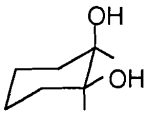
c) 

d) 

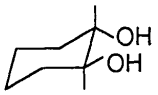
Which of the following statements is not true for the Williamson synthesis of ethers?

a) The rate of reaction depends on the leaving group.
b) The rate of reaction is proportional to the concentration of the nucleophile.
c) The mechanism involves one step.
d) Rearrangements occur in some situations.

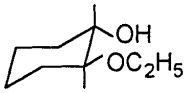
What is the major product from the reaction of cyclohexene oxide with aqueous acid?



a)



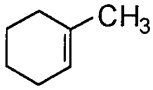
b)



c)

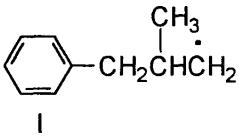
d)

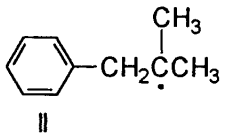
How many sets of equivalent hydrogen atoms are there for the following compound?

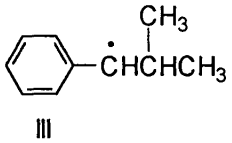


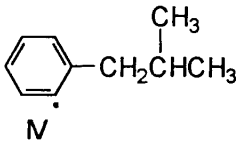
a) 3 b) 4 c) 5 d) 6

What is the order of increasing stability for the following radicals (least first)?


I


II


III


IV

a) I, III, II, IV b) IV, III, II, I c) IV, I, II, III d) I, II, III, IV

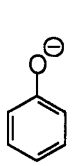
Which of the following substituents on benzene are activating for electrophilic aromatic substitution?

— Br (I) — NO_2 (II) — OCH_3 (III) — $COCH_3$ (IV)

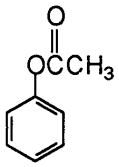
— $N(CH_3)_2$ (V) — $C(CH_3)_3$ (VI) — $\overset{\oplus}{N}(CH_3)_3$ (VII) — SO_3H (VIII)

a) I, II, VII b) II, IV, V c) II, VII, VIII d) III, V, VI

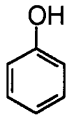
What is the order of increasing reactivity for electrophilic substitution of the following compounds (least first)?



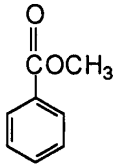
I



II



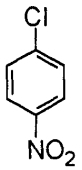
III

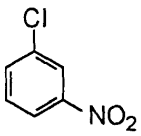


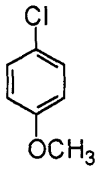
IV

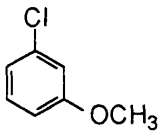
a) IV, III, II, I b) I, II, III, IV c) IV, II, III, I d) III, II, IV, I

Which of the following compounds reacts fastest in a hydrolysis reaction with aqueous base?

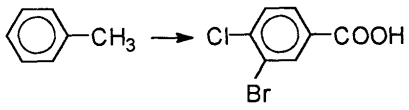
a) 

b) 

c) 

d) 

What is the best procedure for the following synthesis?



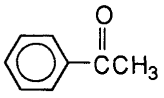
a) $\xrightarrow[FeCl_3]{Cl_2}$ $\xrightarrow[FeBr_3]{Br_2}$ $\xrightarrow[\ominus OH]{KMnO_4}$ $\xrightarrow{H_3O^{\oplus}}$

b) $\xrightarrow[FeCl_3]{Cl_2}$ $\xrightarrow[\ominus OH]{KMnO_4}$ $\xrightarrow{H_3O^{\oplus}}$ $\xrightarrow[FeBr_3]{Br_2}$

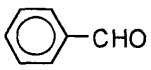
c) $\xrightarrow[\ominus OH]{KMnO_4}$ $\xrightarrow{H_3O^{\oplus}}$ $\xrightarrow[FeBr_3]{Br_2}$ $\xrightarrow[FeCl_3]{Cl_2}$

d) $\xrightarrow[\ominus OH]{KMnO_4}$ $\xrightarrow{H_3O^{\oplus}}$ $\xrightarrow[FeCl_3]{Cl_2}$ $\xrightarrow[FeBr_3]{Br_2}$

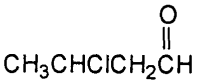
Which of the following structures have the correct names?



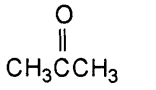
benzophenone
I



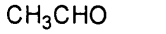
benzaldehyde
II



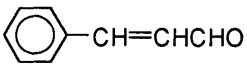
3-chlorobutanal
III



acetophenone
IV



acetaldehyde
V



cinnamaldehyde
VI

a) I, II, IV, VI b) I, II, V, VI c) II, III, V, VI d) III, IV, V, VI

Which of the following reaction conditions is best for preparing hexanal from hexanol?

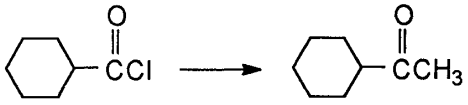
a) $Na_2Cr_2O_7$ in aqueous H_2SO_4

b) Zn in acetic acid

c) CrO_3 and pyridine in chloroform

d) $HgSO_4$ in aqueous H_2SO_4

Which reagents can be used for the following conversion?



Zn / acetic acid (I)

$CH_3Cl / AlCl_3$ (II)

CH_3Li (III)

CH_3MgBr (IV)

$LiAlH(OCMe_3)_3$ (V)

$(CH_3)_3CuLi$ (VI)

$(CH_3)_2Cd$ (VII)

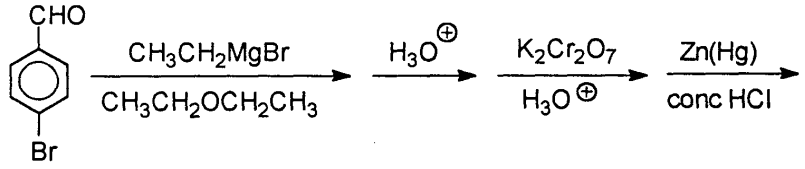
a) I, II, III

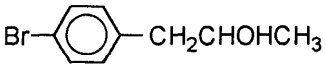
b) VI, VII

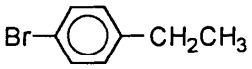
c) V, VII

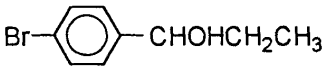
d) IV, VI, VII

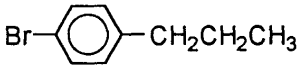
What is the product from the following series of reactions?



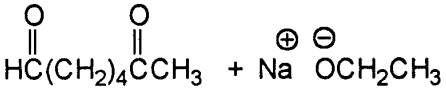
a) 

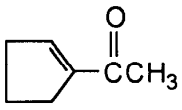
b) 

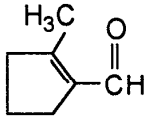
c) 

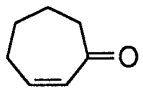
d) 

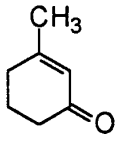
What is the major product from the following reaction?



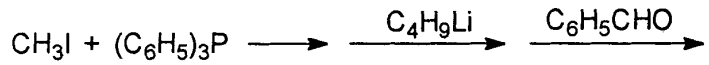
a) 

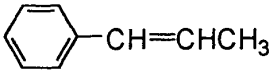
b) 

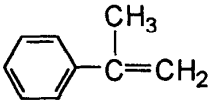
c) 

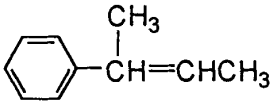
d) 

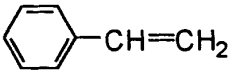
What is the most likely product from the following series of reactions?



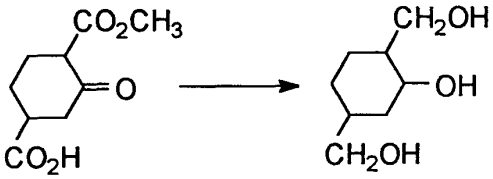
a) 

b) 

c) 

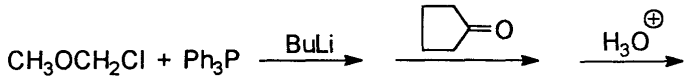
d) 

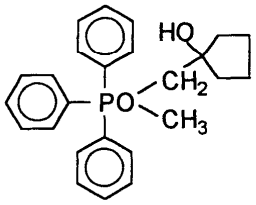
Which reagent is best for the following conversion?

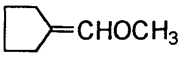


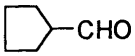
a) $NaBH_4$ b) $LiAlH_4$ c) Na / liquid NH_3 d) $K_2Cr_2O_7$ / H_2SO_4

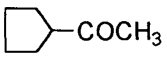
What is the product from the following series of reactions?



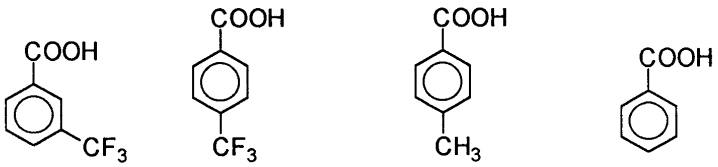
a) 

b) 

c) 

d) 

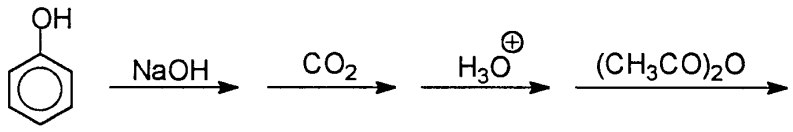
Arrange the following compounds in the order of increasing acid strength (lowest first).

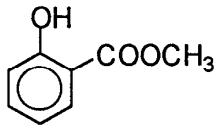


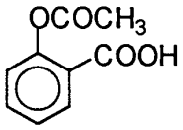
I II III IV

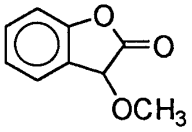
a) IV, III, I, II b) II, IV, III, I c) III, IV, II, I d) I, II, IV, III

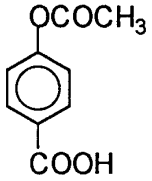
What is the major product from the following reaction sequence?



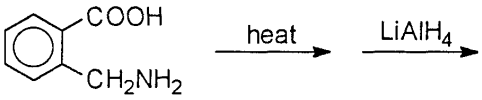
a) 

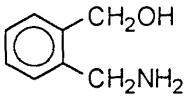
b) 

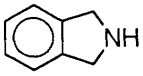
c) 

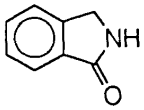
d) 

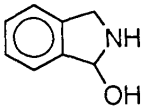
What is the major product from the following reactions?



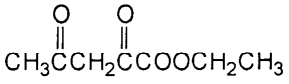
a) 

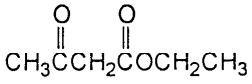
b) 

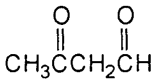
c) 

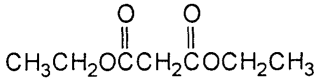
d) 

What is the major product from the crossed Claisen condensation reaction of acetone and diethyl oxalate?

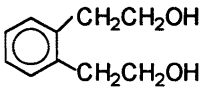
a) 

b) 

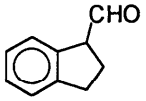
c) 

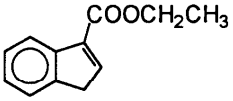
d) 

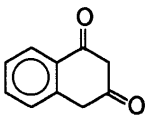
Compound A is treated with sodium dichromate in sulfuric acid and water to give Compound B. Compound B is reacted with ethanol and hydrochloric acid to give Compound C. Reaction of Compound C with sodium ethoxide followed by treatment with dilute acid gives Compound D, the final product. Given the structure of Compound A as follows, what is the most likely structure for Compound D?

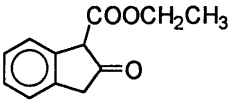


Compound A

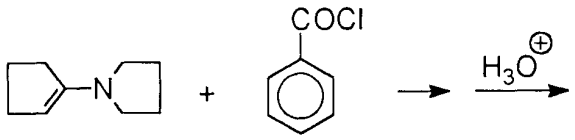
a) 

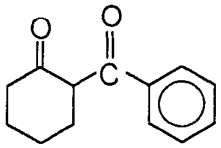
b) 

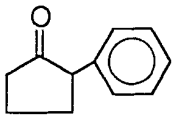
c) 

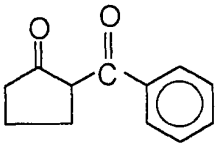
d) 

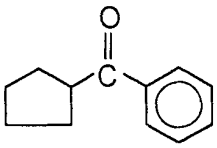
What is the major product from the following reaction?



a) 

b) 

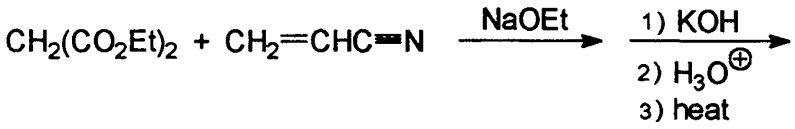
c) 

d) 

Diethyl malonate and which halide can be used to prepare butyric acid?

a) methyl bromide
b) ethyl bromide
c) 1-bromopropane
d) isopropyl chloride

What is the major product from the following series of reactions?



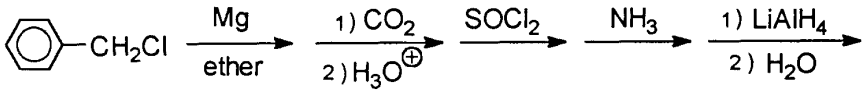
a) $HOOC(CH_2)_2COOH$

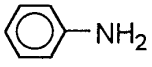
b) $HOOC(CH_2)_3COOH$

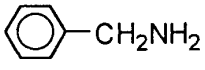
c) $HOOC(CH_2)_4COOH$

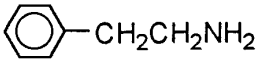
d) $HOOC(CH_2)_5COOH$

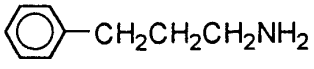
Which compound is prepared from the following reaction scheme?



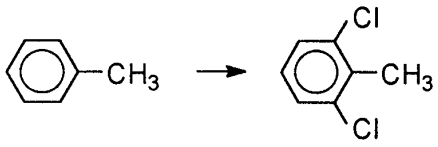
a) 

b) 

c) 

d) 

What are the best conditions for the following synthesis?



a) HNO_3, H_2SO ; Cl_2, $FeCl_3$; Sn, HCl ; HONO ; H_3PO_2

b) HNO_3, H_2SO_4 ; Sn, HCl ; Cl_2. $FeCl_3$; HONO ; H_3PO_2

c) Cl_2, $FeCl_3$; HNO_3, H_2SO_4 ; Sn, HCl ; HONO ; H_3PO_2

d) HNO_3, H_2SO_4 ; Sn, HCl ; HONO ; H_3PO_2 ; Cl_2, $FeCl_3$