

Solutions to Chem1040 Practice Exam

- 1) Calculate the number of moles of carbon atoms present in a 12.3 g sample of $\text{CH}_4\text{CH}_3\text{OH}$ (molar mass = 48.1 g/mol).

Answer: 0.512 moles of carbon in $\text{CH}_4\text{CH}_3\text{OH}$

Solution:

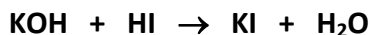
First determine the number of moles of $\text{CH}_4\text{CH}_3\text{OH}$ in the sample.

$$\frac{12.3 \text{ g}}{48.1 \text{ g/mol}} = 0.256 \text{ moles}$$

Next, note that there are 2 moles of carbon for every mole of $\text{CH}_4\text{CH}_3\text{OH}$. Thus, this gives us

$$0.256 \text{ moles of } \text{CH}_4\text{CH}_3\text{OH} \times \frac{2 \text{ mol C}}{1 \text{ mol } \text{CH}_4\text{CH}_3\text{OH}} = 0.512 \text{ moles of carbon in } \text{CH}_4\text{CH}_3\text{OH}$$

- 2) When 2 moles of KOH are added to 3 moles of HI and the following reaction proceeds, what will be in the final mixture when the reaction comes to completion? (The reaction is practically not reversible.)

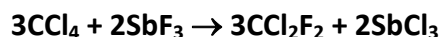


- (a) HI and KI
- (b) KI and H_2O
- (c) HI and H_2O
- (d) HI, KI and H_2O
- (e) KOH, HI, KI and H_2O

Answer: D

Solution: Because the reaction is one to one for KOH and HI there will be excess HI as 3 moles of HI are added to 2 moles of KOH. Therefore the final mixture will contain the two products, KI and H_2O , and excess HI reagent.

- 3) Freon-12 (CCl_2F_2), which is now a banned refrigerant, is prepared by the reaction,



If 0.486 moles of CCl_4 is allowed to react with 0.376 moles of SbF_3 , which chemical substance will be the limiting reagent?

- (a) CCl_4
- (b) CCl_2F_2
- (c) SbCl_3
- (d) SbF_3
- (e) Cannot be determined from the given information.

Answer: A

Solution:

$$0.486 \text{ moles } \text{CCl}_4 \times \frac{3 \text{ moles } \text{CCl}_2\text{F}_2}{3 \text{ moles } \text{CCl}_4} = 0.486 \text{ moles } \text{CCl}_2\text{F}_2$$

$$0.376 \text{ moles } \text{SbF}_3 \times \frac{3 \text{ moles } \text{CCl}_2\text{F}_2}{2 \text{ moles } \text{SbF}_3} = 0.564 \text{ moles } \text{CCl}_2\text{F}_2$$

Therefore CCl_4 is the limiting reagent.

- 4) Calculate the volume in mL of 0.8 M $\text{HCl}_{(\text{aq})}$ needed to completely react with 10.0 mL of 0.4 M $\text{Ba}(\text{OH})_{2(\text{aq})}$.

Answer: 10 mL of HCl.

Solution:

First calculate the moles of OH^- which are produced from $\text{Ba}(\text{OH})_2$:

$$(0.4 \text{ M})(0.01 \text{ L}) = 0.004 \text{ moles of } \text{Ba}(\text{OH})_2$$

Note that 1 mole of $\text{Ba}(\text{OH})_2$ produces 2 moles of OH^- . Therefore, multiple 0.004 moles by 2:

$$0.004 \text{ moles} \times 2 = 0.008 \text{ moles of } \text{OH}^-.$$

In order to completely neutralize the OH^- , we need an equivalent amount of H^+ from HCl. Since 1 mole of HCl = 1 mole of H^+ , we need 0.008 moles of HCl:

$$0.008 \text{ mol} = (0.8 \text{ mol/L})(x \text{ L})$$

$$x \text{ L} = \frac{0.008 \text{ mol}}{0.8 \text{ mol/L}} = 0.001 \text{ L} = 10 \text{ mL}$$

- 5) Place the following in the order basicity (strong to weak) of their conjugate base.

A. HF ($\text{pK}_a = 3.45$)

B. HCOOH ($\text{pK}_a = 3.75$)

C. HClO ($\text{pK}_a = 7.53$)

D. HIO ($\text{pK}_a = 10.64$)

E. CH_3COOH ($\text{pK}_a = 4.75$)

Answer: $\text{IO}^- > \text{ClO}^- > \text{CH}_3\text{COO}^- > \text{HCOO}^- > \text{HF}^-$

Solution:

The strongest conjugate base will result from the compound with the largest K_a or pK_a as $pK_w = pK_a + pK_b$. A small pK_b will result in a stronger base.

6) What is the pH of a 0.12 M aqueous solution of the weak base morphine ($K_b = 1.6 \times 10^{-6}$)?

- (a) 8.20
- (b) 3.56
- (c) 10.64
- (d) 11.10
- (e) 11.56

Answer: C

Solution:

$$B^- + H_2O \rightarrow HB + OH^-$$
$$K_b = \frac{[OH^-][HB]}{[B^-]} = \frac{x \cdot x}{0.12M} = 1.6 \times 10^{-6}$$

Solving for $x = [OH^-] = 4.38 \times 10^{-4}$
Thus, $pOH = -\log[OH^-] = 3.39$
 $pH = 14 - pOH = 14 - 3.39 = 10.64$

7) Calculate the H^+ and OH^- concentration for an aqueous solution with a pH of 10.9.

Answer: $[H^+] = 1.26 \times 10^{-11} M$; $[OH^-] = 7.9 \times 10^{-4} M$

Solution:

$$pH = -\log[H^+], \therefore [H^+] = 10^{-10.9} = 1.26 \times 10^{-11} M$$

For $[OH^-]$, recall that $pK_w = 14 = pH + pOH$
Thus, $pOH = 14 - pH = 14 - 10.9 = 3.1$
 $\therefore [OH^-] = 10^{-3.1} = 7.9 \times 10^{-4} M$

8) Methanoic acid (formic acid) is a weak acid with $K_a = 1.8 \times 10^{-4}$ in water at 25°C.

(a) Calculate pK_b for the conjugate base of methanoic acid at 25°C.

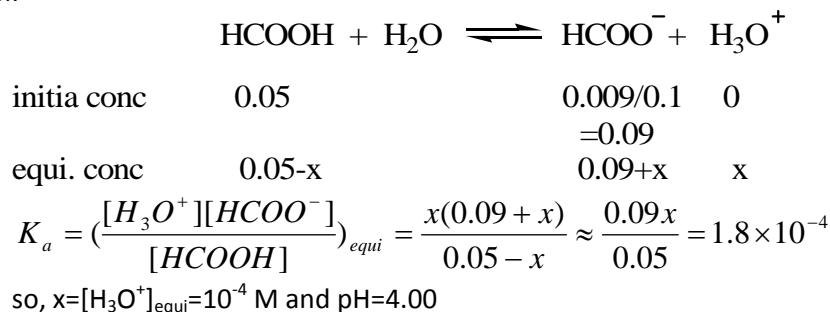
Answer: 10.26

Solution:

$$K_b = \frac{K_w}{K_a} = 5.6 \times 10^{-11} \text{ and } pK_b = -\log_{10}(5.6 \times 10^{-11}) = 10.26$$

(b) A buffer solution is to be prepared from methanoic acid and sodium methanoate. What would be the pH of a solution prepared by dissolving 9.0×10^{-3} moles of sodium methanoate in 100 mL of 0.050 M methanoic acid? (Neglect any change in volume.)

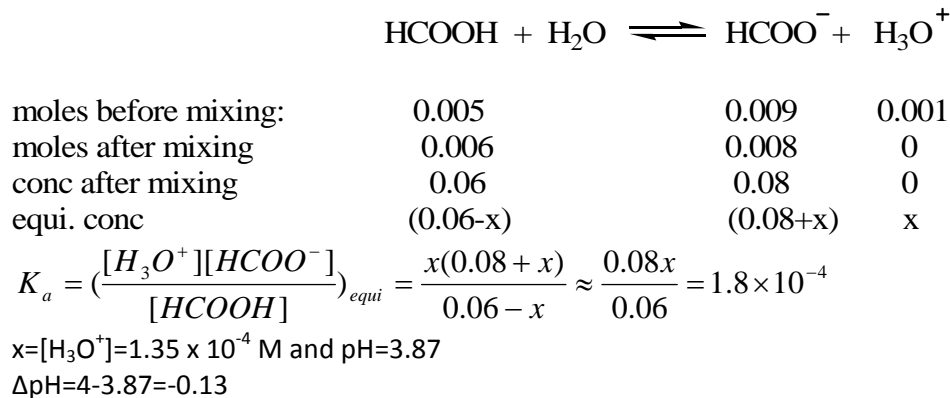
Solution:



(c) What would be the change in the pH of the above solution following the addition of 0.2 mL (4 drops) of 5.0 M HCl? (Neglect any change in volume)

Answer: -0.13

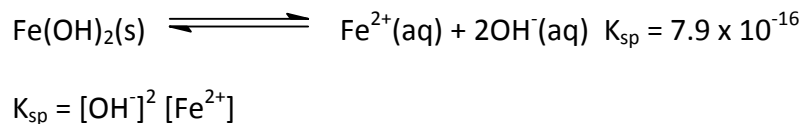
Solution:



9) Not all inorganic salts dissolve completely in water, the degree of dissolution is given by the equilibrium constant, K_{sp} .

i) Write an expression for K_{sp} for $\text{Fe}(\text{OH})_2(\text{s})$ in terms of chemical activities given the following expression:

Solution:



ii) 10g of $\text{Fe}(\text{OH})_2(\text{s})$ (M.W. 89.85g mol^{-1}) is added to 100mL of water. Calculate the concentration of Fe^{2+} and the pH of the solution at equilibria.

Solution:

This requires the employment of an "I. C. E." table. This will allow $[\text{Fe}^{2+}]$, $[\text{OH}^-]$ and consequently pH to be solved for.

First determine the number of moles of $\text{Fe}(\text{OH})_2(\text{s})$ in 10g:

$$\begin{aligned} \text{Moles} &= \frac{(\text{Mass of } \text{Fe}(\text{OH})_2(\text{s}))}{(\text{M.W. of } \text{Fe}(\text{OH})_2(\text{s}))} \\ &= \frac{10\text{g}}{89.5\text{g mol}^{-1}} = 0.112 \text{ mol} \end{aligned}$$

	Moles of $\text{Fe}(\text{OH})_2(\text{s})$	Moles of Fe^{2+}	Moles of OH^-
Initial	0.112 mol	0	0
Change	-x	x	2x
Equilibrium	0.112mol - x	x	2x

$$K_{\text{sp}} = [\text{OH}^-]^2 [\text{Fe}^{2+}]$$

$$7.9 \times 10^{-16} = (2x)^2(x)$$

$$= 4x^3$$

$$x^3 = \frac{7.9 \times 10^{-16}}{4}$$

$$x^3 = 1.975 \times 10^{-16}$$

$$x = (1.975 \times 10^{-16})^{1/3}$$

$$= 5.8235 \times 10^{-6} \text{ moles}$$

x = the moles of Fe^{2+} So,

$$[\text{Fe}^{2+}] = x / \text{volume}$$

$$= \frac{5.8235 \times 10^{-6} \text{ moles}}{0.100\text{L}}$$

$$= 5.8235 \times 10^{-5} \text{ M}$$

To Find pH recall:

$$\text{pH} = 14 - \text{pOH}$$

$$= 14 - (-\log [\text{OH}^-])$$

$$= 14 + \log \frac{(2x)}{\text{Volume}}$$

$$= 14 + \log \frac{(1.1647 \times 10^{-5})}{0.100\text{L}}$$

$$= 14 - 3.934$$

$$= 10.07$$

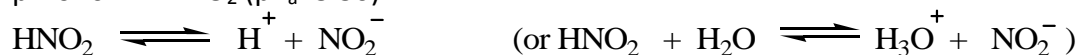
10) On the diagram given in part (e) you are asked to draw a titration curve for the addition of 0.1M NaOH to 25 mL of freshly prepared 0.1M nitrous acid (HNO₂), whose pK_a=3.30 at 25 °C, by evaluating the pH at the following points.

(a) Point A, evaluate the pH of the original HNO₂ solution, before any NaOH is added.

Answer: pH=2.15

Solution:

pH of 0.1M HNO₂ (pK_a=3.30)



$$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{[\text{H}^+]^2}{[\text{HNO}_2]} \quad \text{assuming } \text{H}^+ \text{ from } \text{H}_2\text{O} \text{ is negligible}$$

$$\text{Thus } 10^{-3.30} = \frac{[\text{H}^+]^2}{0.1 - [\text{H}^+]} \quad \text{assume small}$$

$$\text{Then } [\text{H}^+]^2 = 10^{-4.30}, \text{ so } [\text{H}^+] = 10^{-2.15}$$

(b) Point B, As NaOH is being added to the HNO₂ solution, before the equivalence point is reached, the solution contains some remaining undissociated HNO₂ plus some salt, NaNO₂. What is the pH when 12.5 mL NaOH have been added?

Answer: pH=3.30

Solution:

When 12.5mL of NaOH have been added, the system is half-way to the equivalence point. ie: has equal amounts of HNO₂ and NaNO₂

$$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]} \quad \text{and } [\text{NO}_2^-] = [\text{HNO}_2]$$

$$\text{Thus } K_a = [\text{H}^+]; \quad \text{pH} = \text{p}K_a = 3.30$$

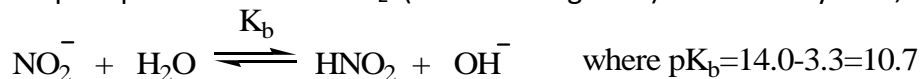
(c) Point C, At the equivalence point the system is "simply" a solution of x M NaNO₂. Determine x and then the pH of the solution.

Answer: x= 0.05 M NaNO₂ pH=8.00

Solution:

At the equivalence point, system has 50mL of 0.05 M NaNO₂ ie: x=0.05 M NaNO₂;

Require pH of 0.05M Na⁺NO₂⁻ (salt of strong base) weak acid system, thus, basic)



$$K_b = \frac{[HNO_2][OH^-]}{[NO_2^-]} \approx \frac{[OH^-]^2}{[NO_2^-]} = 10^{-10.7}$$

$$10^{-10.7} = \frac{[OH^-]^2}{0.05} \quad \therefore [OH^-] = 10^{-1.3} \times 10^{-10.7} = 10^{-12}$$

$$[OH^-] = 10^{-6} \quad \therefore [H^+] = 10^{-8}, \quad pH = 8$$

$$K_B = \frac{K_w}{K_a} = \frac{[OH^-]}{[NO_2^-]} = \frac{K_w^2}{[H^+]^2 [NO_2^-]}$$

$$[H^+]^2 = \frac{K_a K_w}{[NO_2^-]} = \frac{10^{-3.3} 10^{-15}}{10^{-1.3}} = 10^{-16}. \quad [H^+] = 10^{-8} \quad pH = 8$$

(d) Point D, after the addition of 50 mL of the NaOH solution, what are the OH⁻ concentration, and hence the pH?

Answer: [OH⁻]=0.0333M; pH=12.52

Solution:

After addition of 50mL of 0.1 M NaOH, solution contains 50 mL 0.05M NaNO₂ and 25 mL excess 0.1M NaOH

$$\frac{0.05MNaNO_2(50mLNaNO_2)}{75mLsolution} = 0.0333M NaNO_2$$

excess NaOH prevents effective

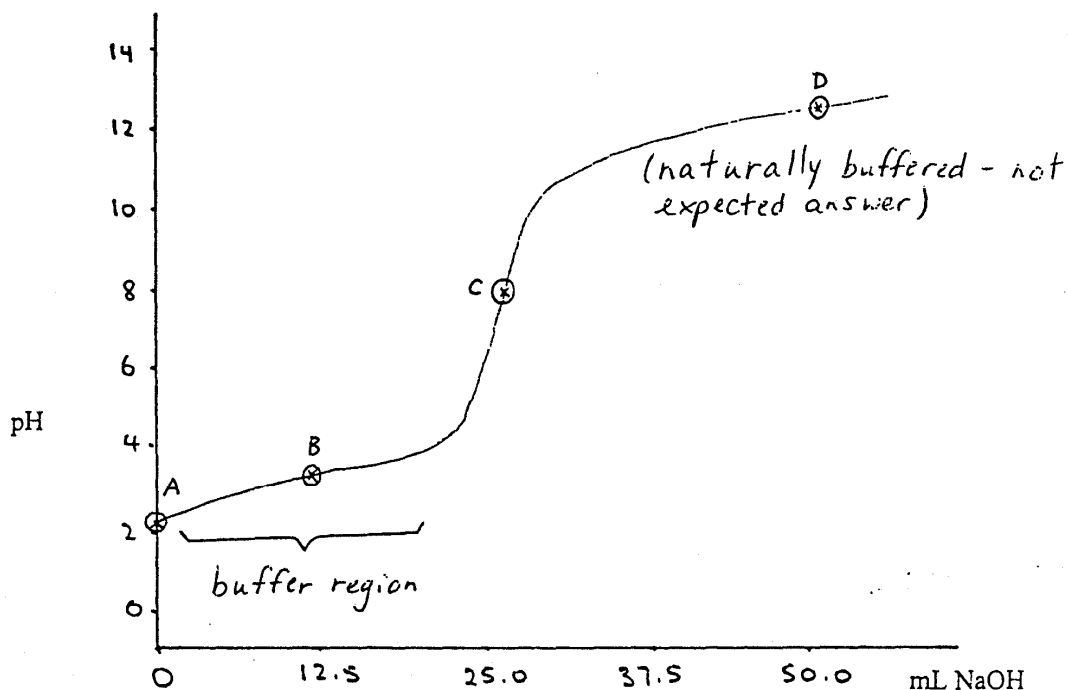
$$\frac{0.1MNaOH(25mLNaOH)}{75mLsolution} = 0.0333M NaOH$$

hydrolysis of the NO₂⁻, thus require of pH of 0.0333M[OH⁻]

pOH=1.477, pH=12.52

(e) Draw the titration curve and identify points A, B, C and D on the curve

Answer:

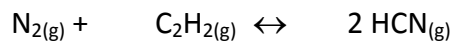


(f) Indicate on the titration curve any region where buffer action is occurring.

Answer: Region where pH changes only very slightly upon the addition of small amounts of acid or base see (e) above.

11) The equilibrium constant for the reaction below is $K_c = 2.5 \times 10^{-4}$ at 25°C . If the initial concentrations were $[\text{N}_2] = [\text{C}_2\text{H}_2] = [\text{HCN}] = 1.00 \text{ mol L}^{-1}$, then what is $[\text{HCN}]$ at equilibrium?

Answer:



i: 1.00 1.00 1.00 \Rightarrow **Q=1>K so then rxn goes to the left**

c: +x +x -2x

e: 1.00+x 1.00+x 1.00-2x

$$\frac{(1.00 - 2x)^2}{(1.00 + x)^2} = K_c \Rightarrow \frac{(1.00 - 2x)}{(1.00 + x)} = \sqrt{K_c}$$

$$x = \frac{1 - \sqrt{K_c}}{2 + \sqrt{K_c}} = 0.488$$

12) Which of the following pairs of solution will give a precipitate when mixed?

$\text{NH}_4\text{Cl}_{(\text{aq})}$ and $\text{Ca}(\text{CH}_3\text{COO})_2_{(\text{aq})}$

$\text{AgNO}_3_{(\text{aq})}$ and $\text{NaCH}_3\text{COO}_{(\text{aq})}$

$\text{Ba}(\text{OH})_2_{(\text{aq})}$ and $(\text{NH}_4)_2\text{SO}_4_{(\text{aq})}$

$\text{Hg}(\text{NO}_3)_2_{(\text{aq})}$ and $\text{KClO}_4_{(\text{aq})}$

$\text{Na}_2\text{SO}_4_{(\text{aq})}$ and $\text{CuCl}_2_{(\text{aq})}$

Answer: C

Solution:

Solubility rules:

Most NO_3^- salts are soluble

AgCl , PbCl_2 and Hg_2Cl_2 are insoluble

BaSO_4 , PbSO_4 , and CaSO_4

Most S^{2-} , CO_3^{2-} and PO_4^{3-} salts are insoluble

13) What is the ground state electron configuration of a) the phosphorus atom? b) the Cr^{2+} ion?

Answer: a) $[\text{Ne}]3s^23p^3$ b) $[\text{Ar}]3d^4$

Solution:

a) Phosphorus is straight forward- $1s^22s^22p^63s^23p^3$ or $[\text{Ne}]3s^23p^3$

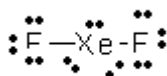
b) First consider the ground state electron configuration for Cr:

$1s^22s^22p^63s^23p^64s^13d^5$. Recall that chromium is a special case when it comes to electron configurations. Both the 4s and 3d orbitals are both half-filled rather than the $1s^22s^22p^63s^23p^64s^23d^4$ electron configuration as predicted by the Aufbau principle. As such, removal of two electrons to form the 2+ ion would result in removal of the $4s^1$ electron and one of the 3d5 electrons to yield $1s^22s^22p^63s^23p^63d^4$ or $[\text{Ar}]3d^4$.

14) Estimate the F-Xe-F bond angle in XeF_2 . Choose from 90, 109, 120, or 180 degrees.

Answer: 180°

Solution:



Total # of valence electrons: $8 + 2(7) = 22$

2 bonding pairs and 3 lone pairs of electrons on Xe atom

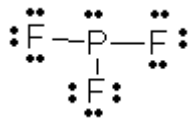
dsp^3 hybridization on Xe atom \rightarrow trigonal bipyramidal basic structure; the F atoms would be 180° apart.

15) What set of hybrid orbitals is used by P atom in PF₃?

- A) sp B) sp² C) sp³ D) dsp³ E) d²sp³

Answer: C) sp³

Solution:



Total # of valence electrons: 5 + 3(7) = 26

3 bonding pairs and 1 lone pair of electrons on the P atom = sp³ hybridization.

16) Consider the molecule NH₂NO₂ shown below:

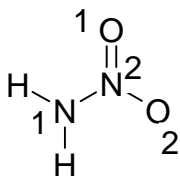
a) Determine the orbital hybridization for N(1), N(2), O(1), O(2) atoms.

b) Predict the magnitude of the angle of:

i) H-N(1)-H

ii) N(1)-N(2)=O(1)

iii) Determine the number of lone pairs of electrons



Answers:

a) N(1): sp³ N(2): sp² O(1): sp² O(2): sp³

b) i) 109° ii) 120° iii) 6 lone pairs

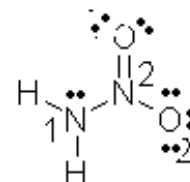
Solutions:

N(1) has 3 bonding pairs and 1 lone pair of electrons → sp³ hybridized

N(2) has 3 bonding pairs of electrons → sp² hybridized

O(1) has 1 bonding pair and 2 lone pairs of electrons → sp² hybridized

O(2) has 1 bonding pair and 3 lone pairs of electrons → sp³ hybridized



i) N(1) is sp³ hybridized; tetrahedral structure; 109° bond angle

ii) N(2) is sp² hybridized; trigonal planar; 120° bond angle

iii) By the Lewis Structure, there are 6 lone pairs of electrons.

17) Which of the following characteristics should apply to PF₃?

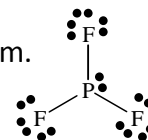
- (I) trigonal planar
- (II) one lone pair of electrons on P
- (III) sp² hybridized phosphorous atom
- (IV) polar molecule
- (V) polar bonds

- A. (I), (IV), and (V)
- B. (II), (III), and (IV)
- C. (I), (II), and (IV)
- D. (II), (IV), and (V)
- E. (I), (III), and (V)

Answer: D

Solution:

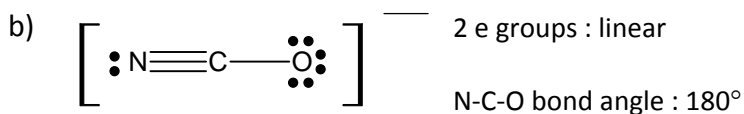
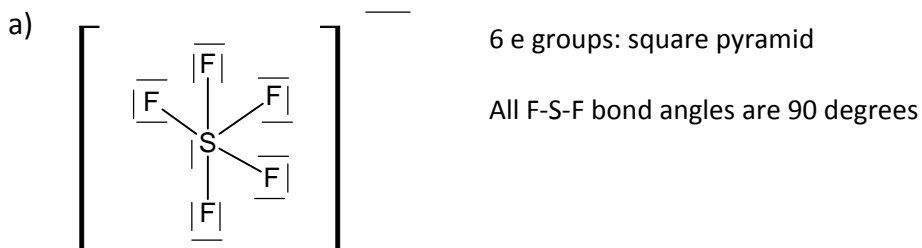
The structure is not trigonal planar due to the lone pair on the central atom. The phosphorus atom is sp³ hybridized, and this molecule is polar and contains polar bonds due to the electronegative F atoms and the less electronegative P atom.



18) For the following molecules, draw the best Lewis structure, showing all valence electrons. You only have to show 1 resonant form if there are multiple resonant forms of equal importance. Give the name of the molecular geometry and state the bond angles in the molecule.

- a) SF₅⁻
- b) NCO⁻

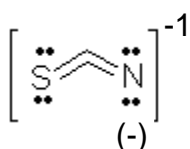
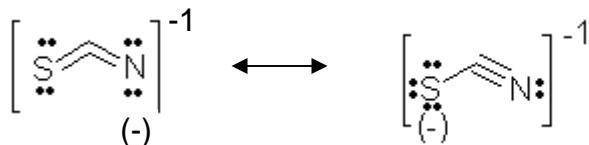
Answers:



19) Write the possible Lewis structures for the thiocyanate anion (SCN^-). (Carbon is central). Determine the formal charge on each atom. From this decide which is the preferred structure.

Answer:

SCN^- : Total # of valence electrons: $6 + 4 + 5 + 1 = 16$



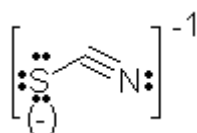
Formal charge = (# of valence electron on a free atom) – (# of valence electrons assigned to the atom in the molecule)

Valence electrons assigned = (# of lone pair electrons) + $\frac{1}{2}$ (# of shared electrons)

For S, formal charge = $6 - [4 + \frac{1}{2}(4)] = 0$

For C, formal charge = $4 - [0 + \frac{1}{2}(8)] = 0$

For N, formal charge = $5 - [4 + \frac{1}{2}(4)] = -1$



For S, formal charge = $6 - [6 + \frac{1}{2}(2)] = -1$

For C, formal charge = $4 - [0 + \frac{1}{2}(8)] = 0$

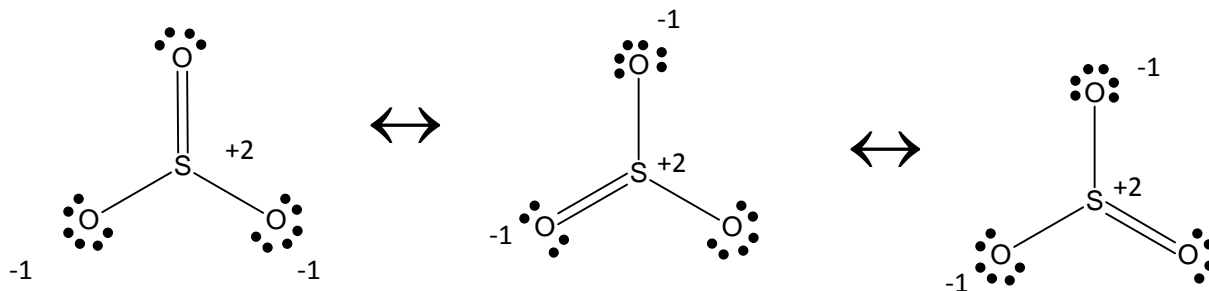
For N, formal charge = $5 - [2 + \frac{1}{2}(6)] = 0$

The first structure is preferred since N is more electronegative than S, and thus is more likely to have the negative charge.

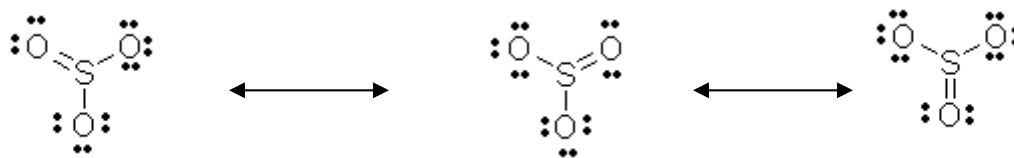
20) Draw the resonance forms for sulphur trioxide (SO_3), in which the central sulphur atom is bonded to the three oxygens, AND indicate the formal charge on all atoms. (Assume that the octet rule is satisfied for all atoms).

Answer:

There are THREE resonance structures.



Total # of valence electrons = $6 + 3(6) = 24$



Formal charge = (# of valence electron on a free atom) – (# of valence electrons assigned to the atom in the molecule)

Valence electrons assigned = (# of lone pair electrons) + $\frac{1}{2}$ (# of shared electrons)

Formal charge of S = $6 - [0 + \frac{1}{2}(8)] = +2$

Formal charge of $-O$ = $6 - [6 + \frac{1}{2}(2)] = -1$

Formal charge of $=O$ = $6 - [4 + \frac{1}{2}(4)] = 0$

21) Using the terms below, indicate the relationship between the following pairs of molecules. Use only one term for each pair.

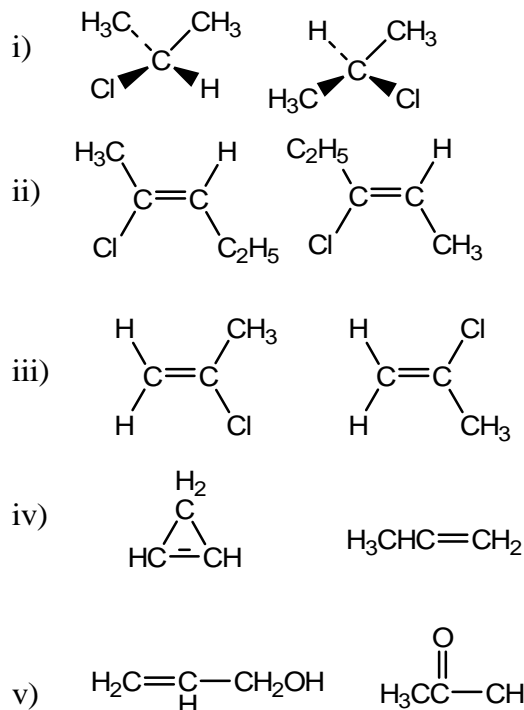
Structural isomers

Geometric (cis/trans) isomers

Enantiomers

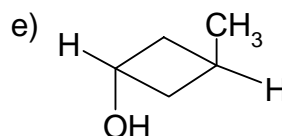
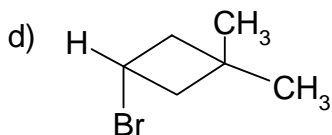
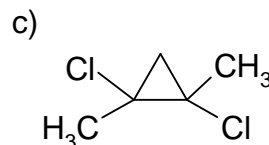
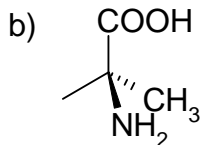
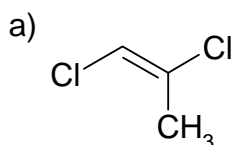
identical molecules

none of the above



Answers: (i) identical; (ii) structural; (iii) identical; (iv) none of the above; (v) structural

22) Which of the following molecules does not have any stereoisomers (geometric or enantiomers)?



Answer: D

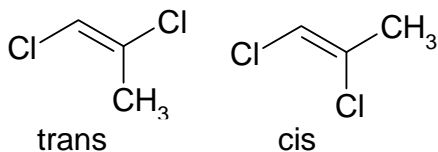
Solution:

Stereoisomers includes **geometric isomers** and **enantiomers**.

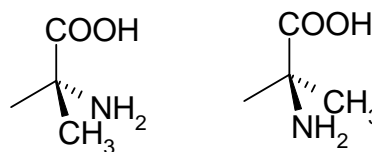
Geometric isomers (also known as cis/trans isomers) result from molecules that are restricted from moving about a double bond or a ring, thus forming different structure.

Enantiomers are a pair of non-superimposable mirror images of each other.

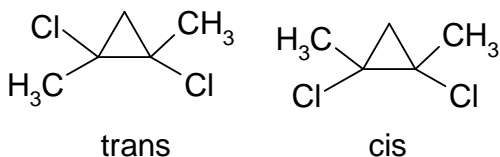
a) Geometric isomers possible



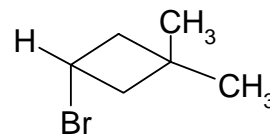
b) Enantiomers possible



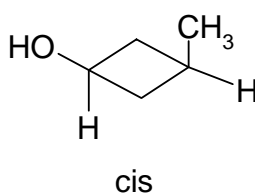
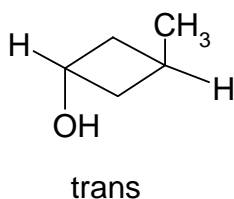
c) Geometric isomers and enantiomers



d) No stereoisomers possible because of the 2 methyl groups on one of the carbons



e) Geometric isomers; plane of symmetry is present so no enantiomers are possible.



23) Rank the following four-carbon compounds based on the decreasing order of boiling point.

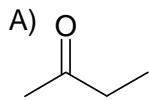
- A. $\text{CH}_3\text{C(O)CH}_2\text{CH}_3$
- B. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
- C. $\text{CH}_3\text{CH}_2\text{CH}_2\text{C(O)NH}_2$
- D. $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$
- E. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

Answer: $C > E > A > D > B$

Solution:

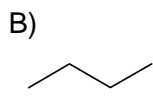
The boiling point depends on the type of intermolecular forces present.

H-bonding > dipole-dipole > London dispersion forces.



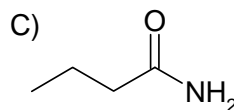
Ketone

Dipole-dipole



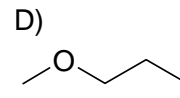
Alkane

London



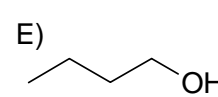
Amide

H-bonding &



Ether

weak



Alcohol

H-bonding

The order of intermolecular bonding strength & hence boiling temp is:

Amide (C) > Alcohol (E) > Ketone (A) > Ether (D) > Alkane (B)

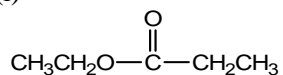
24) Arrange the following compounds according to boiling point (i.e. list them starting with the one with the lowest boiling point and finish with the one with the highest boiling point):

propane, 1-pentanol, methane, dimethyl ether, 1-propanol.

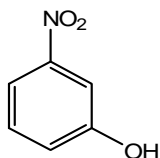
Answer: Methane < propane < dimethyl ether < 1-propanol < 1-pentanol

25) Name the following compounds by the IUPAC system.

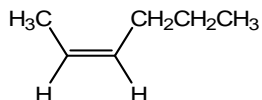
(i)



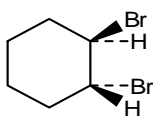
(ii)



(iii)



(iv)



(v) $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{CH}_3$

Solution:

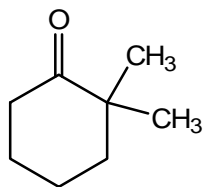
- (i) ethyl propanoate
- (ii) 2-or m-nitrophenol
- (iii) cis-2-hexene
- (iv) trans-1,2-dibromocyclohexane
- (v) 2,2,3,3-tetramethylpentane

26) Draw the structural formula of the following compounds.

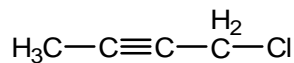
- (i) 2,2-dimethylcyclohexanone
- (ii) 3-methylcyclopentene
- (iii) potassium benzoate
- (iv) 1-chloro-2-butyne
- (v) 2,6-dimethyl-2,5-heptadiene

Answer:

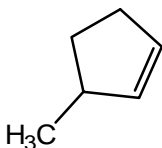
(i)



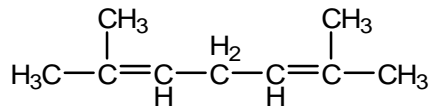
(iv)



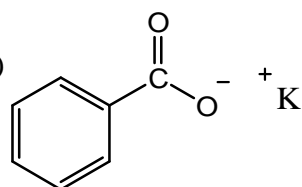
(ii)



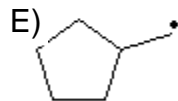
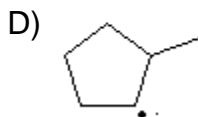
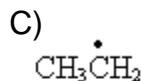
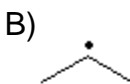
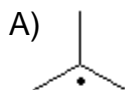
(v)



(iii)



27) Which of the following free radical intermediate is the least stable?



Ans: C

Solution:

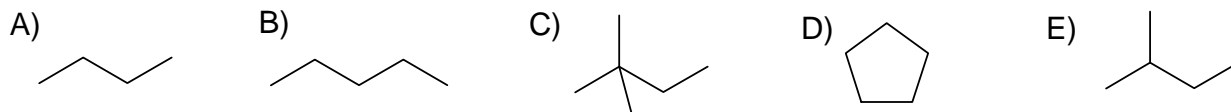
Primary carbon radicals are the least stable compared to 2° or 3° carbons. Carbon radicals are electron-deficient like carbocations; thus structure E, which contains a cyclopentane group attached to the 1° carbon, is more stable than structure C, which has a methyl group attached to the 1° carbon.

28) Which of the following compounds has the most reactive kind of C-H bond for reaction with Br₂ under ultraviolet light?

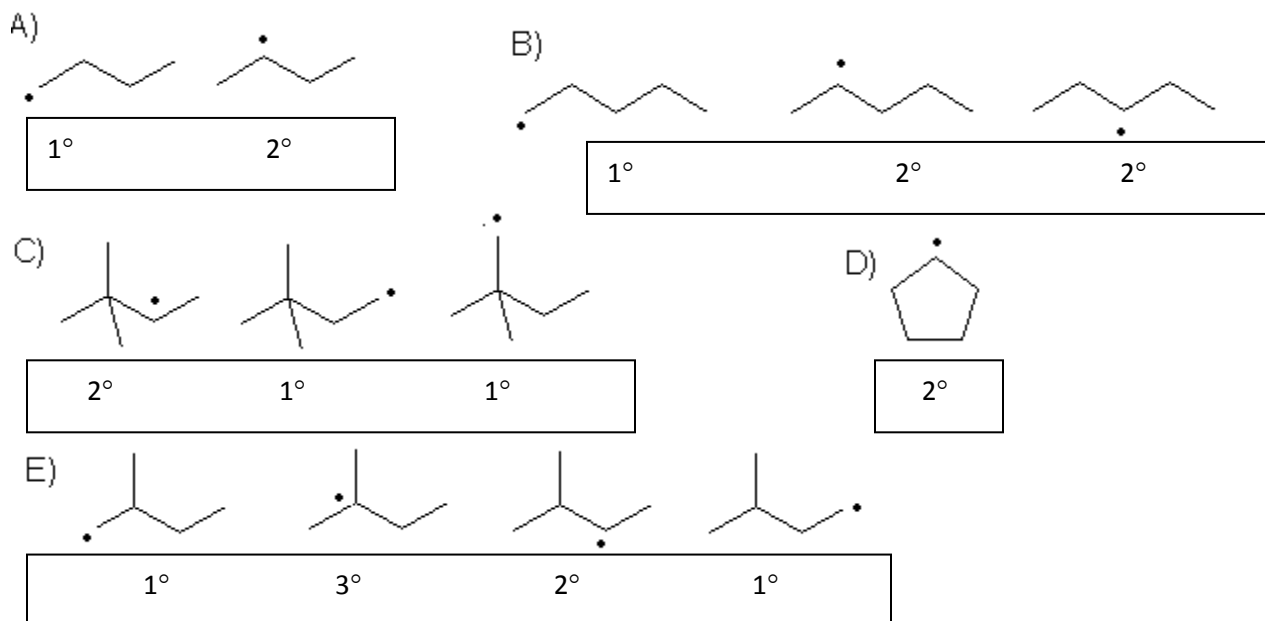
- a) butane
- b) pentane
- c) 2,2-dimethylbutane
- d) cyclopentane
- e) 2-methylbutane

Answer: e) 2-methylbutane

Solution:

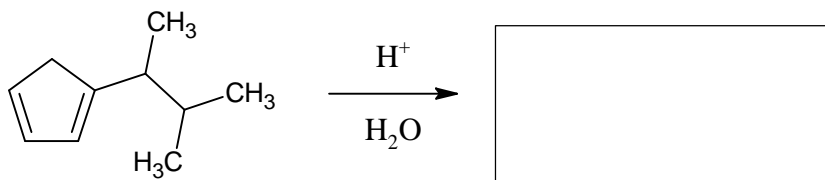


The structure containing the most reactive C-H bond would be the one that forms the most stable radical. The order of radical stability is as follows: 3° carbons $>$ 2° carbons $>$ 1° carbons. Structure E would be the most reactive as the radical would be on a 3° carbon.

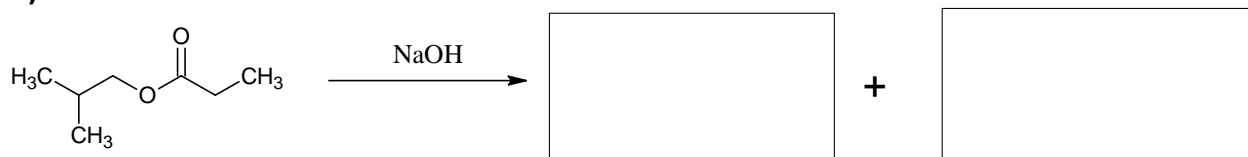


29) Complete the following reactions by providing the appropriate products in the boxes provided:

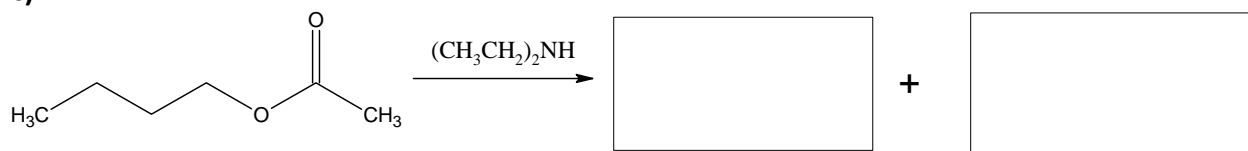
a)



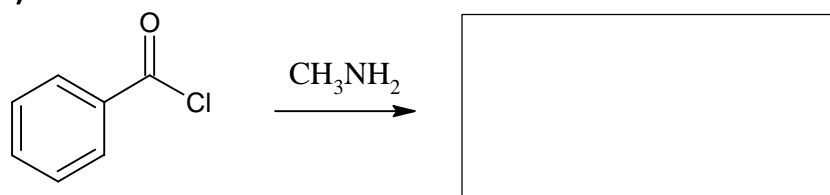
b)



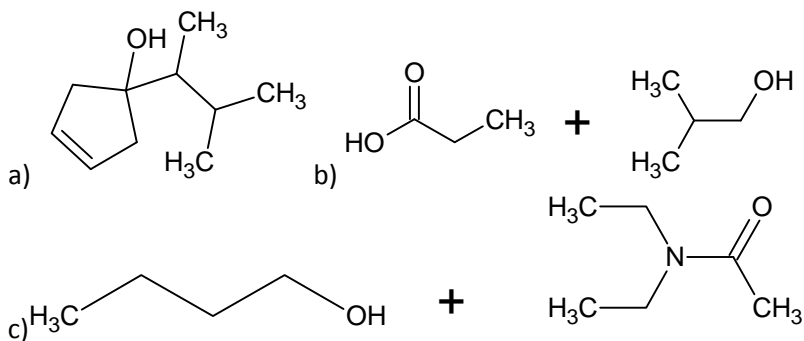
c)

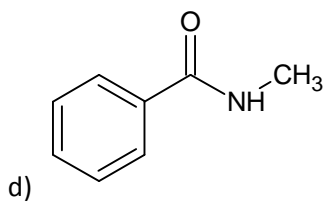


d)



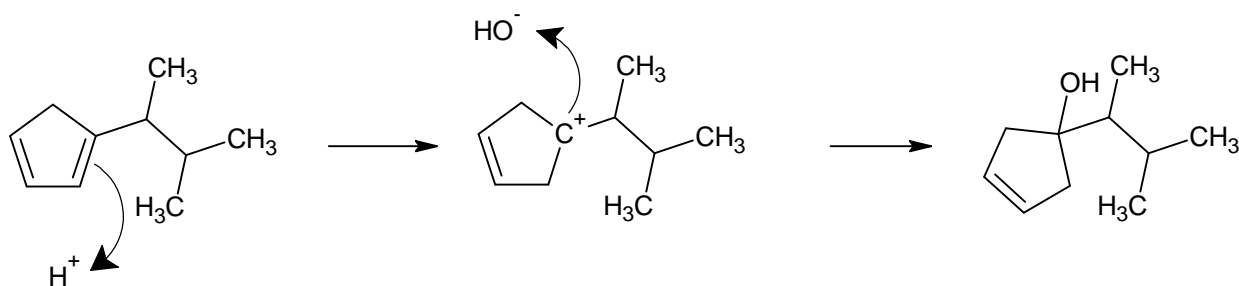
Answers:



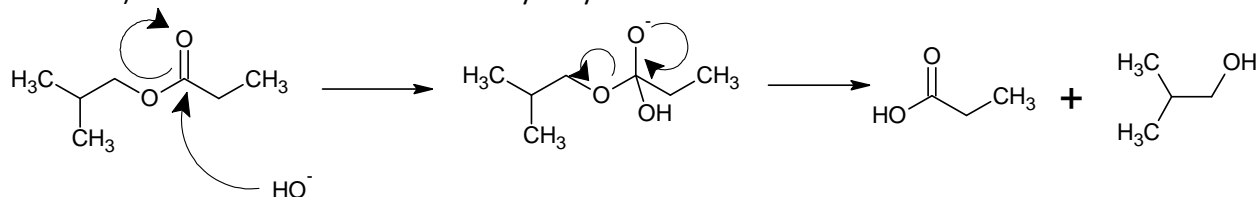


Solutions:

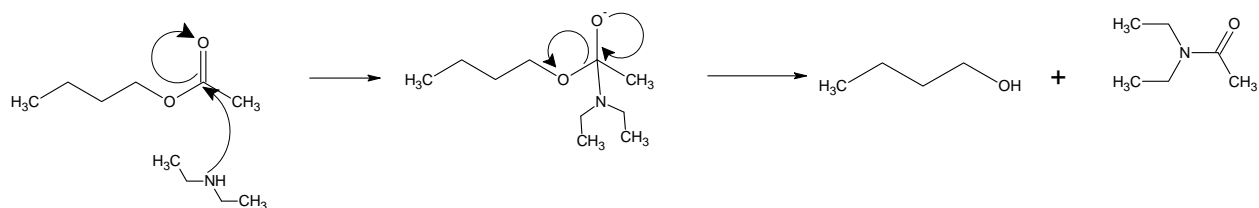
a) Electrons in the alkene bond will react with the H^+ , followed by electrophilic addition of the OH^- to the newly created tertiary carbocation. Recall that tertiary carbocations are more stable than primary or secondary carbocations.



b) This reaction involves an ester hydrolysis in a basic solution.

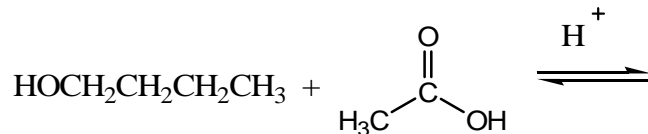


c) This is a synthesis of an amide by reacting an ester with an amine.

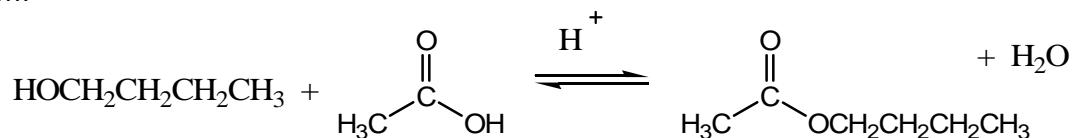


d) This reaction results in the synthesis of an amide from an acid halide and a primary amine.

30) Butanol and ethanic acid react in acidic solution to give a compound that smells fruity. Draw the structures of the products formed from this reaction. Also, what can be done to improve the yield of the reaction?



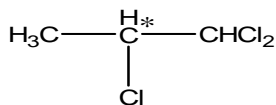
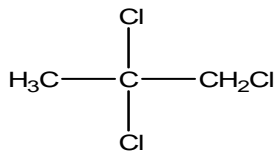
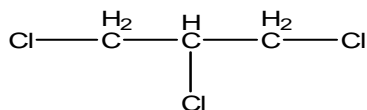
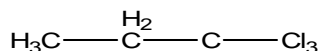
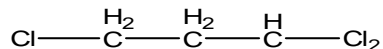
Solution:



The reaction shown above is actually an equilibrium process. In order to improve this reaction, consider Le Chatelier's principle. If we wanted to shift the equilibrium to the right, we need to either add more reactants or remove water as it is formed.

31) Draw all structures possible for $\text{C}_3\text{H}_5\text{Cl}_3$. Indicate with an asterisk (*) any chiral carbon atoms which are present. Be sure to include all hydrogen atoms.

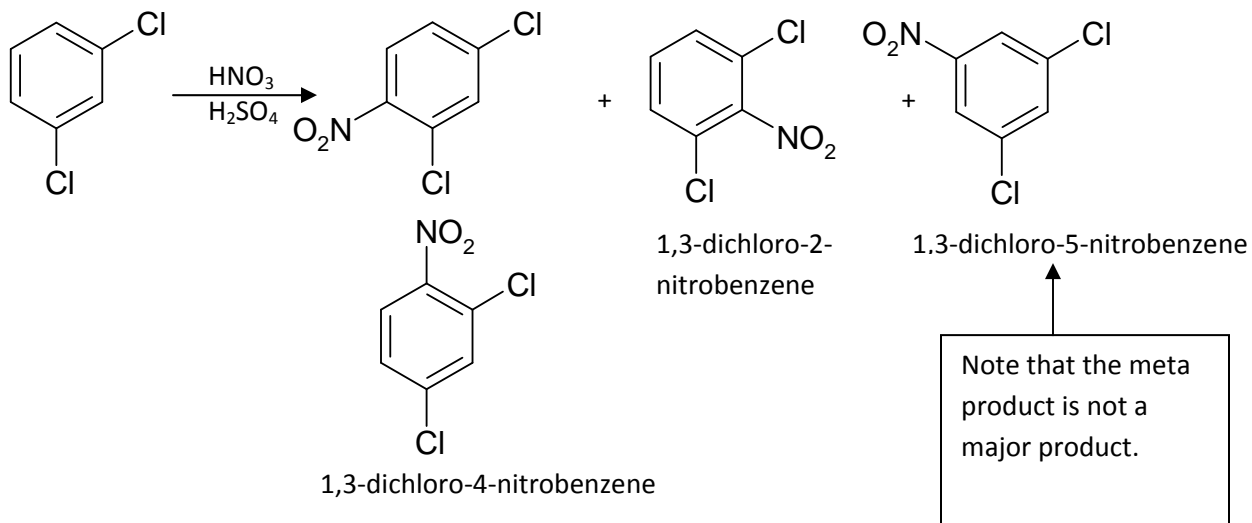
Solution:



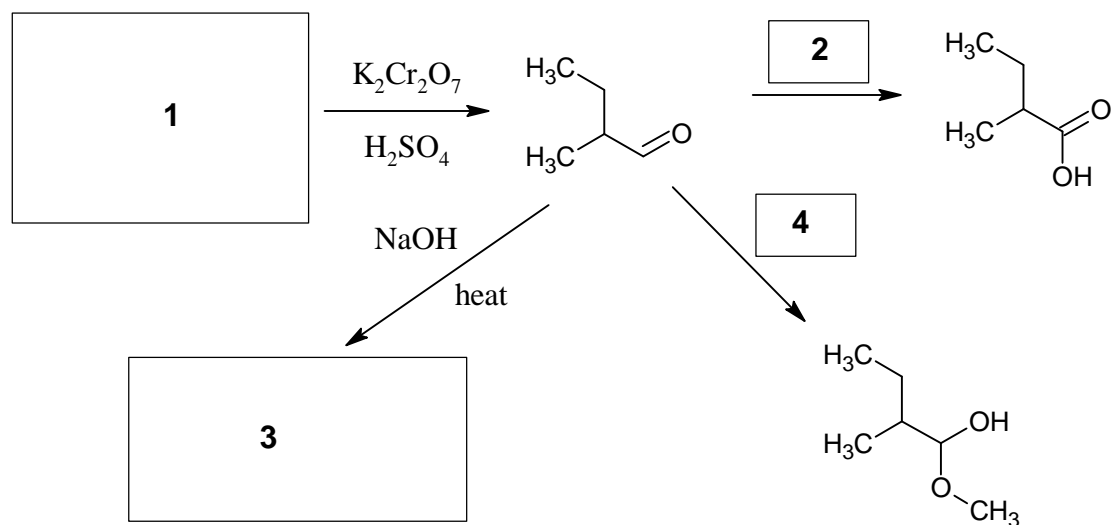
32) How many products are possible in the reaction of 1,3-dichlorobenzene with $\text{HNO}_3/\text{H}_2\text{SO}_4$? Draw and name each of the products.

Solution:

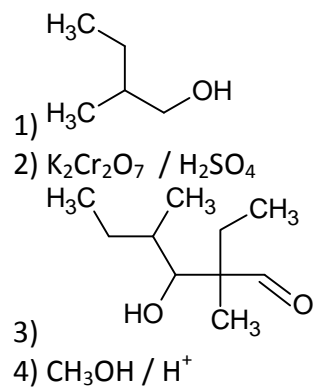
Halogen-containing aromatic compounds are ortho & para-directing deactivators. Though halogens are electron withdrawing groups, they can have electron donating effects as a result of resonance at the ortho and para positions. As such, the following structures can be formed:



33) Fill in the missing reagents and products.



Answer:



Solution:

- 1) This is an oxidation reaction to an aldehyde. As such, we need to start off with the primary alcohol.
- 2) This is another oxidation reaction so we need a strong oxidizing agent such as $\text{K}_2\text{Cr}_2\text{O}_7$ and an acid such as H_2SO_4 .
- 3) This reaction will result in a dimerization reaction. It is an aldol reaction of an aldehyde with a strong base to yield a beta-hydroxy aldehyde.
- 4) The product is a hemi-acetal. In order for this reaction to occur, our aldehyde has to react with methanol under acidic conditions.