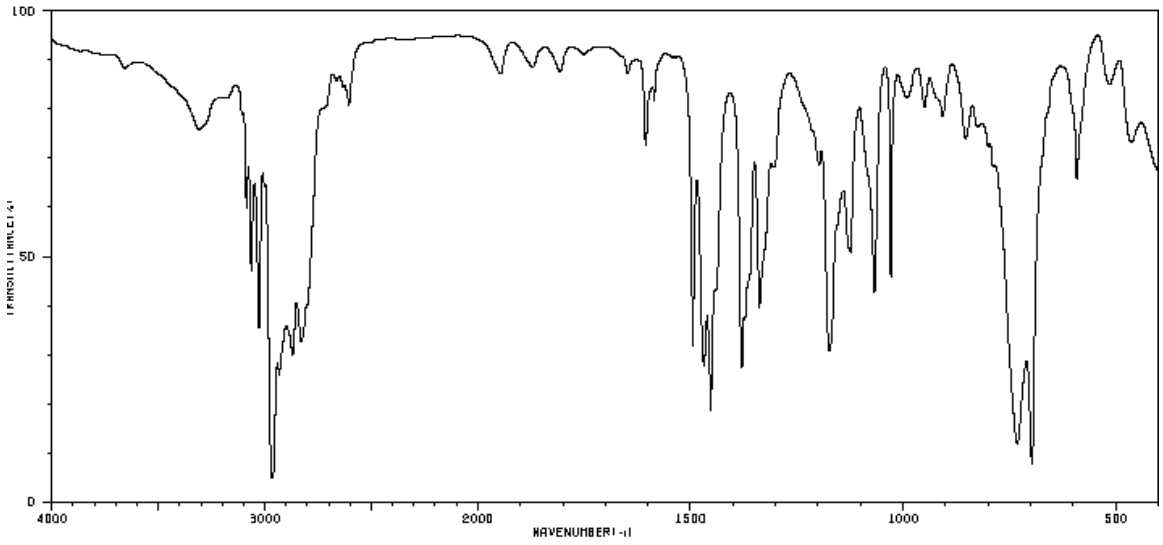
Chemistry Department

University of Alberta

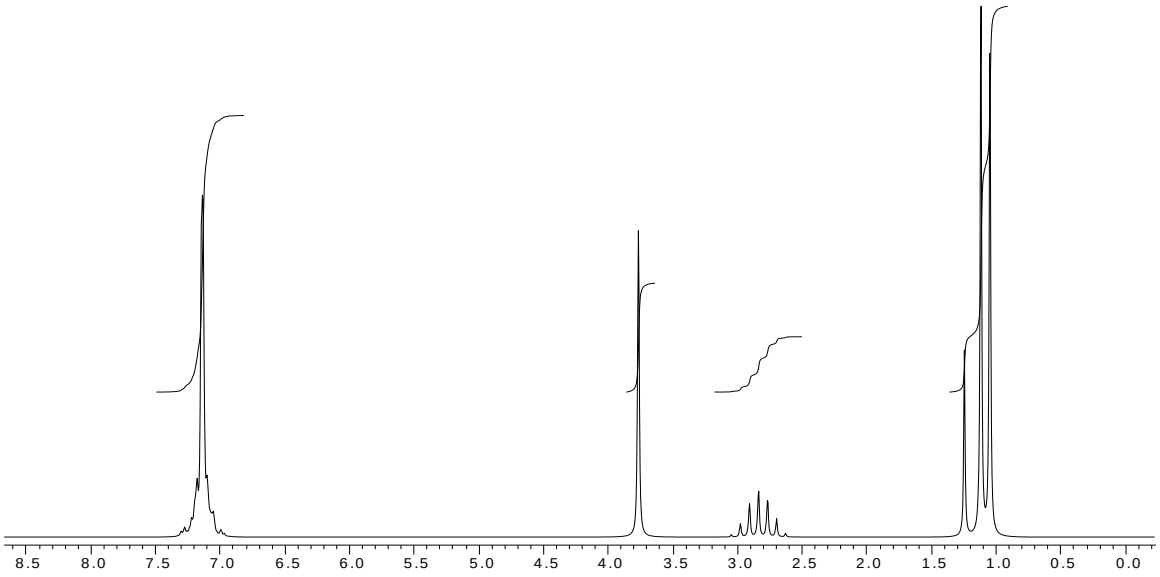
CHEM 263
Final Exam

June 17, 2011

1. The IR and ^{1}H NMR spectra of a compound of molecular formula $C_{10}H_{15}N$ are given below.



SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology, 30 March 2011)



a. Calculate the degree of unsaturation. (1 point)

(2 x 10 + 1 – 15 + 2)/2 =4

b. List the possible non-hydrocarbon functional groups using the molecular formula and your calculated degree of unsaturation. (2 points)

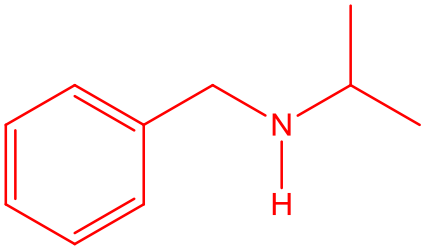
nitrile, primary, secondary, or tertiary amine

c. What is the functional group in this molecule? (1 point)

Secondary amine

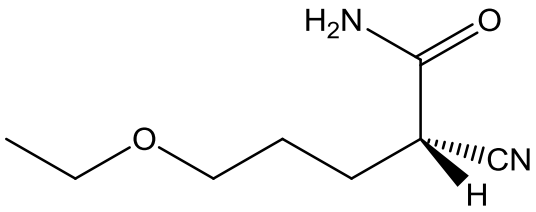
d. Draw a table that lists chemical shifts and multiplicity. Then propose a structure for this compound. (11 points)

δ (ppm)	multiplicity	neighbours	# hydrogens	origin
7.1	s		5	Monosubstituted benzene
3.75	s	0	2	-CH_2- between N and benzene ring
2.8	7	6	1	-CH- with two CH_3 groups on this carbon
1.25	s	0	1	N-H
1.1	d	1	6	$(CH_3)_2C$-



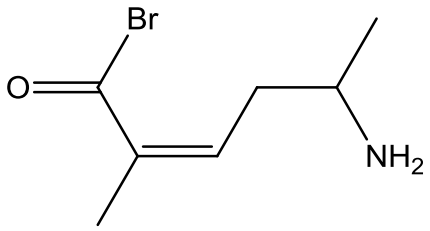
2. Name <u>five</u> (5) of the following structures: (15 points)

a.



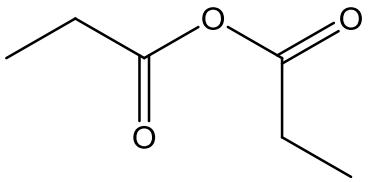
(S)-2-cyano-5-ethoxypentanamide

b.



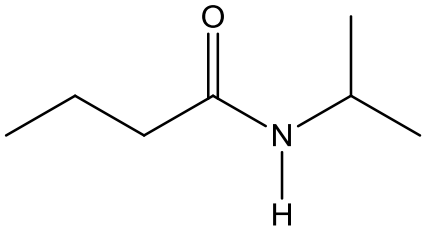
(Z)-5-amino-2-methyl-2-hexenoyl bromide

c.



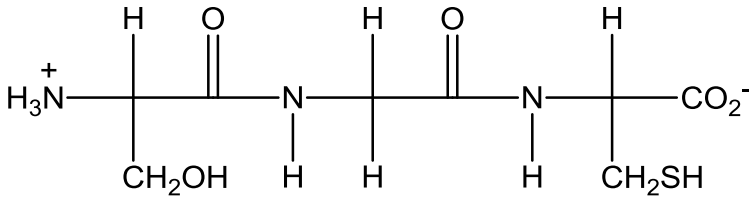
propanoic anhydride

d.



N-isopropylbutanamide

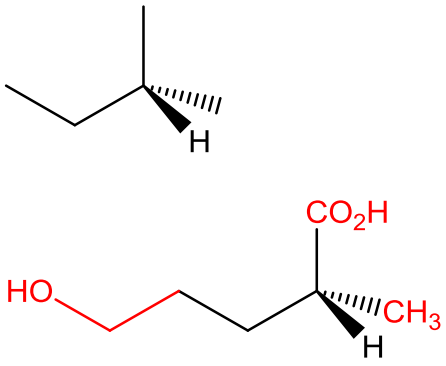
e.



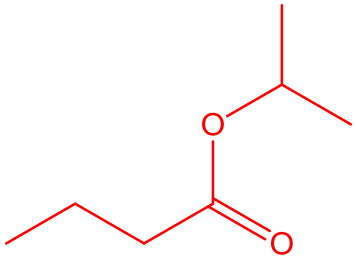
serylglycylcysteine

3. Give the structural formula of <u>five</u> (5) of the following compounds. Where given, complete the partial structures: (15 points)

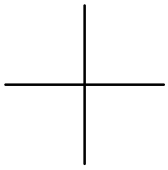
a. (R)-5-hydroxy-2-methylpentanoic acid

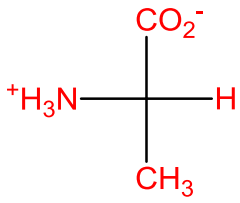


b. isopropylbutanoate

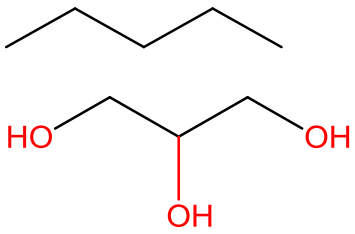


c. L-Alanine (as a zwitterion)

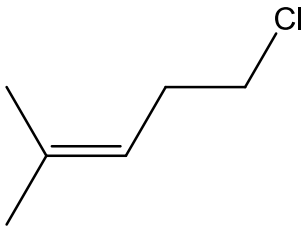


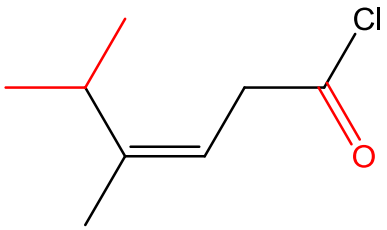


d. Glycerol



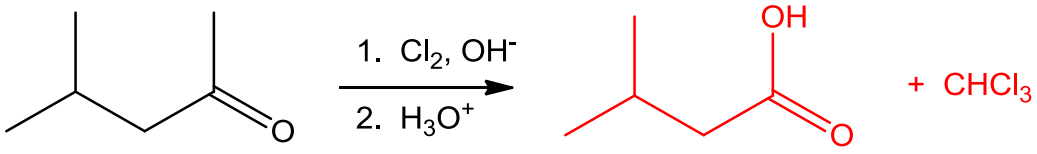
e. (Z)-4,5-dimethyl-3-hexenoyl chloride



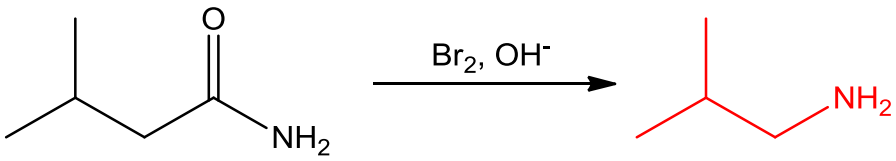


4. Give the structure(s) of the principle organic products of ten (10) of the following reactions: (30 points)

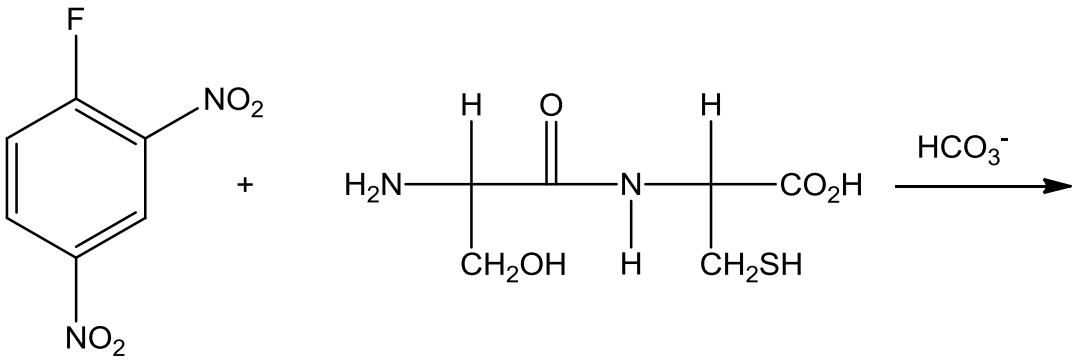
a.

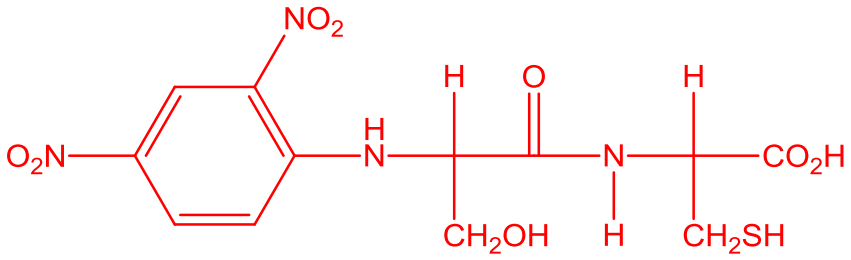


b.

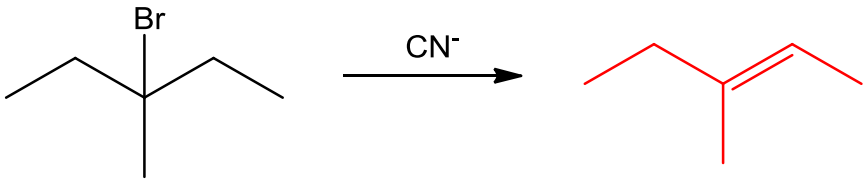


c.

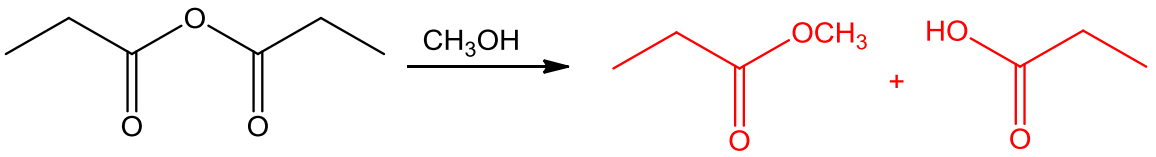




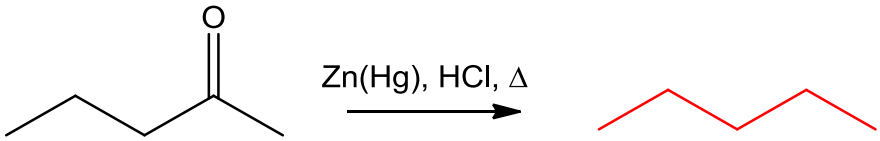
d.


Br
CN-

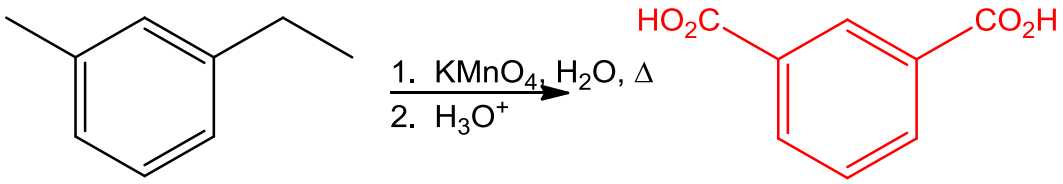
e.


O
O
O
CH3OH
OCH3
O
+
HO
O

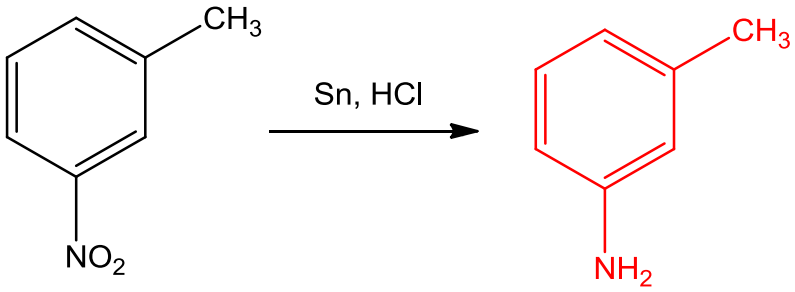
f.


O
Zn(Hg), HCl, Δ

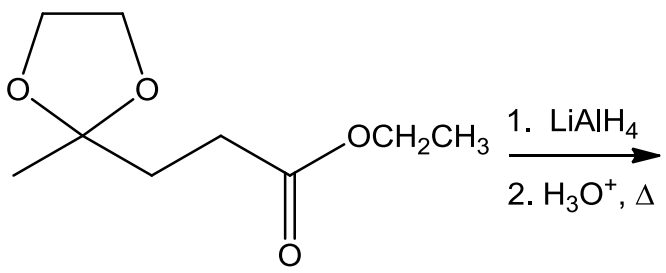
g.

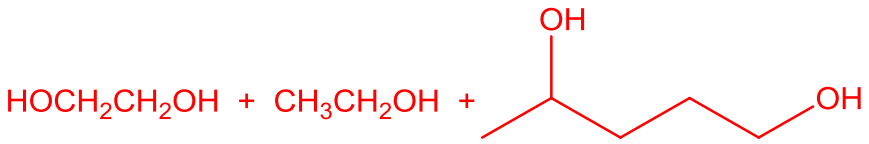

1. KMnO4, H2O, Δ
2. H3O+
HO2C
CO2H

h.

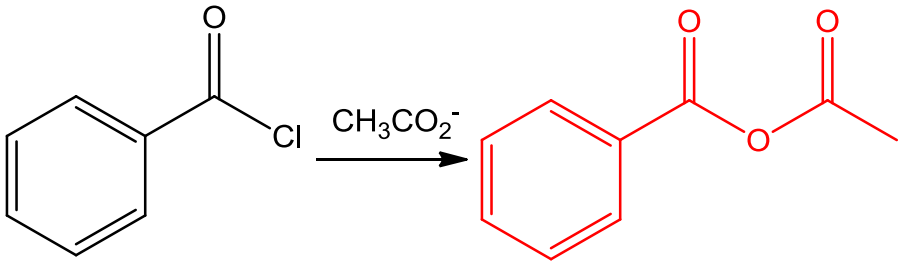

CH3
NO2
Sn, HCl
CH3
NH2

i.



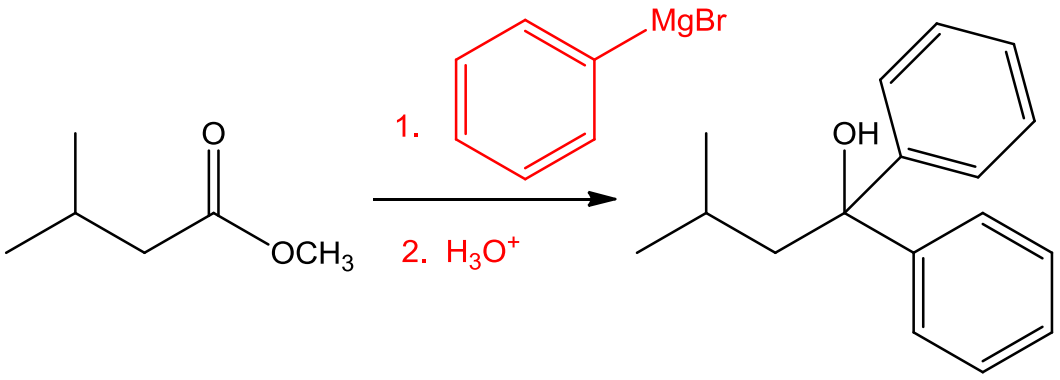


j.

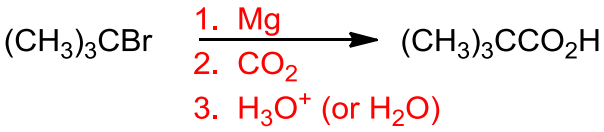


5. What reagent(s) would you use to effect <u>ten</u> (10) of the following conversions? (30 points)

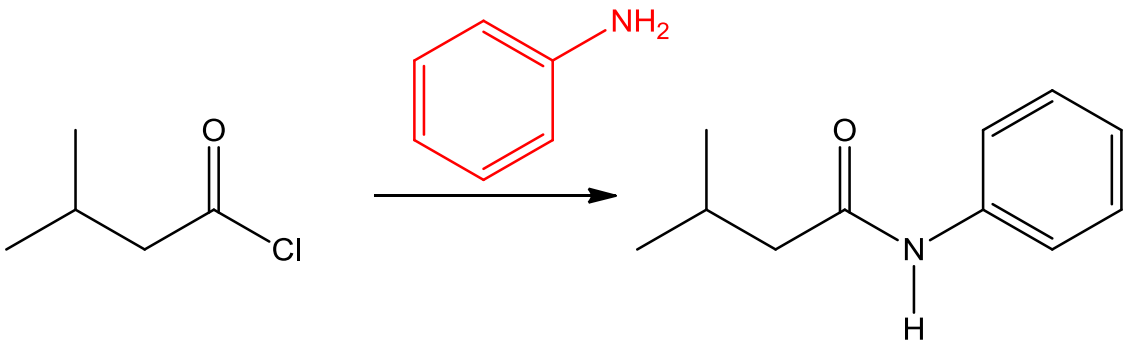
a.



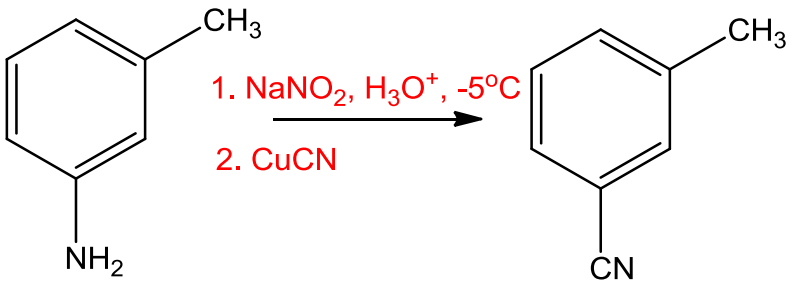
b.


(CH3)3CBr
1. Mg
2. CO2
3. H3O+ (or H2O)
(CH3)3CCO2H

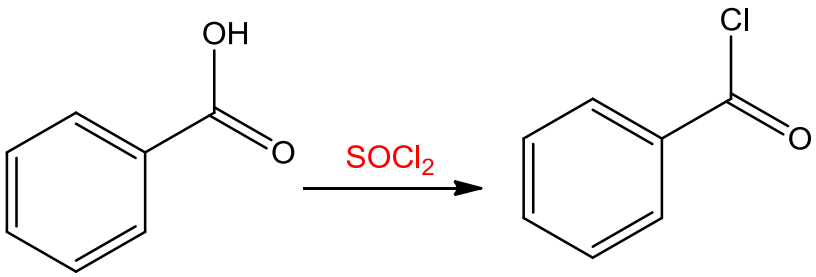
c.


NH2
O
Cl
O
N
H

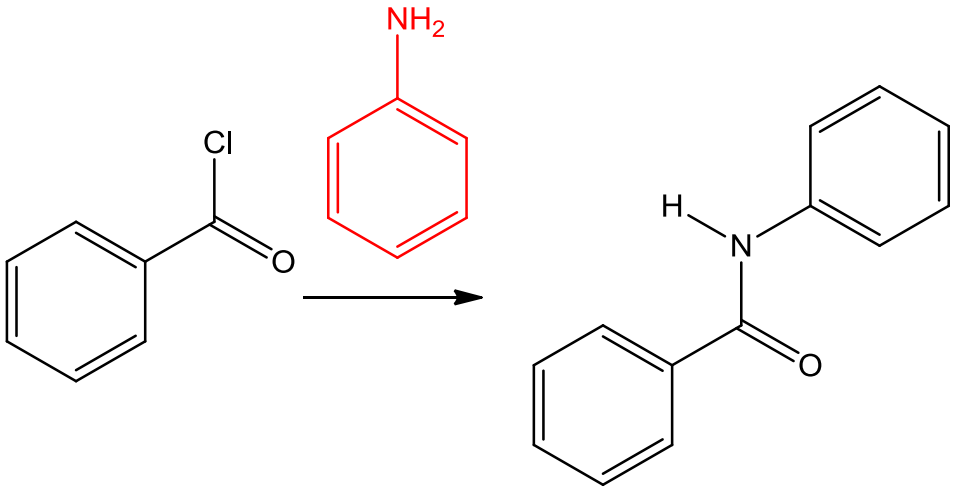
d.


CH3
NH2
1. NaNO2, H3O+, -5°C
2. CuCN
CH3
CN

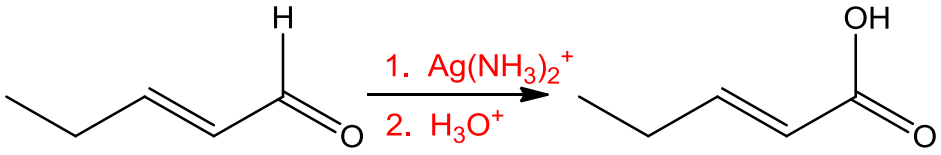
e.


OH
O
SOCl2
Cl
O

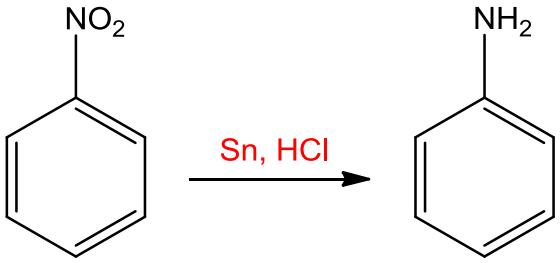
f.


NH2
Cl
O
H
N
O

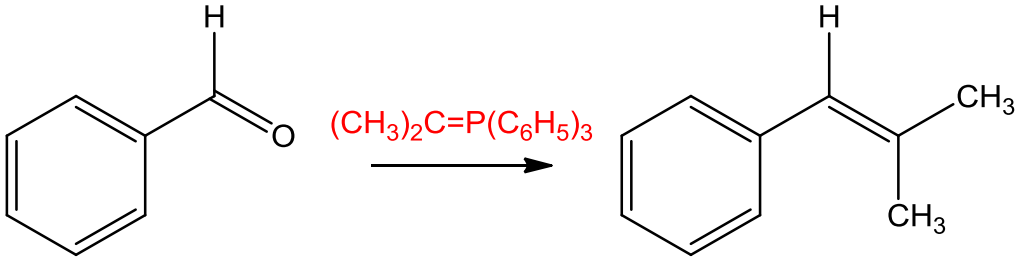
g.


H
O
1. Ag(NH3)2+
2. H3O+
OH
O

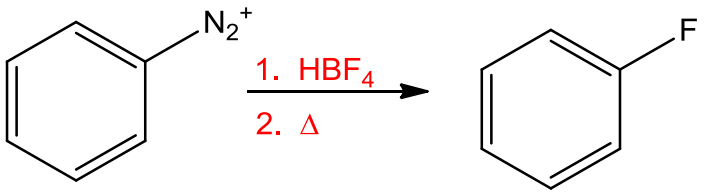
h.


NO2
Sn, HCl
NH2

i.

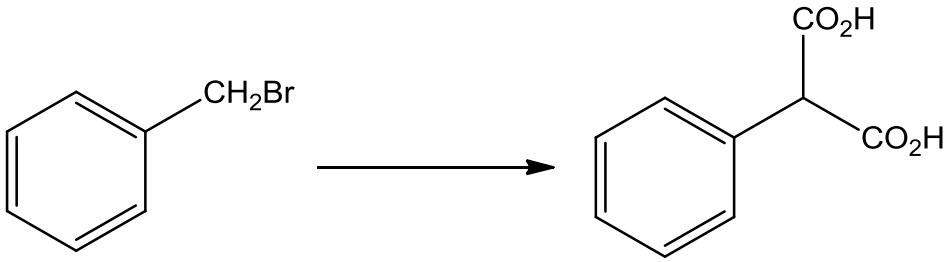

H
O
(CH3)2C=P(C6H5)3
H
CH3
CH3

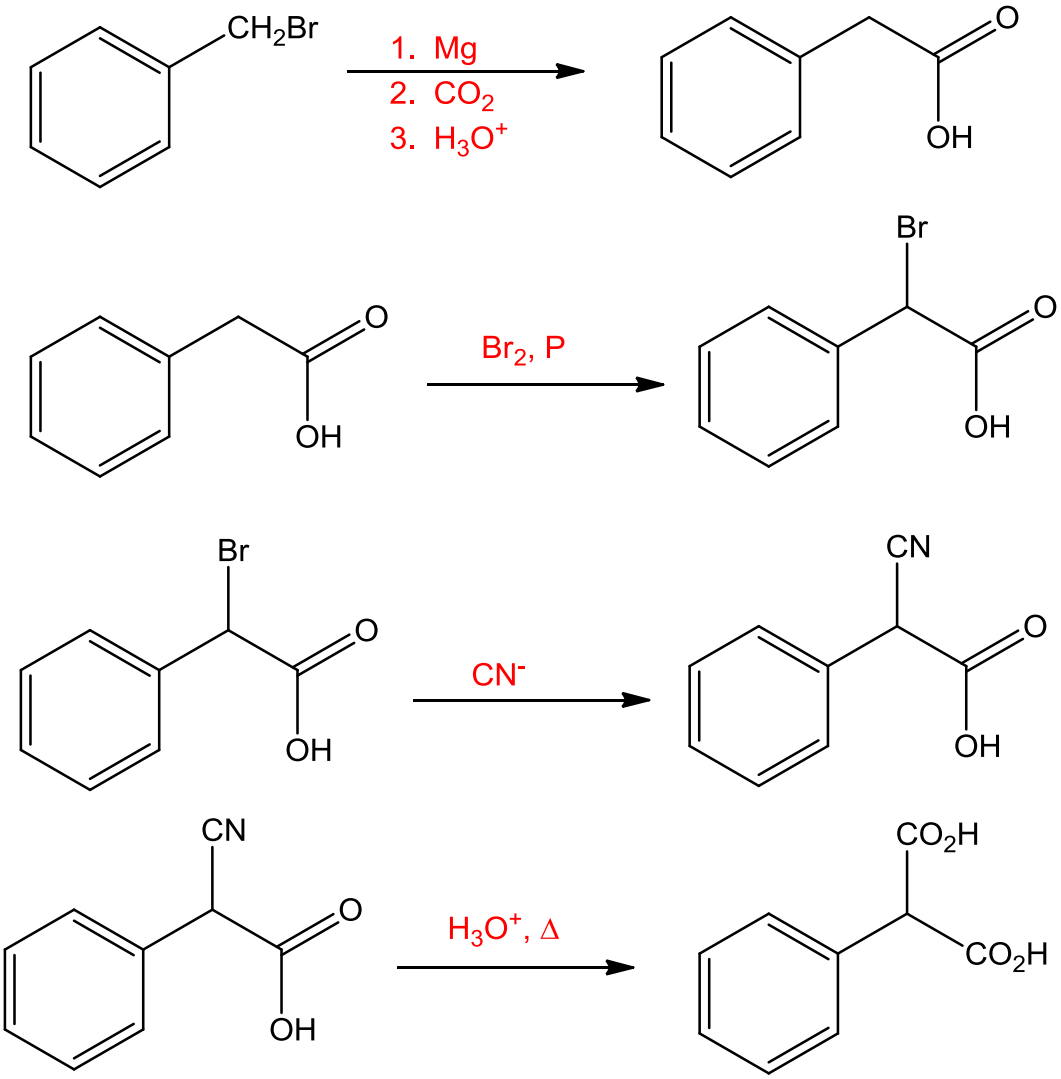
j.



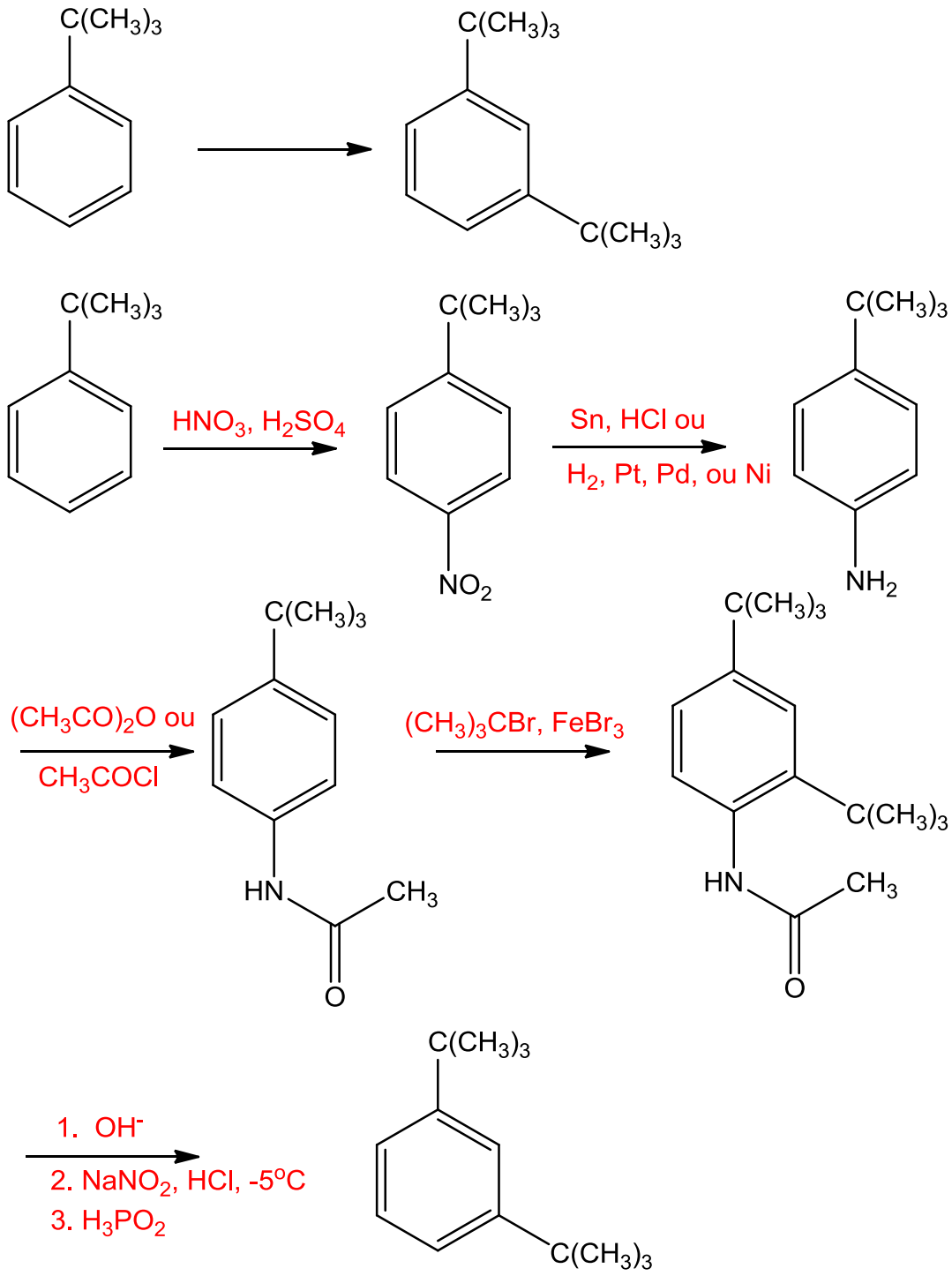
6. Provide synthetic pathways for <u>three</u> (3) of the following transformations (30 points):

a.

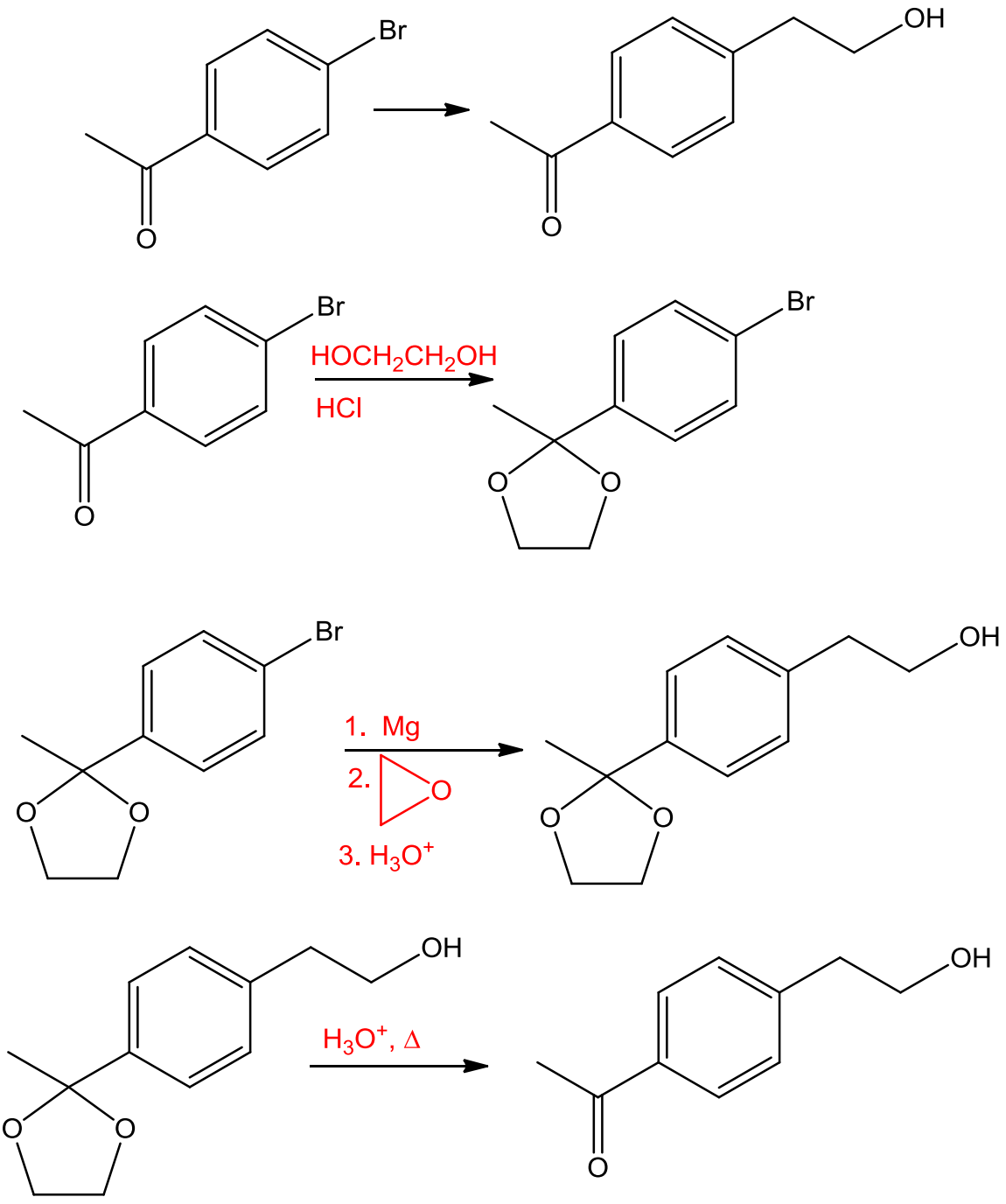



CH2Br
1. Mg
2. CO2
3. H3O+
O
OH
Br2, P
Br
CN-
CN
H3O+, Δ
CO2H

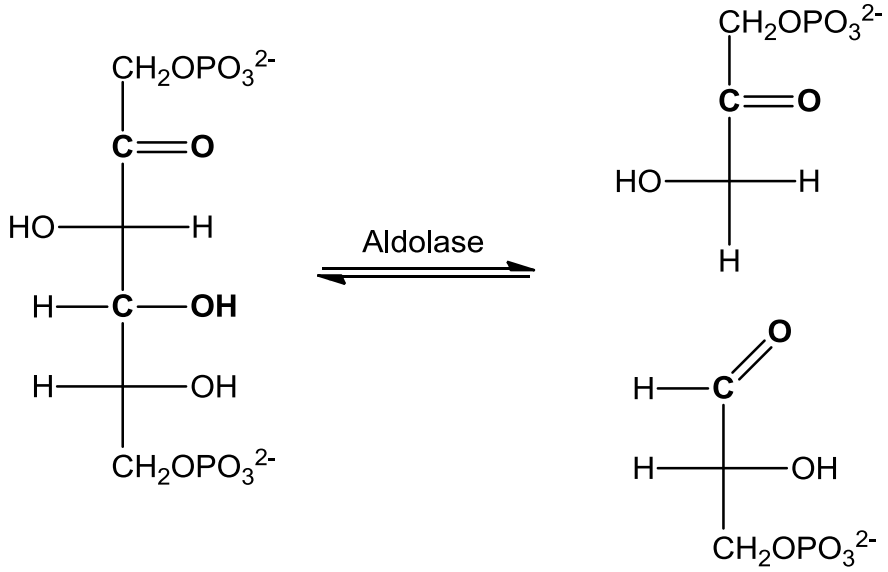
b.


C(CH3)3
C(CH3)3
C(CH3)3
HNO3, H2SO4
NO2
Sn, HCl ou
H2, Pt, Pd, ou Ni
NH2
(CH3CO)2O ou
CH3COCl
HN
CH3
O
(CH3)3CBr, FeBr3
1. OH-
2. NaNO2, HCl, -5°C
3. H3PO2

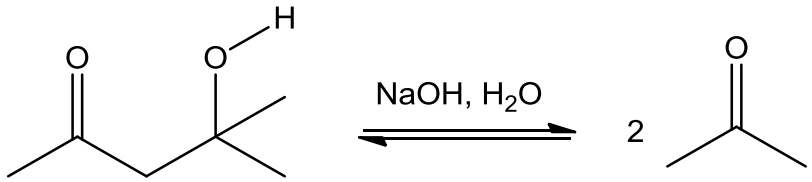
c.

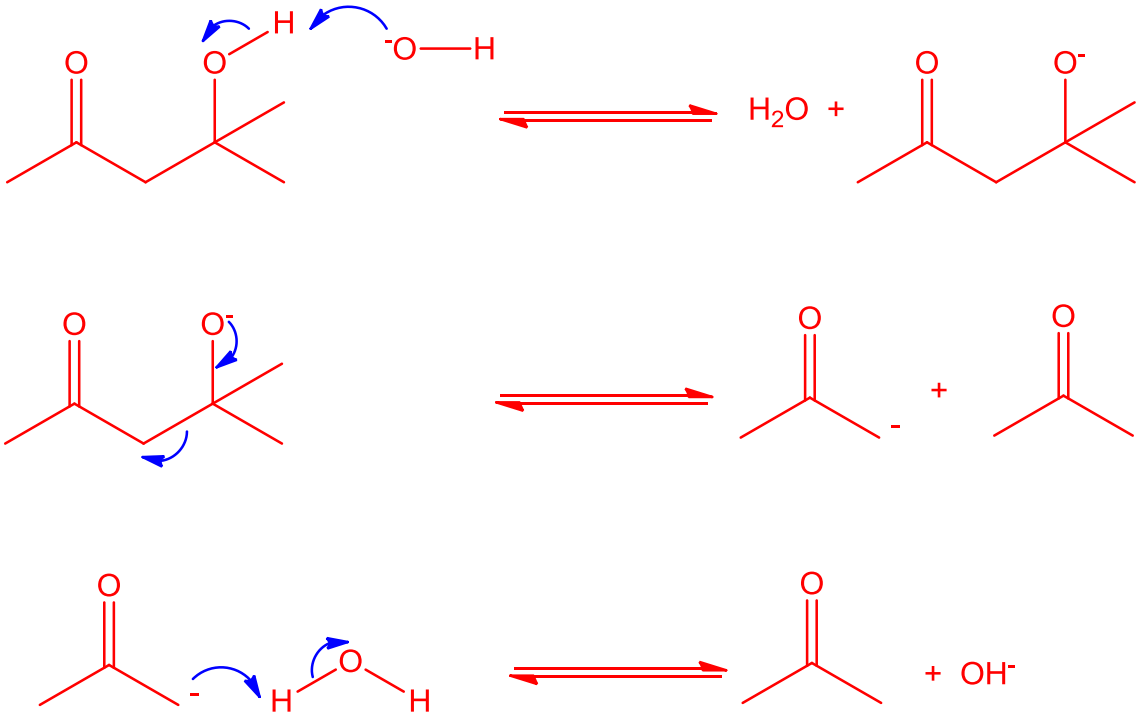

Br
OH
O
O
Br
HOCH2CH2OH
HCl
O
O
O
Br
Br
1. Mg
2.
O
3. H3O+
O
O
O
OH
OH
H3O+, Δ
O
O
O
OH
O

7. One of the steps involved in glycolysis is a retro-aldol reaction which occurs in the presence of an enzyme called aldolase:



Propose a mechanism for the following retro-aldol reaction (i.e. the reverse of the aldol reaction): (9 points)





8.

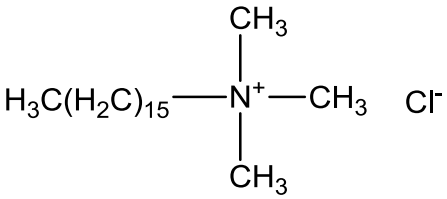
a. What term refers to a mixture that acts as a pure substance; it boils at a constant temperature because its composition in the liquid phase is identical to that in the vapour phase? (1 point)

azeotrope

b. What is the name of a spherical cluster of soap molecules in aqueous solution? (1 point)

micelle

c. Could the following molecule act as a detergent? (1 point)

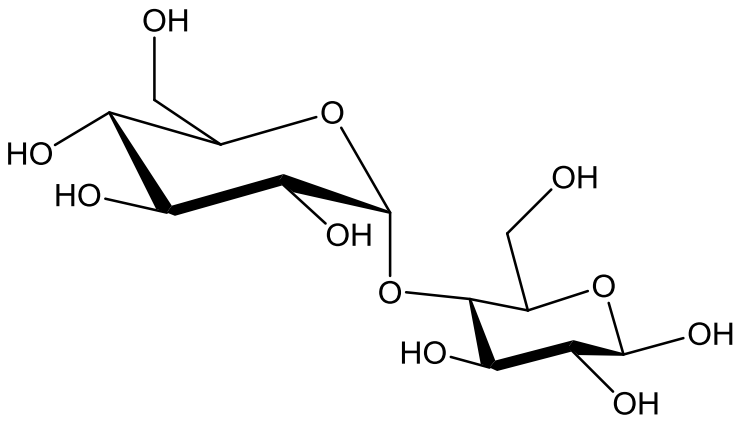


Yes

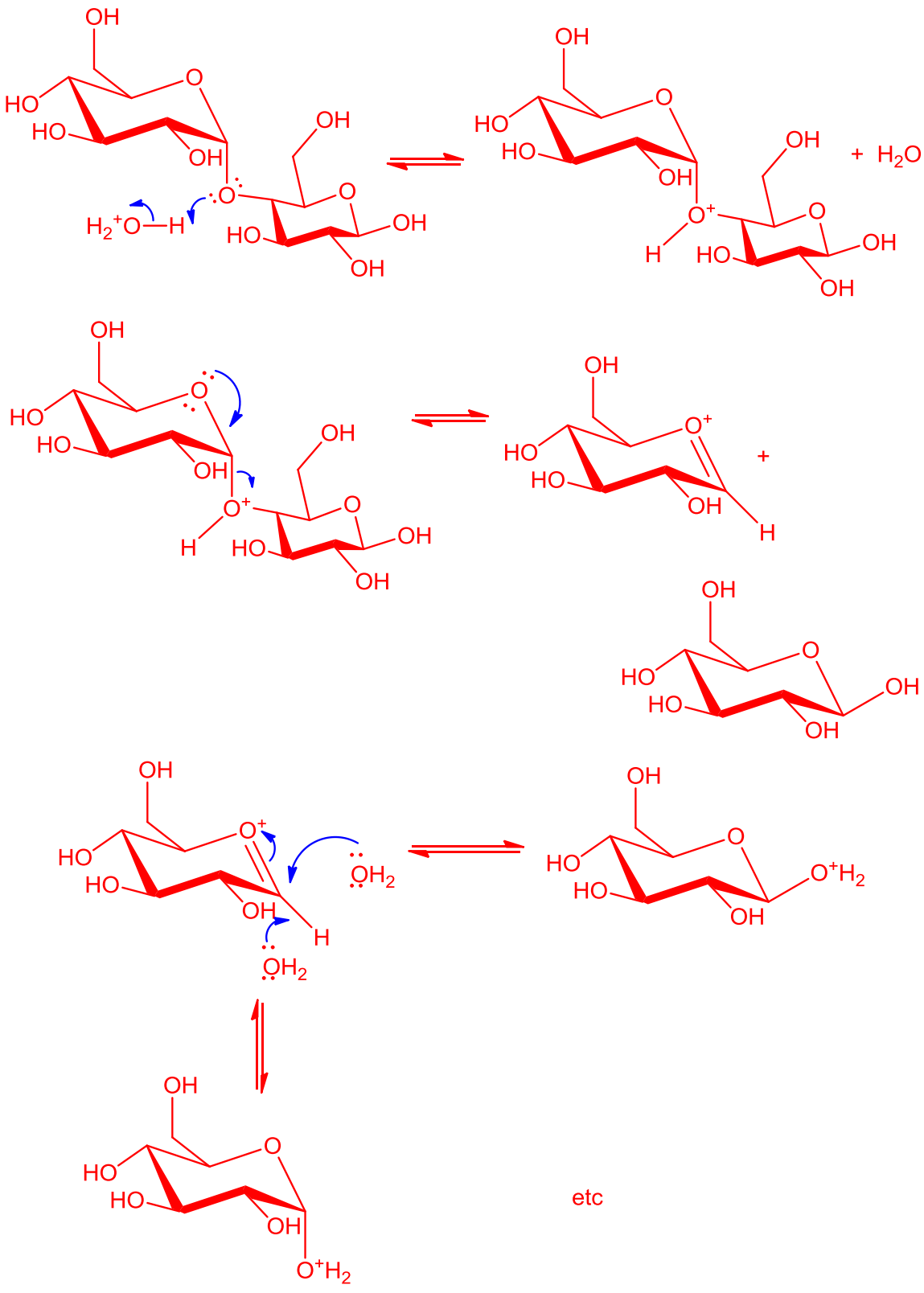
d. What term refers to two diastereomers that only differ in the configuration around carbon 1. (1 point)

anomer

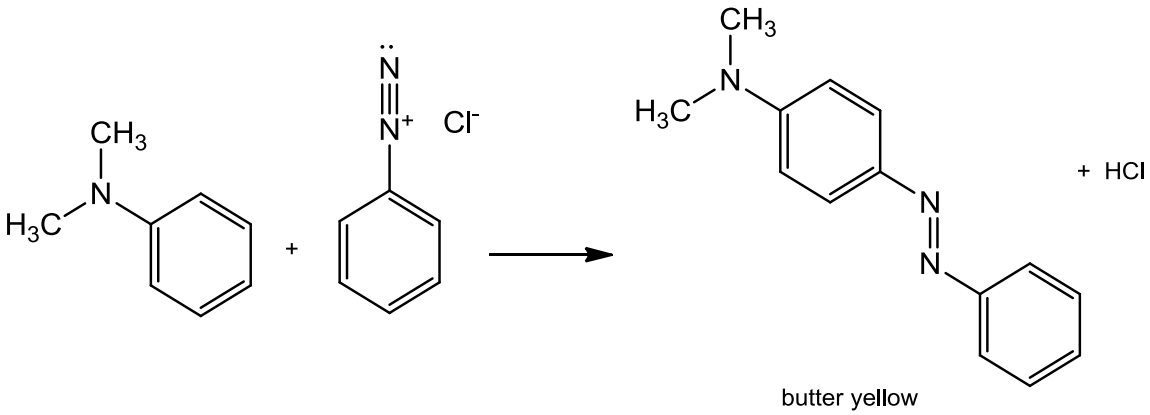
e. When an aqueous solution of maltose is made acidic it undergoes hydrolysis to produce a mixture of α-D-glucose and β-D-glucose. Propose a mechanism that accounts for this reaction. (10 points)



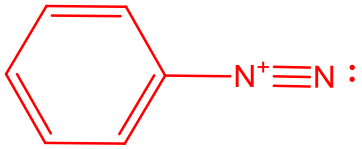
maltose


OH
HO
HO
O
OH
H_2^+O
H
+ H_2O
O^+
+
OH_2
O^+H_2
etc

9. Butter yellow is a dye that was used to colour margarine. However it has been found to be carcinogenic and therefore is no longer permitted in the food industry. The dye can be made by the following reaction:



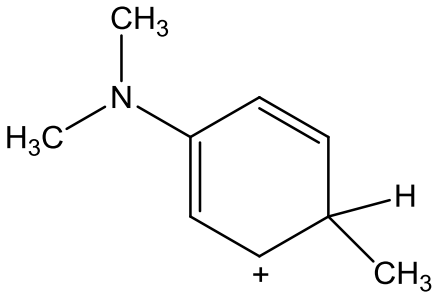
a. Identify the electrophile. (1 point)

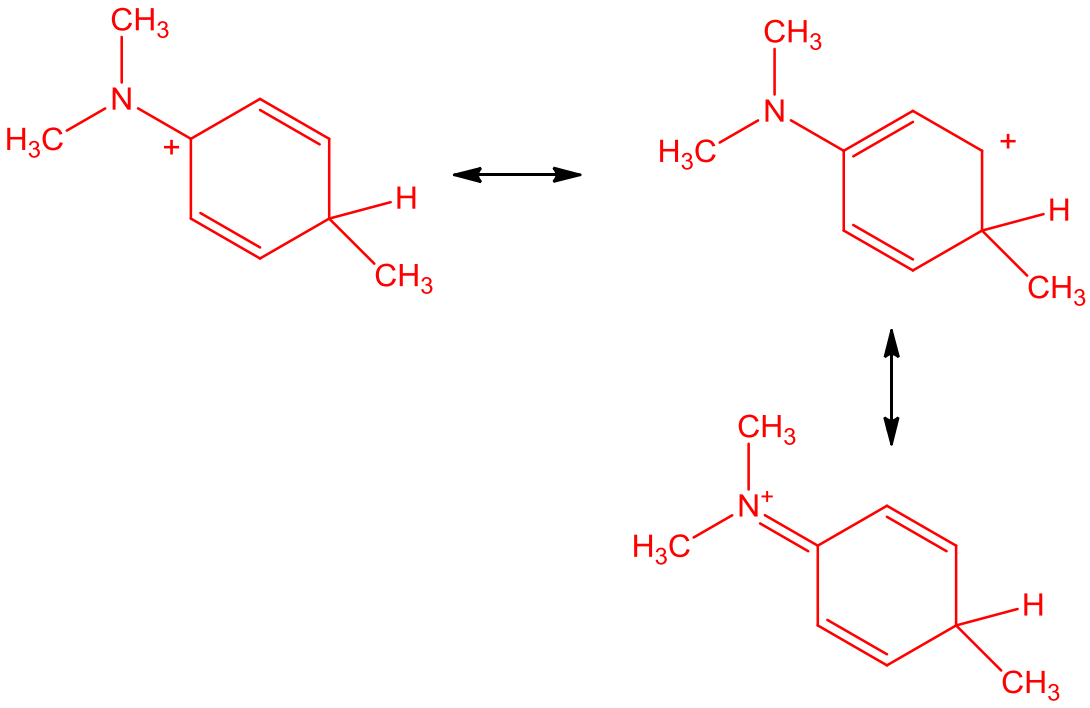


b. Name the nucleophile. (2 points)

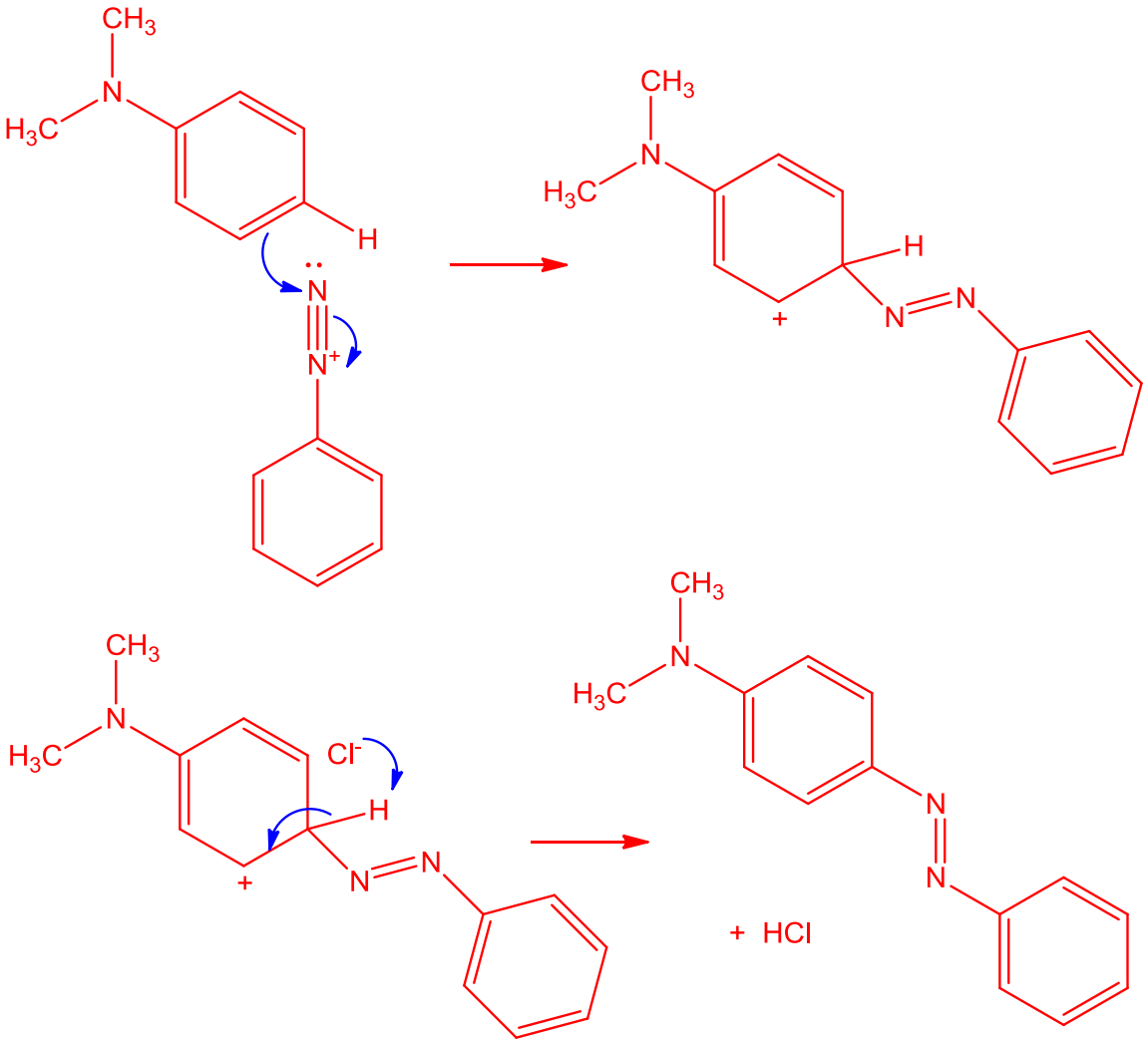
N,*N*-dimethylaniline

c. Draw the remaining resonance structures for the following cation: (3 points)





d. Draw the mechanism for this synthesis of butter yellow. (6 points)


CH3
N
H3C
H
N
N+
CH3
N
H3C
H
+
N
N
CH3
N
H3C
Cl-
H
+
N
N
CH3
N
H3C
N
N
+ HCl

10.

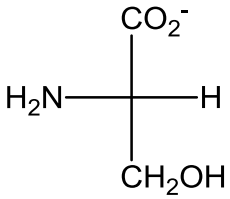
a. Give an example of an essential amino acid. (1 point)

One of Valine, Leucine, Isoleucine, Threonine, Methionine, Lysine, Arginine, Phenylalanine, Histidine, or Tryptophan

b. Explain the term isoelectric point. (1 point)

The pH at which there is no net charge.

c. The isoelectric point of serine is 5.68. This is its structure in a buffer of a certain pH. Is this pH lower or higher than the isoelectric point? (1 point)



Higher

d. A peptide has the following amino acid composition:

2 Arg, 2 Ile, Glu, 2 Gly, Leu, Lys, Phe, Pro, Ser, Trp

Determine its structure from the following information: (3 points)

Reaction with Edman's reagent releases PTH-Leu.

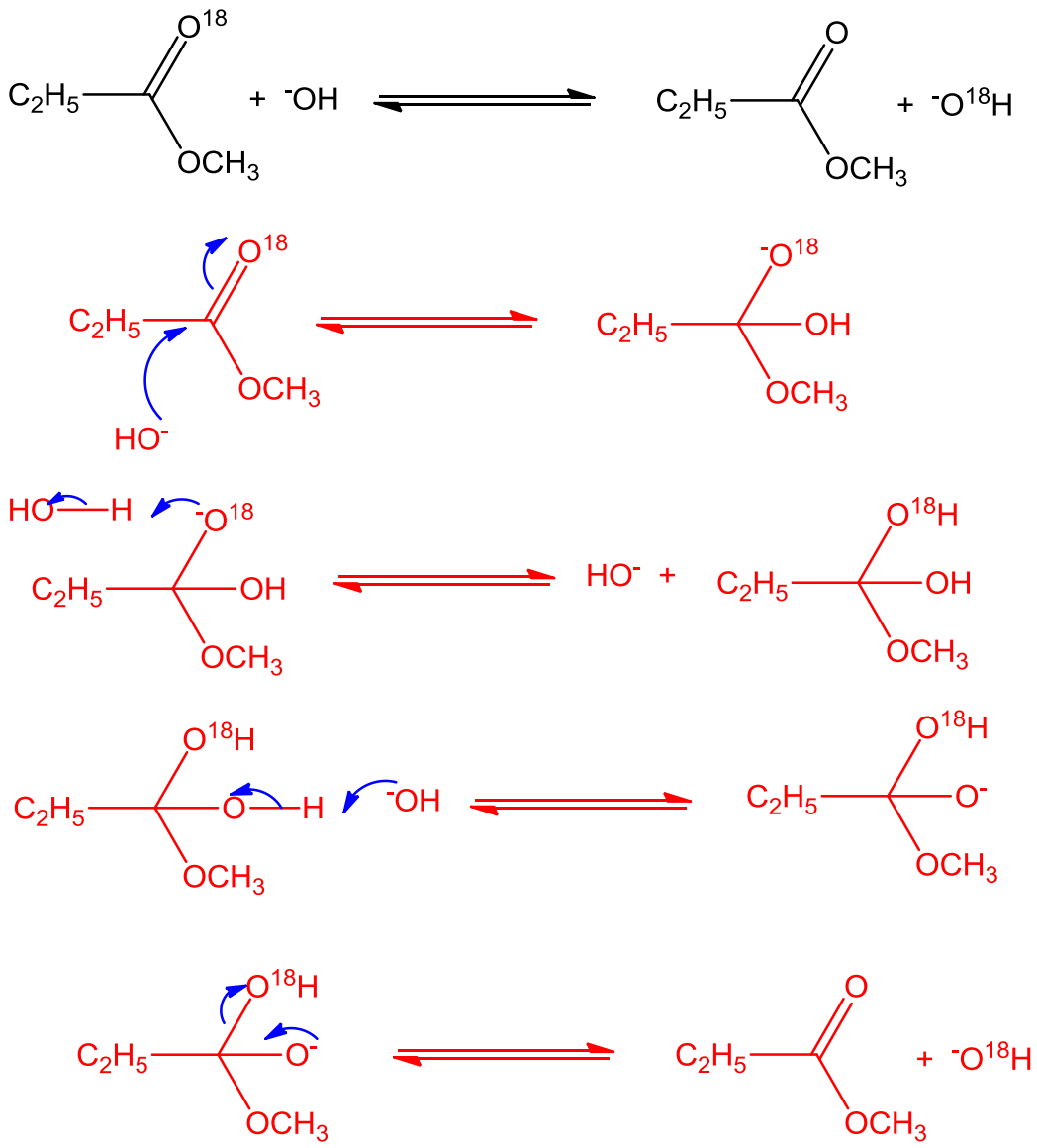
Trypsin, a digestive enzyme of intestinal liquids, cleaves polypeptides only at the carboxy (acid) end of arginine (Arg) and Lysine (Lys). Chymotrypsin which is also found in mammalian intestines, cleaves the carboxy end of phenylalanine (Phe), tryptophan (Trp) and tyrosine (Tyr).

Hydrolysis by trypsin produces Gly-Arg, Ile-Trp-Phe-Pro-Gly-Arg, Leu-Lys, and Ser-Glu-Ile.

Hydrolysis by chymotrypsin produces one peptide with a partial sequence of Leu-Lys-Gly … and another with partial sequence Phe-Pro-Gly-Arg-Ser ...

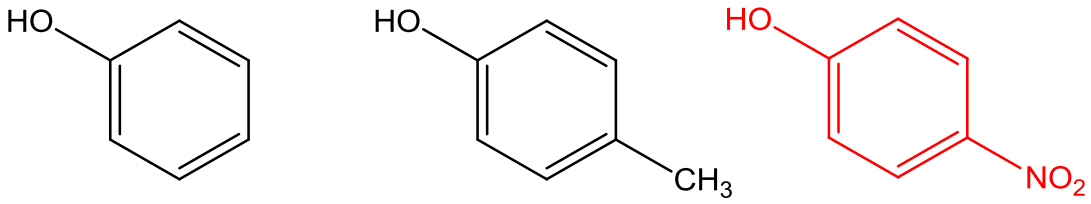
Leu-Lys-Gly-Arg-Ile-Trp-Phe-Pro-Gly-Arg-Ser-Glu-Ile

11. Propose a mechanism to explain the following transformation that occurs in aqueous solution: (12 points)

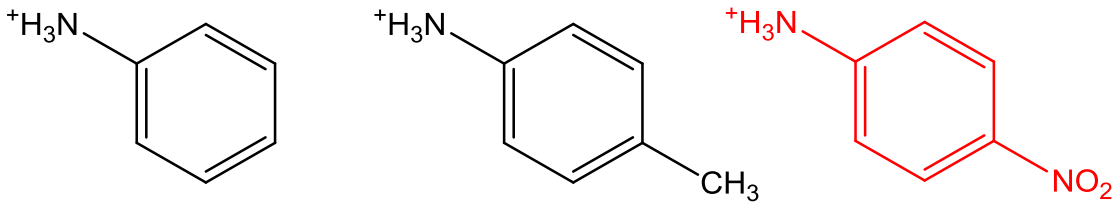


12. In each of the following groups, label the strongest acid: (4 points)

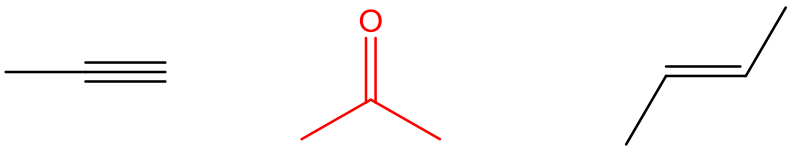
a.



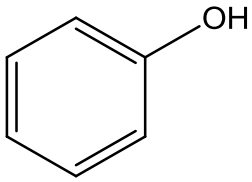
b.



c.



d.



CH_3CO_2H CH_2ClCO_2H