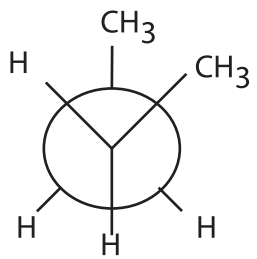
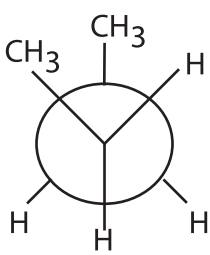
Medicinal & Organic Chemistry- Q & A

2024-2025 Edition



n-Butane

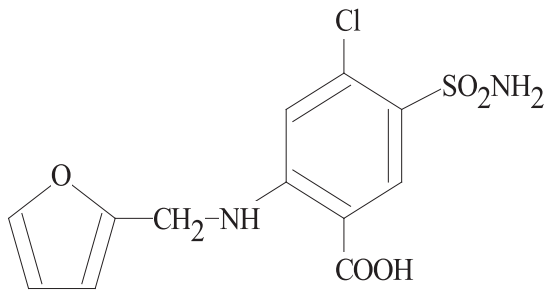
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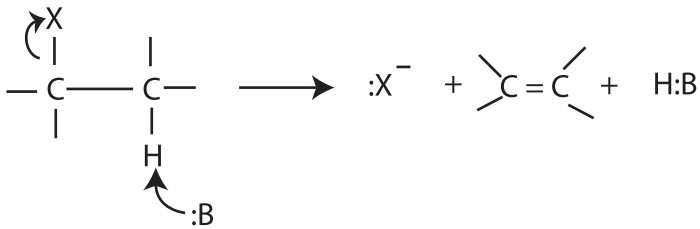
n-Butane

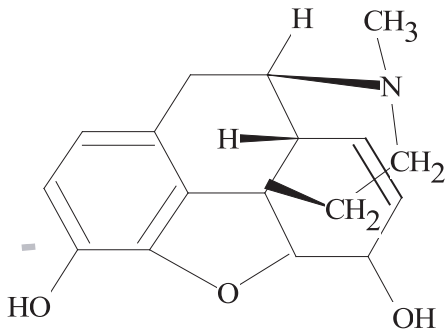
III

Gauche Conformations



Furosemide





Morphine

PREPARATION

CHEMISTRY

Questions & Answers

By Manan H. Shroff, R.Ph 2024-2025 Edition

RXEXAM - MEDICINAL & ORGANIC CHEMISTRY QUESTIONS & ANSWERS

2025 Edition

Manan H. Shroff

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Preface:

RxExam - Medicinal and Organic Chemistry - Questions & Answers is specifically written for students preparing for the FPGEE and Canadian Evaluating Exams. It has 500 questions with answers and complete explanations. Recently, the exam puts more emphasis on graph- and structure-based questions, therefore an effort was made to include all of these topics in a review guide.

Each answer is explained thoroughly to refresh your memory on specific topics. Please do not go through only the questions and answers. Try to understand and learn the answer's explanations. It is the best way to get the most out of this review guide.

I hope my efforts will help you to pass your key exam. I wish you the very best of luck, and any questions or comments are always welcome.

Manan Shroff

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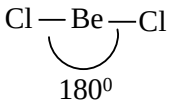
SECTION-I

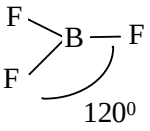
QUESTIONS **7**

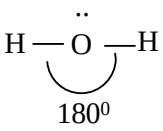
SECTION-II

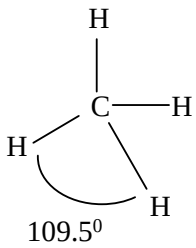
ANSWERS **87**

1. Which of the following is incorrectly presented?

a. 

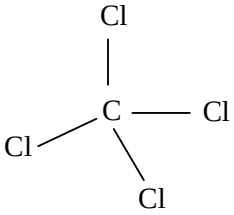
b. 

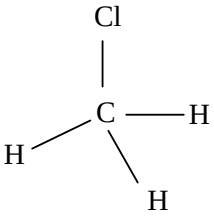
c. 

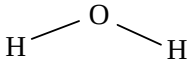
d. 

2. Which of the following molecules has the largest dipole?

a. 

b. 

c. 

d. 

3. Which of the following is falsely presented?

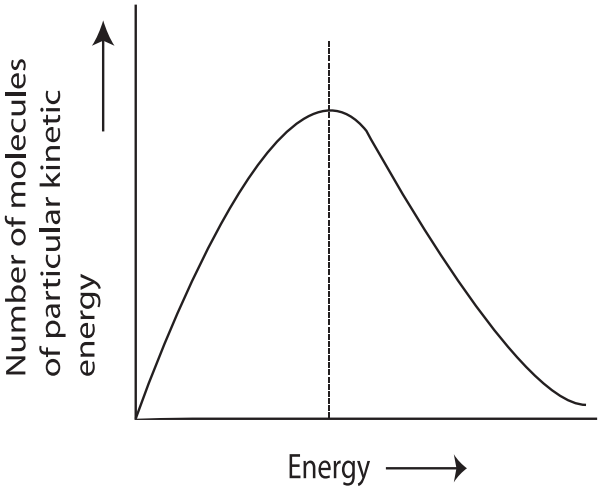
a. $CH_4 \xrightarrow{F_2} CH_3F + HF$

b. $CH_4 \xrightarrow{Cl_2} CH_3Cl + HCl$

c. $CH_4 \xrightarrow{Br_2} CH_3Br + HBr$

d. $CH_4 \xrightarrow{I_2} CH_3I + HI$

4. Which of the following statements is true about the following chart?



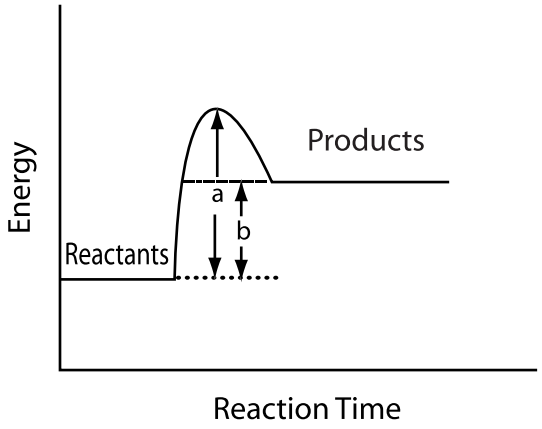
a. The temperature is a measure of the average kinetic energy.

b. Kinetic energy of the moving molecules is not the source of the energy needed for reaction.

c. The number of molecules with a particular kinetic energy is greatest for an energy near the average and decreases as the energy becomes larger or smaller than the average.

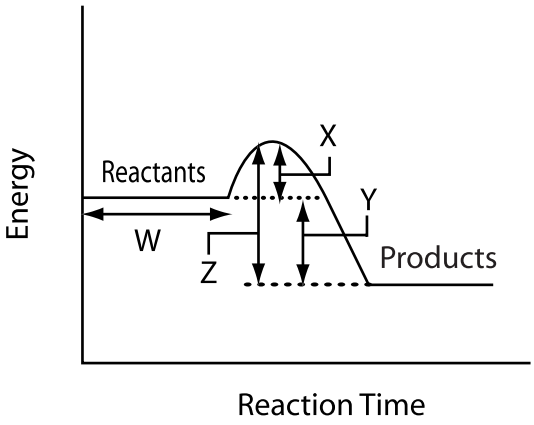
d. The size and weight of the particles are characteristic of each reaction and cannot be changed.

5. Which of the following is true about the graphic presentation?



a. It is an endothermic reaction.
b. The b-portion is called activation energy.
c. The a-portion is the energy given off.
d. It is an exothermic reaction.

6. On a following graphical presentation, identify the activation energy for a reaction.

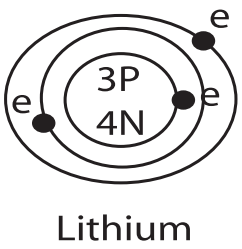


a. W
b. X
c. Y
d. Z

7. From the graph of question 6, one can say that:

a. Z = exothermic energy
b. Z-Y = exothermic energy
c. Z-X = exothermic energy
d. X + Y = exothermic energy

8. What is the mass number of lithium?



Lithium

a. 3
b. 4
c. 7
d. 1

9. Which of the following is an isotope of hydrogen?

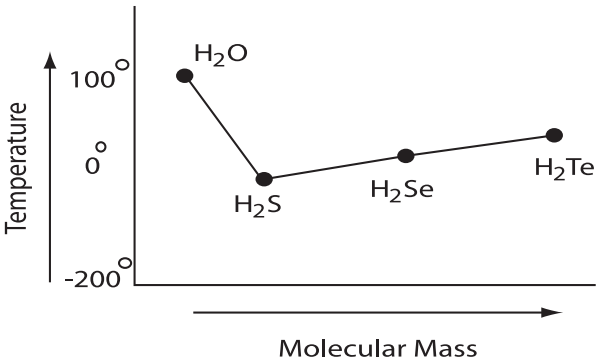
a. 

b. 

c. 

d. 

10. Which of the following statements are TRUE about the following graphical presentation?



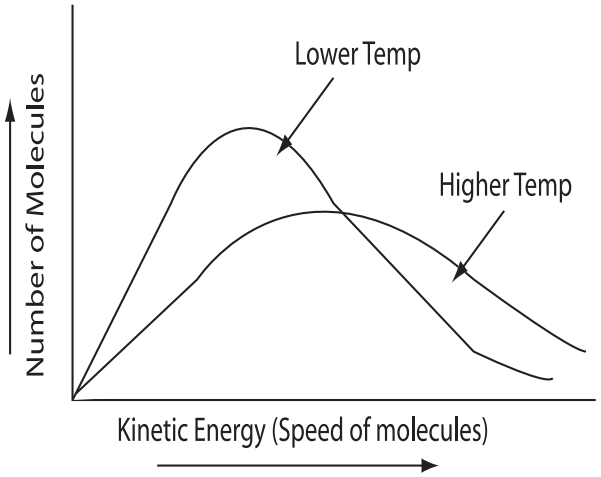
I. The high boiling point of water is due to its ability to form strong H-bonding.

II. The H-bond formation is the strongest in H_2Te.

III. The increase of the boiling point of a compound is directly proportional to its molecular mass.

a. I only
b. I and II only
c. II and III only
d. All

11. Which of the following statements are TRUE about the relationship between kinetic energy and number of molecules?



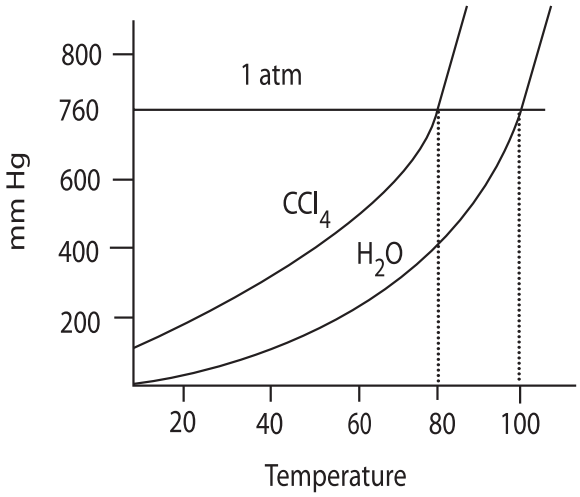
I. As the temperature of a gas increases, its kinetic energy is increased.

II. Temperature increases a measure of the average kinetic energy of the particles.

III. The average kinetic energy of molecules is found at the peak of the curve.

a. I only
b. I and II only
c. II and III only
d. All

12. What is the boiling point of CCl_4?



a. 760 °
b. 100 °
c. 20 °
d. 80 °

13. Which of the following pentane structures has the lowest boiling point?

a. $CH_3—CH_2–CH_2–CH_2–CH_3$

b. $CH_3–CH_2–CH(CH_3)—CH_3$

c. $CH_3—C(CH_3)_2—CH_3$

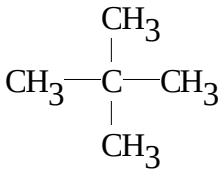
d. $CH_3–CH(CH_3)—CH_2–CH_3$

14. Which of the following arrangements lists the compounds below in the order of decreasing the bond dissociation energy (high-energy first, least-energy last)?

1. CH_4

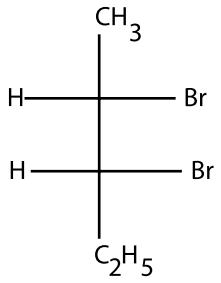
2. CH_3CH_3

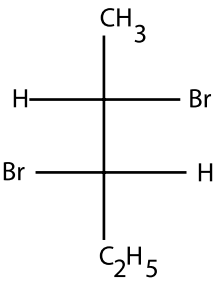
3. $CH_3CH_2CH_3$

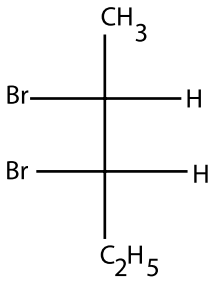
4. 

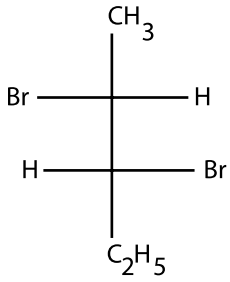
a. 1 > 2 > 3 > 4
b. 4 > 3 > 1 > 2
c. 2 > 4 > 3 > 1
d. 1 > 4 > 3 > 2

15. Which of the following compounds represents a pair of diastereomers?

1. 

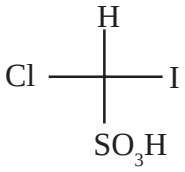
2. 

3. 

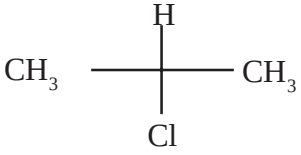
4. 

a. 1 and 3
b. 2 and 4
c. 3 and 2
d. 4 only

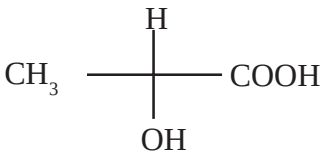
16. Which of the following compounds does NOT contain a chiral carbon?

1. 

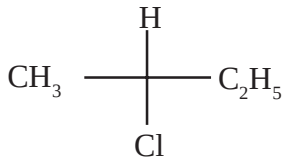
(Chloroiodomethanesulfonic acid)

2. 

Isopropyl chloride

3. 

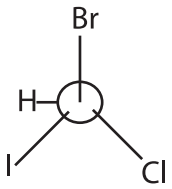
(Lactic acid)

4. 

(sec-Butyl chloride)

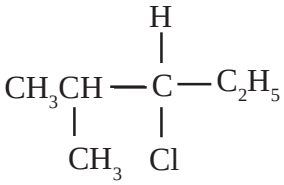
a. 1
b. 2
c. 3
d. 4

17. What is the complete name for the optically active compound listed below?



a. (+)-Bromochloroiodomethane
b. (S)-Bromochloroiodomethane
c. (R)-Bromochloroiodomethane
d. (RS)-Bromochloroiodomethane

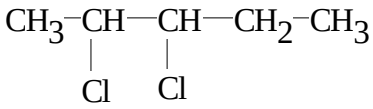
18. In the following compound what would be the correct configuration sequence of atoms attached to the chiral carbon?



3-chloro-2-methylpentane

a. Ethyl > Cl > Isopropyl > H
b. Cl > Ethyl > H > Isopropyl
c. Cl > Isopropyl > Ethyl > H
d. Isopropyl > Cl > Ethyl > H

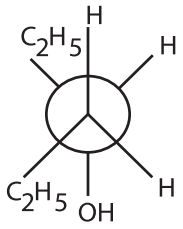
19. How many enantiomers are possible for 2,3-Dichloropentane?



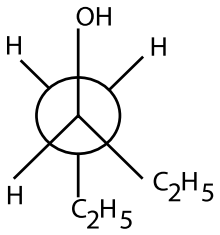
2,3-Dichloropentane

a. 1
b. 3
c. 4
d. 5

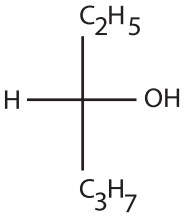
20. Which of the following is (R)-3-hexanol?



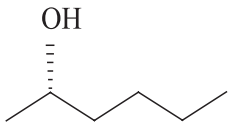
(fig-1)



(fig-2)



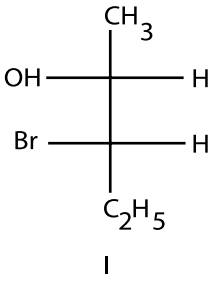
(fig-3)



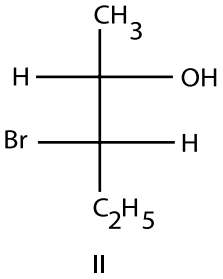
(fig-4)

a. fig-1
b. fig-2
c. fig-3
d. fig-4

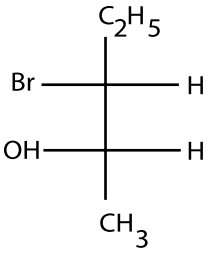
21. Which two fischer formulas represent a pair of enantiomers?



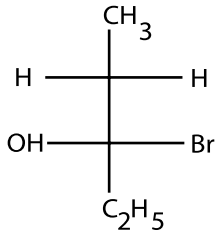
I



II



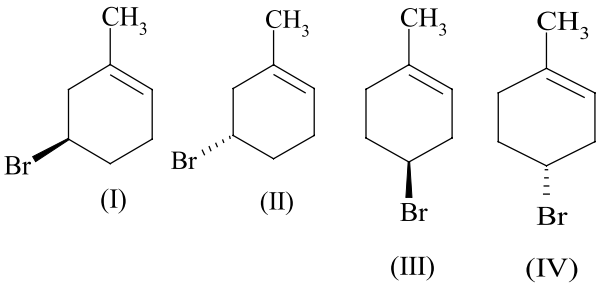
III



IV

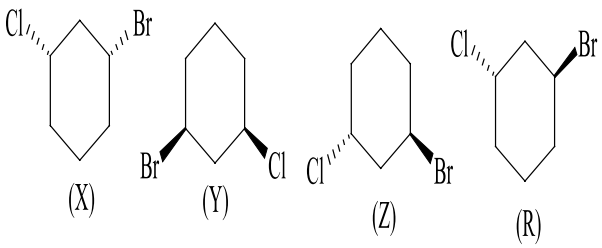
a. I and IV
b. II and III
c. III and I
d. II and IV

22. Which of the following compounds is (S)-4-bromo-1-methylcyclohexene?



a. I
b. II
c. III
d. IV

23. Which of the following compounds represents a pair of enantiomers?

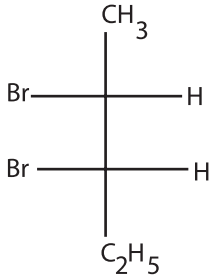


a. X and Y
b. X and Q
c. Z and Y
d. Z and R

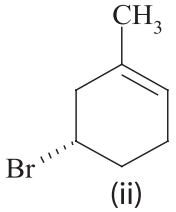
24. Pure (R)-2-pentanol has a specific rotation of -10.50 degrees. You have purified a sample that has a calculated specific rotation of -2.625 degrees. What can you conclude about this sample?

a. The sample has completely racemized
b. 75% of the sample has rearranged into a meso-isomer
c. 50% of the sample has racemized
d. 75% of the sample has racemized

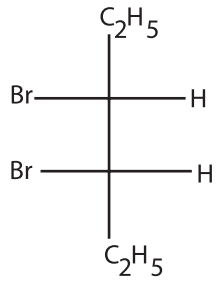
25. Which of the following is classified as a meso- compound?



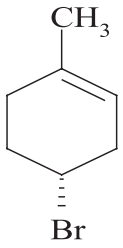
(i)



(ii)



(iii)



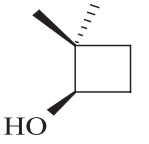
(iv)

a. i
b. ii
c. iii
d. iv

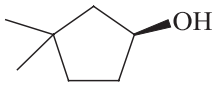
26. How many stereoisomers of $(CH_3)_2CHCH=CHCH_2CH(OH)CH_2Br$ are possible?

a. 5
b. 4
c. 2
d. 0

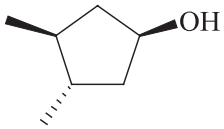
27. A $C_7H_{14}O$ optically active alcohol (3,3-Dimethylcyclopentanol) is oxidized by Jones' reagent to an optically inactive (achiral) ketone. What is the correct structural formula for this compound?



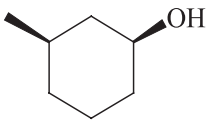
(1)



(2)



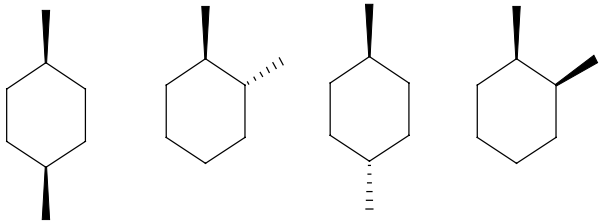
(3)



(4)

a. 1
b. 2
c. 3
d. 4

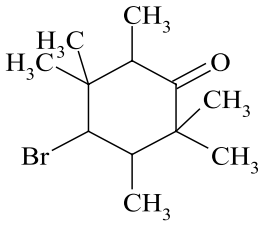
28. Which of the following C_8H_{16} isomers is thermodynamically most stable?



R S T U

a. R
b. S
c. T
d. U

29. How many stereoisomers are possible for the following compound?

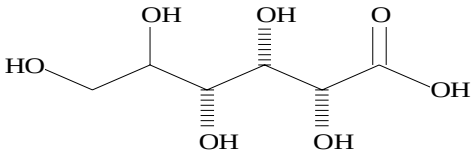


a. 2
b. 4
c. 8
d. 10

30. Which of the following compounds has the highest boiling point?

a. $CH_3CH_2CH_2CH_2CH_3$
b. CH_3CH_2OH
c. CH_3Cl
d. NH_4

229. What is a chemical formula of gluconic acid?



Gluconic acid

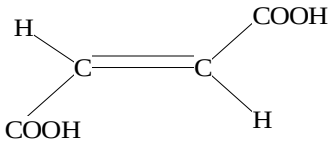
a. $C_7H_{13}O_8$

b. $C_6H_{12}O_7$

c. $C_5H_{12}O_9$

d. $C_6H_{12}O_{10}$

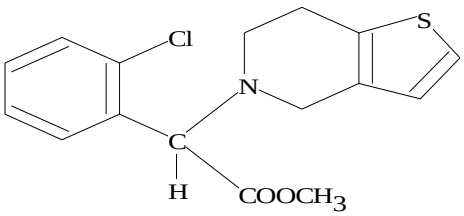
230. Below is the structure of fumaric acid. What is the name of the cis isomer of it?



Fumaric acid

a. Ascorbic acid
b. Lactic acid
c. Formic acid
d. Maleic acid

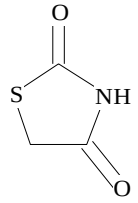
231. Below is the structure of a well known anti-platelets aggregation inhibitor, clopidogrel. What is the name of heterocyclic group present in the structure?



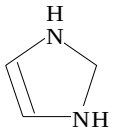
Clopidogrel

a. Imidazoline
b. Imidazole
c. Thienopyridine
d. Benzofuran

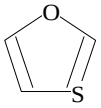
232. Rosiglitazone (Avandia) is a derivative of the parent:



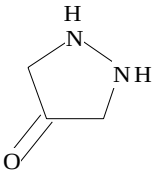
Compound A



Compound B



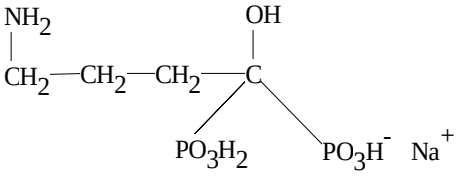
Compound C



Compound D

a. Compound A
b. Compound B
c. Compound C
d. Compound D

233. The compound shown below is used for the treatment of:



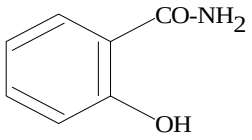
a. Hypertension
b. Diabetes
c. Osteoporosis
d. Aluminum toxication

234. The chances of methemoglobinemia and hemolytic anemia are higher when administering:

I. Acetaminophen
II. Phenacetin
III. Acetanilide

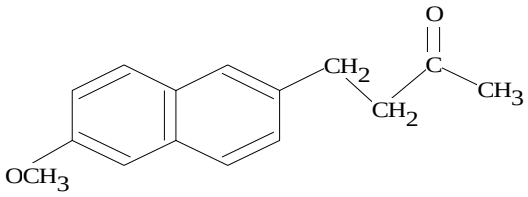
a. I only
b. I and II only
c. II and III only
d. All

235. The structure shown below is known as:



a. acetyl salicylic acid
b. salicylsalicylic acid
c. salicylamide
d. 5-(2,4-difluorophenyl)-salicyclic acid

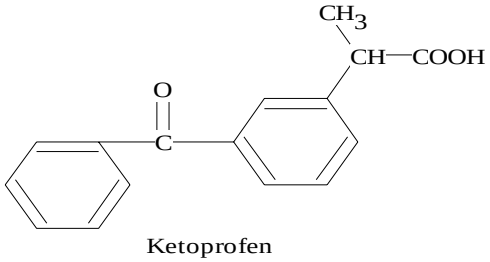
236. What is the name of the functional aromatic group in nabumetone?



Nabumetone

a. naphthalene
b. phenanthrene
c. pentacene
d. benzopyrene

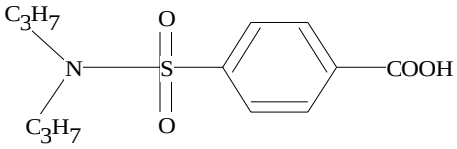
237. In the following structure, please identify the major functional group.



Ketoprofen

a. Ether
b. Ester
c. Ketone
d. Phenol

238. Below is the structure of probenecid. Which of the following statements are TRUE if we replace both (C_3H_7) groups at the nitrogen position with (CH_3) groups?



Probenecid

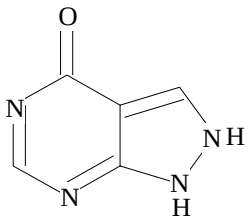
I. Uricosuric activity decreases with the substitution of methyl groups.

II. Renal clearance of the compound decreases with substitution of methyl groups.

III. The reabsorption of uric acid in proximal tubules increases with substitution of methyl groups.

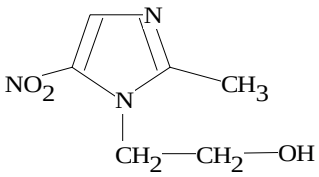
a. I only
b. I and II only
c. II and III only
d. All

239. The compound shown below inhibits which of the following enzymes?



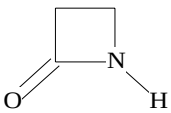
a. MAO
b. COMT
c. Xanthine oxidase
d. Dihydro folate reductase

240. What is the name of the heterocyclic group found in the following structure?



a. pyridine
b. pyrazole
c. imidazole
d. pyrrole

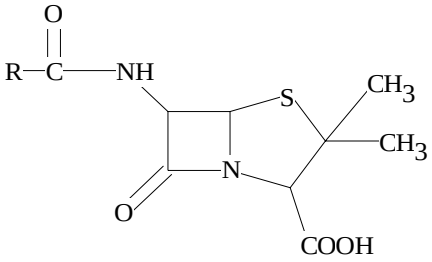
241. The beta-lactam ring is also known as:



Beta lactam ring

a. cyclic ketone
b. cyclic amide
c. cyclic ester
d. cyclic amine

242. Which of the following statements is TRUE about improving the acid stability of penicillin?



Penicillin

a. The R substituent group should be highly lipophilic.

b. The R substituent group should be highly hydrophilic.

c. The R substituent group should be a strong electron-withdrawing group.

d. The R substituent group should be a strong electron-donating group.

243. To prepare beta-lactamase resistant penicillin, one should use:

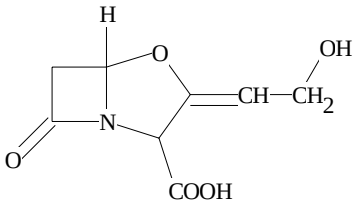
a. The aromatic ring that is directly attached to the side-chain carbonyl and both ortho positions should be substituted by methoxy groups.

b. The aromatic ring that is directly attached to the side-chain carbonyl and ortho and para positions should be substituted by methoxy groups.

c. The aromatic ring that is directly attached to the side-chain carbonyl and meta and para positions should be substituted by methoxy groups.

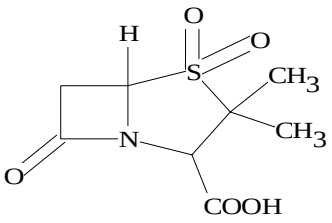
d. A methylene between the aromatic ring and carbonyl group of side chain.

244. The compound shown below functions as:



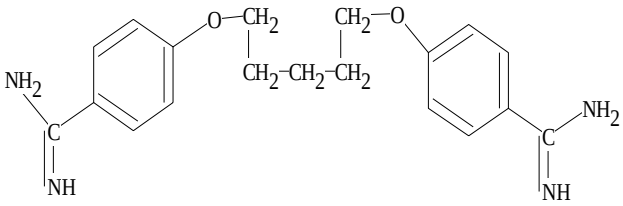
a. An MAO inhibitor
b. A xanthine oxidase inhibitor
c. A 5-alpha azo reductase inhibitor
d. A beta-lactamase inhibitor

245. The compound shown below has the similar indication as:



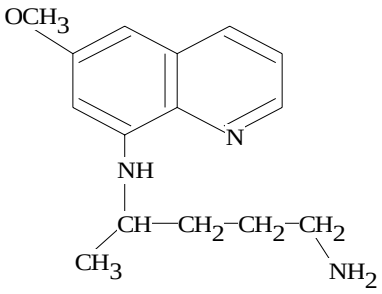
a. Hydralazine
b. Sulfonamide
c. Clavulanic acid
d. Finasteride

246. The compound shown below is mainly indicated for the prophylaxis and treatment of:



a. Legionnaires' disease
b. Pneumocystis carinii pneumonia
c. Parkinson's disease
d. Traveller's diarrhea

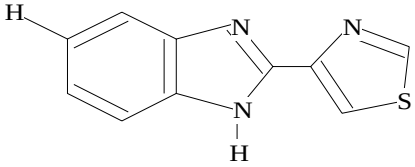
247. What is the name of the heterocyclic organic compound present in Primaquine?



Primaquine

a. Quinoline
b. Isoquinoline
c. Pyridazole
d. Indole

248. What is the name of the heterocyclic organic compounds in the following structure?

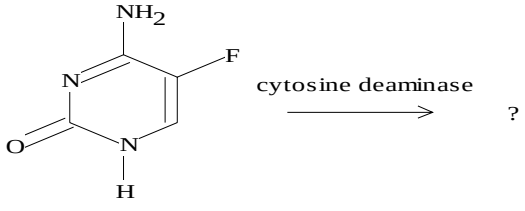


Thiabendazole

I. Benzimidazole
II. Thiazole
III. Isothiazole

a. I only
b. I and II only
c. II and III only
d. All

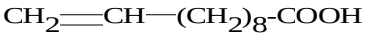
249. Below is the structure of flucytosine. It is converted to an active drug by fungal cytosine deaminase to:



Flucytosine

a. Griseofulvin
b. Capsofungin
c. 5-Fluorouracil
d. Micafungin

250. What is the name of the following compound?

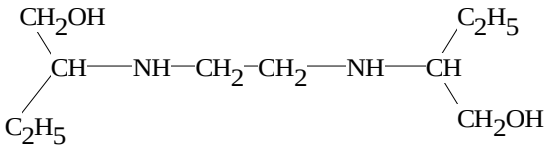


a. Oleic acid
b. Undecylenic acid
c. Arachidic acid
d. Stearic acid

251. 5-hydroxypyrazinoic acid is the metabolite of which of the following?

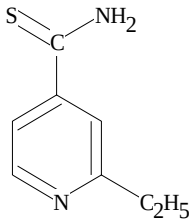
a. Isoniazid
b. Nicotinamide
c. Pyrazinamide
d. Rifampin

252. What is the name of the drug shown in the structure below?



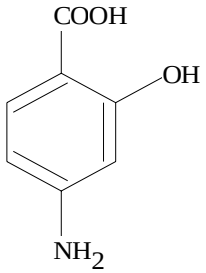
a. Rifabutin
b. Ethambutol
c. Isoniazid
d. Ethionamide

253. What is an IUPAC name of the following compound?



a. 4-pyridine-1-ethylthiocarbomide
b. 3-ethyl carbothiamidine
c. 2-ethylpyridine-4-carbothioamide
d. 2-ethyl-4-thioamide

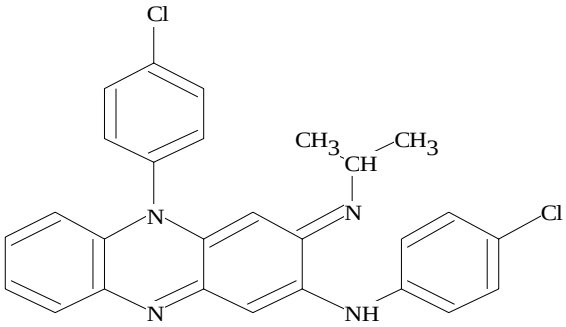
254. When administering simultaneously, p-aminosalicylic acid increases the plasma concentration of:



p-aminosalicylic acid

a. Streptomycin
b. Sulfonamide
c. Isoniazid
d. Ethambutol

255. Discoloration of pink, red or brownish-black of the sputum, tears and urine has been reported with Clofazimine. What is the name of the organic compound in Clofazimine that is responsible for this?



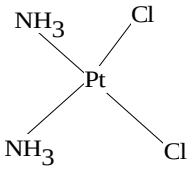
Clofazimine

a. Chlorobenzene
b. Para-aminochlorobenzene
c. Dibenzopyrazine
d. 2-aminopropane

256. 4,4'-diaminodiphenylsulfone is the chemical name for:

a. Sulfamethoxazole
b. Rifampin
c. Dapsone
d. Thalidomide

257. The principal side effect of the compound shown below is:



a. Cardiac toxicity
b. Severe nausea and vomiting
c. Respiratory failure
d. Severe rash

258. Cis-diamminedichloridoplatinum shall be carefully prescribed with:

I. Cyclophosphamide
II. Ifosfamide
III. Streptomycin

a. I only
b. I and II only
c. II and III only
d. All

259. Which of the following statements are TRUE about Cisplatin-induced nephrotoxicity?

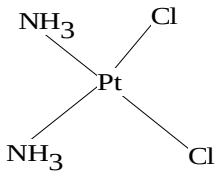
I. Patients should be hydrated with chloride- containing solution prior to therapy.

II. Saline or mannitol diuretics should be used continuously throughout the therapy.

III. Prolonged dialysis shall be used to minimize cisplatin induced nephrotoxicity.

a. I only
b. I and II only
c. II and III only
d. All

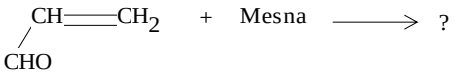
260. Cisplatin-induced nephrotoxicity can be minimized by administering:



Cisplatin

a. Sodium bicarbonate
b. Mesna
c. Sodium thiosulfate
d. Aluminum phosphate

261. What is the water-soluble non-toxic product of the following reaction?



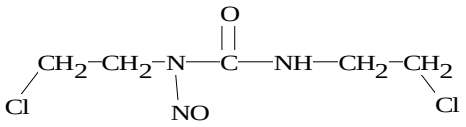
(Acrolein)

a. CH_3CH_2CHO
b. CH_3CH_2SHCHO
c. $CHOCH_2CH_2SCH_2CH_2SO_3^-$
d. $CH_3CH_2CH_2SHCHCOO^-$

262. Triethylenephosphoramide is an active metabolite of:

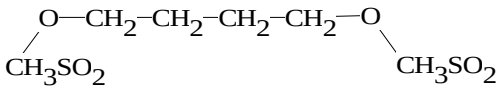
a. Procarbazine
b. Carmustine
c. Thiotepa
d. Ifosfamide

263. The compound shown below is classified as:



a. Nitrogen mustard
b. Triazenes
c. Nitrosoureas
d. Mitosis inhibitor

264. The compound shown below is known as:



a. Cisplatin
b. Dacarbazine
c. Chlorambucil
d. Busulfan

265. What is the backbone structure of Doxorubicin?

a. Sulfonamide
b. Tetracycline
c. Anthracyclins
d. Phenylhydrazine

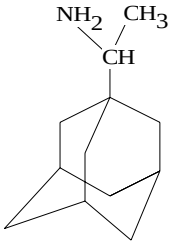
266. Which of the following free radicals produced by anthracycline antibiotics may induce severe irreversible cardiac tissue damage?

a. H_3O^+
b. .OH
c. $.O_2^-$
d. Fe^{+2}

267. Which of the following is NOT a pyrimidine antagonist?

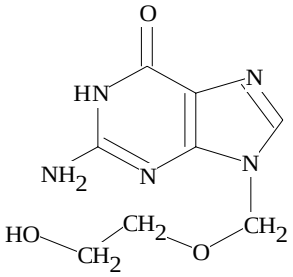
a. Fluorouracil
b. Methotrexate
c. Capecitabine
d. Thioguanine

268. The compound shown below is pharmacologically and structurally related to:



a. Metoprolol
b. Nifedipine
c. Amantadine
d. Diphenhydramine

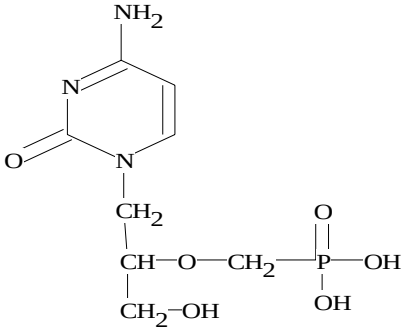
269. Below is the structure of the well known antiviral drug acyclovir. What is the name of the heterocyclic organic compound present in the structure?



Acyclovir

a. Guanine
b. Adenine
c. Cytosine
d. Uracil

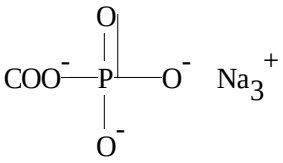
270. Below is the structure of Cidofovir (Vistide). It is a nucleotide analogue of cytosine where cytosine is classified as:



Cidofovir

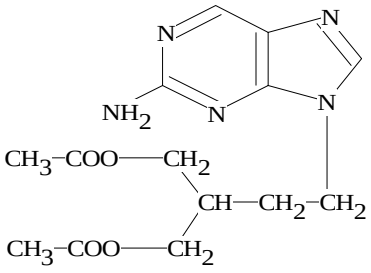
a. Pyrimidine base
b. Purine base
c. Indole base
d. Pyrrole base

271. The compound shown below may cause:



a. Severe hypotension
b. Seizure
c. Electrolyte disturbances
d. Severe nausea and vomiting

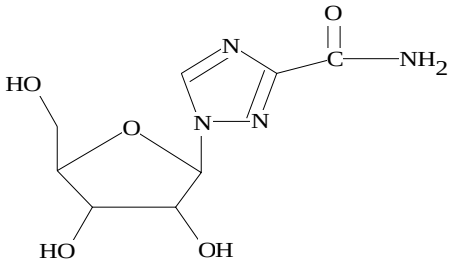
272. Below is the structure of antiviral drug Famciclovir. It is a prodrug of:



Famciclovir

a. Acyclovir
b. Griseofulvin
c. Idoxuridine
d. Penciclovir

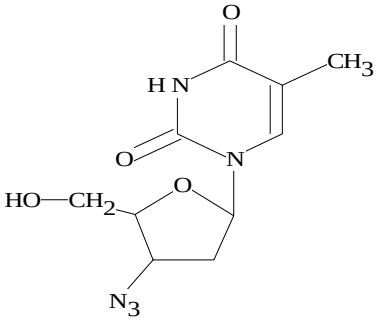
273. The name of heterocyclic aromatic compound present in Ribavirin is:



Ribavirin

a. Phenol
b. Triazole
c. Pyrazole
d. Benzoic acid

274. Below is the structure of the very well known anti-HIV drug Zidovudine. Please identify heterocyclic, aliphatic and organic functional groups in it.

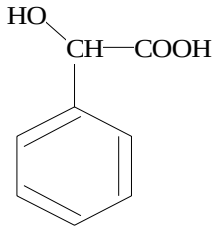


Zidovudine

I. Tetrahydrofuran
II. Thymidine
III. Azido

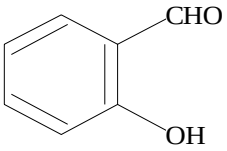
a. I only
b. I and II only
c. II and III only
d. All

275. The compound shown below is known as:



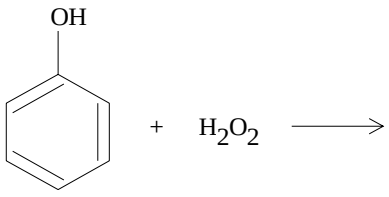
a. Benzoic acid
b. Tartaric acid
c. Mandelic acid
d. Linoleic acid

276. What is the IUPAC name of the following compound?



a. 2-al phenol
b. Benzaldehyde
c. Benzoxyphenol
d. 2-hydroxybenzaldehyde

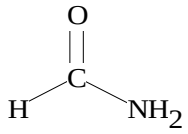
277. What is the name of the final product of the following reaction?



Phenol

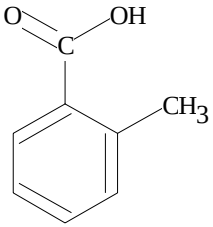
a. 1,2-dihydrophenol
b. 2-hydroxybenzoic acid
c. 2-hydroxyphenol
d. 1,2,5,6-tetrahydropehol

278. What is the name of the functional organic group in the following compound?



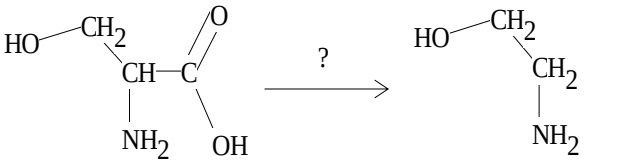
a. ketone
b. aniline
c. aldehyde
d. ether

279. What is the name of the following compound?



a. stearic acid
b. o-phthalic acid
c. o-toluic acid
d. citric acid

280. What is the name of the enzyme participating in the following reaction?

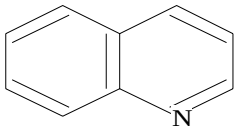


2-amino-3-hydroxypropanoic acid

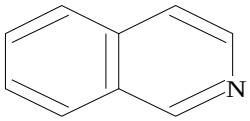
2-aminoethanol

a. choline-n-methyl transferase
b. monoamine oxidase
c. serine decarboxylase
d. peroxidase

Pneumocystis pneumonia. It is a member of the 8-aminoquinoline group of drugs.

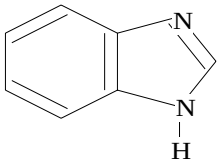


Quinoline

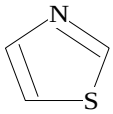


Isoquinoline

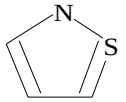
248. (b) I and II only. Thiabendazole (Mintezol) is classified as anthelmintic drug. It is indicated for the treatment of helminth infections. There are two heterocyclic organic compounds present in Thiabendazole: benzimidazole and thiazole.



Benzimidazole

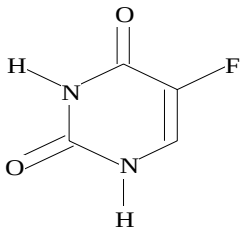


Thiazole



Isothiazole

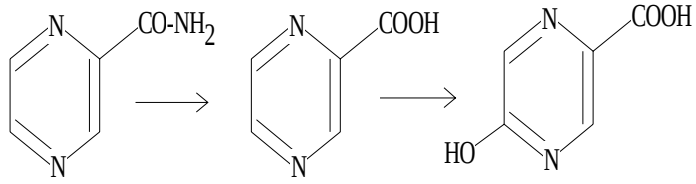
249. (c) Flucytosine (Ancobon), a pro-drug, is converted by fungal cytosine deaminase to 5-fluorouracil. This reaction does not occur in mammalian cells. The 5-fluorouracil is then converted to cytotoxic agent, 5-fluorodeoxyuridine monophosphate. Human cells do not contain cytosine deaminase and therefore do not convert flucytosine to 5-fluorouracil. It is indicated only in the treatment of serious infections caused by susceptible strains of Candida and/or Cryptococcus.



5-fluorouracil

250. (b) Undecylenic / undecenoic acid is an organic unsaturated fatty acid derived from natural castor oil. It is the common name of the 10-undecenoic acid ($CH_2CH(CH_2)_8COOH$). It is used in the manufacture of pharmaceuticals, cosmetics and perfumery including anti-dandruff shampoos, and anti-microbial powders. Undecylenic acid is produced by the cracking of Castor oil under pressure. Undecylenic acid is a natural fungicide and is FDA approved in over-the-counter medications for skin disorders or problems. It is the active ingredient in medications for skin infections and relieves itching, burning, and irritation. For example, it is used against fungal skin infections such as athlete's foot, ringworm and candida albicans. It is also used in the treatment of psoriasis.

251. (c) Pyrazinamide (PZA) is a drug used to treat tuberculosis in afflicted patients. The drug is largely bacteriostatic, but can be bacteriocidal on actively replicating tuberculosis bacteria. It is only used in combination with other drugs such as isoniazid and rifampicin in the treatment of Mycobacterium tuberculosis. It metabolizes to pyrazinoic acid and then subsequently to 5-hydroxypyrazinoic acid.



Pyrazinamide Pyrzinoic acid 5-hydroxypyrazinoic acid

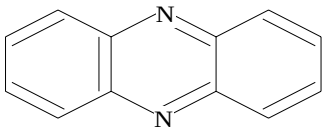
252. (b) Ethambutol (Myambutol) is a bacteriostatic anti-mycobacterial drug prescribed to treat tuberculosis (Mycobacterium tuberculosis). It is usually given in combination with other tuberculosis drugs, such as isoniazid, pyrazinamide and rifampicin. It may reduce visual acuity, including irreversible blindness, which appears to be due to optic neuritis. Optic neuropathy, including optic neuritis or retrob-

ulbar neuritis, occurring in association with ethambutol therapy may be characterized by one or more of the following events: decreased visual acuity, scotoma, color blindness, and/or visual defect. These events have also been reported in the absence of a diagnosis of optic or retrobulbar neuritis. Patients should be advised to report promptly to their physician any change of visual acuity.

253. (c) The compound shown in the structure is ethionamide (Trecator). The IUPAC name for this compound is 2-ethylpyridine-4-carbothioamide. It is antibacterial agent indicated for the treatment of tuberculosis.

254. (c) Para-aminosalicylic acid is used as second-line agent for the treatment of tuberculosis. It is thought to act as an antimetabolite interfering with the incorporation of p-aminobenzoic acid into folic acid. When coadministered with INH (Isoniazid), para-aminosalicylic acid (PAS) is found to reduce the acetylation of INH, itself being the substrate for acetylation, thus increasing the plasma level of INH.

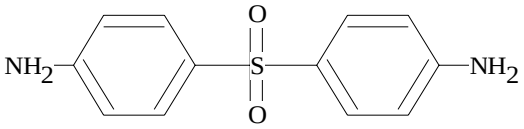
255. (c) Phenazine, also called dibenzopyrazine, is a dibenzo annulated pyrazine and the parent substance of many dyestuffs, such as the eurhodines, toluylene red, indulines and safranines. Being a phenazine derivative water-insoluble dark-red dye, it leads to pigmentation of the skin and discoloration of tears, sweat, sputum and urine.



phenazine or dibenzopyrazine

Clofazimine (Lamprene) is used in combination with rifampicin and dapsone as multidrug therapy (MDT) for the treatment of leprosy.

256. (c) Dapsone or 4,4'-diaminodiphenylsulfone or 4,4'-Sufonyldianiline is an pharmacological medication most commonly used in combination with rifampicin and clofazimine as multidrug therapy (MDT) for the treatment of Mycobacterium leprae infections (leprosy).



4,4'-Diaminodiphenylsulfone
(Dapsone)

257. (b) Cisplatin (Platinol) is organometallic neoplastic agent. It is used for the treatment of metastatic testicular, ovarian and advanced bladder cancer. Severe nausea and vomiting are reported with Cisplatin. Use of antiemetic agent is required prior to cisplatin therapy. Myelosuppression and ototoxicity, including irreversible hearing loss, is also reported with the therapy.

258. (d) Cis-diamminedichloridoplatinum or Cisplatin or Platinol is highly nephrotoxic in nature. It should be carefully prescribed with other nephrotoxic agents such as cyclophosphamide, ifosfamide and streptomycin.

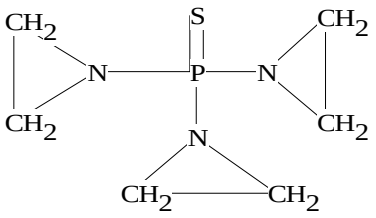
259. (b) To protect patients against cisplatin-induced nephrotoxicity, patients should be hydrated with chloride containing solution prior to therapy. Use of saline or mannitol diuretics is also recommended to promote continuous excretion of the drug and its water soluble metabolite. Cisplatin is very strongly bound to plasma protein, and therefore dialysis cannot rescue patients from cisplatin induced toxicity.

260. (c) Sodium thiosulfate is used to minimize cisplatin -induced bladder and kidney toxicity. The drug accumulates in renal tubules where it neutralizes active drugs in the kidney. The serum

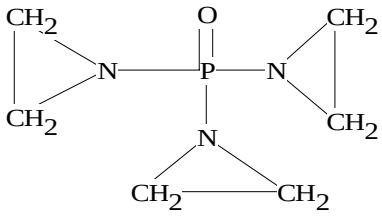
concentration of cisplatin is very low due to the fact that the drug is highly bound to plasma protein, and therefore reaction of sodium thiosulfate with cisplatin in blood is very slow and low (Fig: 11.14, page 149).

261. (c) The water-soluble non-toxic product of the reaction is $CHOCH_2CH_2SCH_2CH_2SO_3^-$ (Fig: 11.15, page 149).

262. (c) N,N'N' triethylenethiophosphoramide, abbreviated "ThioTEPA," is an organophosphorus compound. It is mostly used to treat breast cancer, ovarian cancer, and bladder cancer. It is also used as conditioning for bone marrow transplantation. Its main toxicity is myelosuppression. Triethylenephosphoramide (TEPA) is the active metabolite of the drug.



Thiotepa



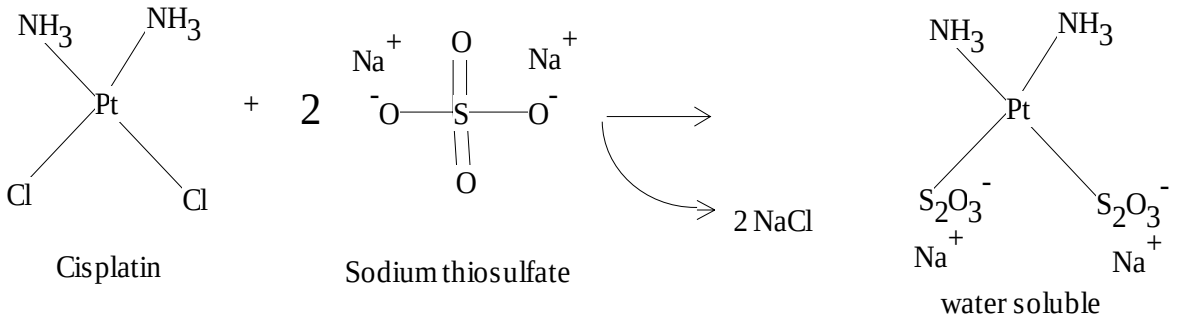
Triethylenephosphoramide
(active metabolite of Thiotepa)

263. (c) Carmustine or BiCNU (Bis-ChloroNitrosoUrea) is classified in the nitrosourea class of chemotherapy agents. It is highly lipophilic and indicated for the treatment of brain tumors and Hodgkin's disease. Thrombocytopenia, leukopenia and severe pulmonary toxicity (dose-related only) are reported side effects of the drug.

264. (d) Busulfan (Myleran) is a chemotherapy drug that is a cell cycle non-specific alkylating agent (slows the growth of cancer cells). More specifically it belongs to a subclass of alkylating agents known as alkyl sulfonates. The IUPAC name for this compound is 1,4-bis(methylsulfonyloxy)butane. It is indicated for the treatment of chronic myelogenous leukemia. Serious bone marrow suppression including pancytopenia is a major side effect of the drug. Recovery from busulfan-induced pancytopenia can take up to 2 years.

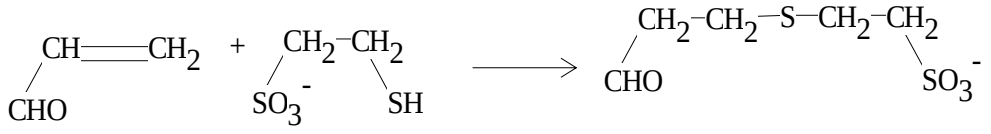
265. (c) Doxorubicin (Adriamycin) is classified as an anthracycline antineoplastic antibiotic. It is structurally very similar to tetracycline antibiotics. Structurally, it is a glycoside and contains a sugar portion (L-daunosamine) and a nonsugar portion. The nonsugar portion of glycoside is generally known as an aglycone. In anthracyclines, the aglycone moiety is specifically called anthracyclinone or anthraquinone.

266. (b) Severe cardiac toxicity is reported with use of anthracyclene antineoplastic antibiotics such as daunorubicin (Cerubidine) and doxorubicin (Adriamycin). The formation of cytotoxic free radicals by anthracyclins is responsible for this. A free radical is normally defined as a highly reactive species with an unpaired electron. When NADPH reductase reduces anthracycline antibiotics, it releases superoxide radical anion ($.O2^{-}$). This anion, with the help of enzyme superoxide dismutase, converts into hydrogen peroxide (H_2O_2). In the presence of the enzyme catalase, this H_2O_2 is readily converted into water and oxygen, which are harmless and non toxic for the body. However in the presence of the ferrous (Fe^{+2}) ion, hydrogen peroxide is converted into a highly toxic free hydroxyl radical through the process called Fenton reaction. When these cytotoxic free radicals are generated within the heart, it may cause severe damage to cardiac tissues since cardiac tissues do not contain enzyme catalase (fig:11.16, page 149).



Cisplatin Sodium thiosulfate water soluble

Fig: 11.14



(Acrolein) (Mesna) water soluble non-toxic product

Fig: 11.15

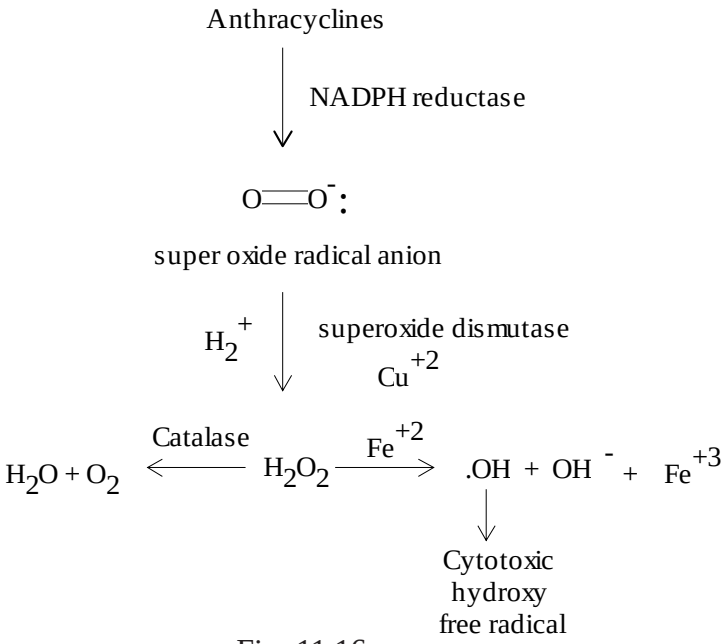
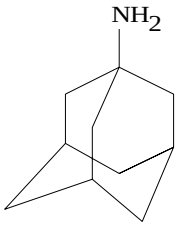


Fig: 11.16

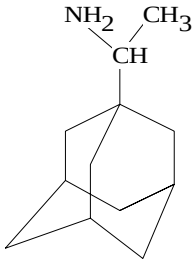
(formation of cytotoxic free radicals by anthracyclenes)

267. (d) Thioguanine (Tabloid) and mercaptopurine (Purinethol) are classified as purine antagonists. Thioguanine is indicated for the treatment of nonlymphocytic leukemias. Fluorouracil, methotrexate, capecitabine, floxuridine and pemetrexed are classified as pyrimidine antagonists.

268. (c) Rimantadine (Flumadine) is structurally and pharmacologically related to amantadine (Symmetrel). Rimantadine appears to be more effective than amantadine against influenza A infection with fewer CNS side effects.



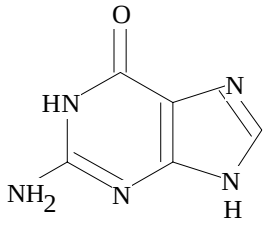
Amantadine



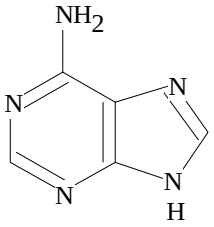
Rimantadine

269. (a) Guanine is one of the five main nucleobases found in the nucleic acids DNA and RNA, the others being adenine, cytosine, thymine, and uracil. With the formula $C_5H_5N_5O$, guanine is a derivative of purine, consisting of a fused pyrimidine-imidazole ring system with conjugated double bonds. Being unsaturated, the bicyclic molecule is planar. The guanine nucleoside is called guanosine.

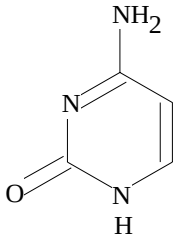
Acyclovir (Zovirax), chemical name acycloguanosine, is a guanosine analogue antiviral drug. One of the most commonly-used antiviral drugs, it is primarily used for the treatment of herpes simplex virus infections, as well as in the treatment of herpes zoster (shingles).



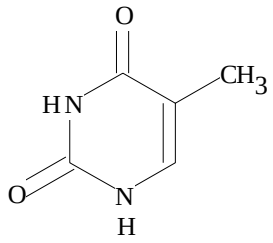
Guanine



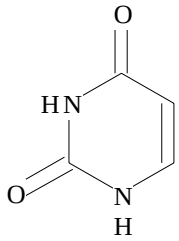
Adenine (6-aminopurine)



Cytosine

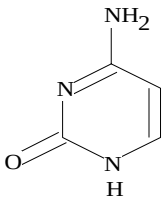


Thymine (5-methyluracil)

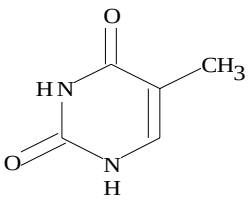


Uracil

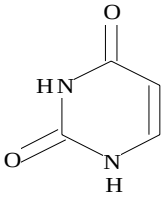
270. (a) Cidofovir (Vistide) is a synthetic acyclic pyrimidine nucleotide analogue of cytosine. Cytosine is one of the five main bases found in DNA and RNA. It is a pyrimidine derivative, with a heterocyclic aromatic ring and two substituents attached (an amine group at position 4 and a keto group at position 2). The nucleoside of cytosine is cytidine. Three nucleobases found in nucleic acids (cytosine, thymine, and uracil) are pyrimidine derivatives:



Cytosine



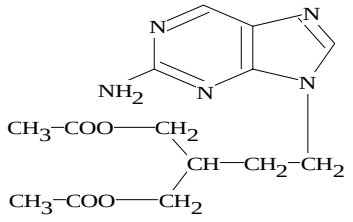
Thymine (5-methyluracil)



Uracil

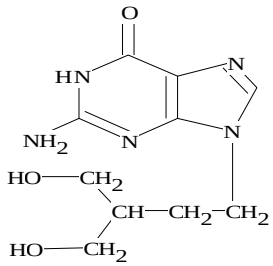
Cidofovir is an injectable antiviral medication for the treatment of cytomegalovirus (CMV) retinitis in patients with AIDS. It suppresses CMV replication by selective inhibition of viral DNA synthesis. Nephrotoxicity is the major side effect of the drug.

271. (c) Foscarnet Na (Foscavir) or phosphonomethanoic acid is a phosphonic acid derivative. It is an antiviral medication used to treat herpes viruses, including cytomegalovirus (CMV) and herpes simplex viruses types 1 and 2 (HSV-1 and HSV-2). It is particularly used to treat CMV retinitis. Nephrotoxicity, severe electrolytes imbalances and genital ulceration are reported side effects of the drug. Increase in serum creatinine levels occurs on average in 45% of patients receiving foscarnet. Other nephrotoxic drugs should be avoided. Nephrotoxicity is usually reversible and can be reduced by dosage adjustment and adequate hydration. Changes in calcium, magnesium, potassium and phosphate levels occur commonly, and regular monitoring of electrolytes is necessary to avoid clinical toxicity.

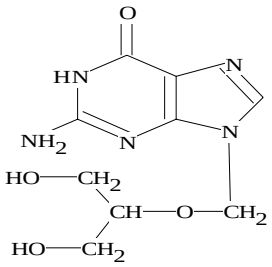


Famciclovir

Hydrolysis Oxidation



Penciclovir



Ganciclovir

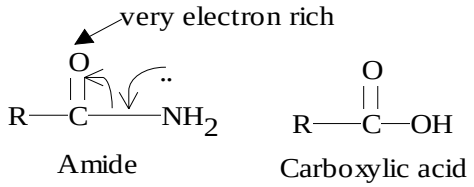
272. (d) Famciclovir (Famvir) is a synthetic purine nucleoside analogue related to guanine. It is the diacetyl 6-deoxy ester of penciclovir. Its pharmacological and microbiological activities are similar to acyclovir. Famciclovir is a prodrug of penciclovir which is formed by hydrolysis of the acetyl groups and oxidation at the 6th position by mixed function oxidase. Famciclovir is indicated for the treatment of recurrent localized herpes zoster and genital herpes in immunocompetent adults. Penciclovir, a prodrug of Famciclovir, is structurally similar to ganciclovir.

273. (b) Ribavirin (Copegus, Rebetol, Virazole) is an anti-viral drug. Ribavirin is a pro-drug, meaning that it is a chemical precursor for the actual pharmacologically active molecule. When the pro-drug is administered, the body converts it into the desired chemical. Ribavirin is activated by cellular kinases which change it into the 5' triphosphate nucleotide. In this form it interferes with aspects of RNA metabolism related to viral replication.

It is indicated for the treatment of hepatitis C, in combination with pegylated interferon drugs. Hemolytic anemia is the major side effect of the drug.

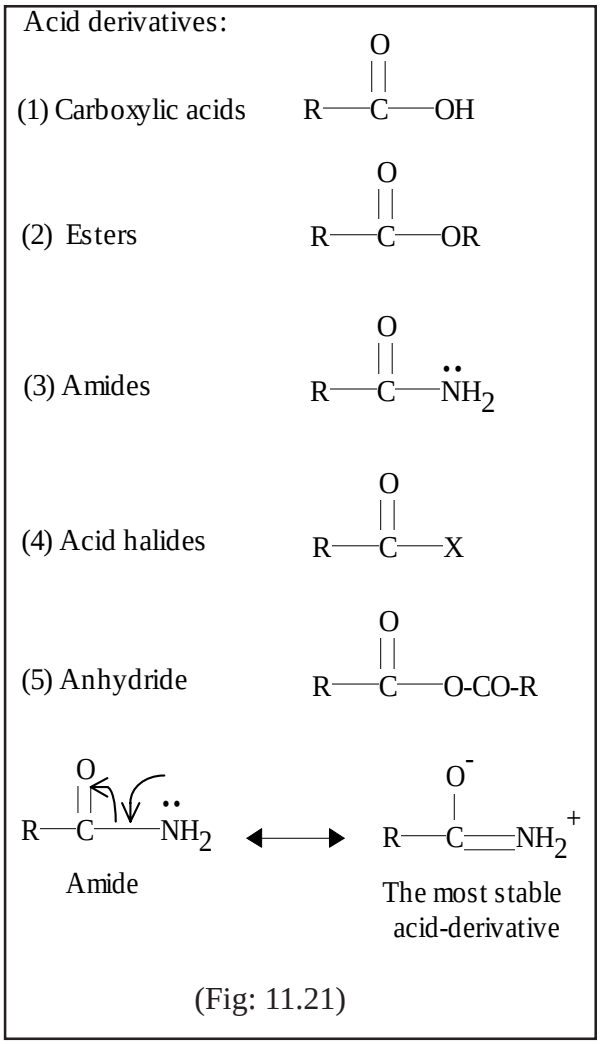
Triazole refers to either one of a pair of isomeric chemical compounds with molecular formula $C_2H_3N_3$, having a five-membered ring of two carbon atoms and three nitrogen atoms. There are two isomers:

hydrogen bond in amides requires a great amount of energy, and hence amides (acetamide) would have the highest boiling point among the given choices.



414. (b) If we carefully observe the given choices, we can conclude that they are all carboxylic acid derivatives. In all these compounds, the hydroxy (-OH) group of carboxylic acid is replaced with some other groups.

When we compared substituted groups, we can find only the nitrogen atom of -NH_2 (amino) group of amide with unshared pair of electrons. This extra pair of unshared electrons donation stabilizes the carbonyl group of carboxylic acid in amides. Due to this, amides are the most stable compounds among all acid derivatives, (Fig: 11.21).



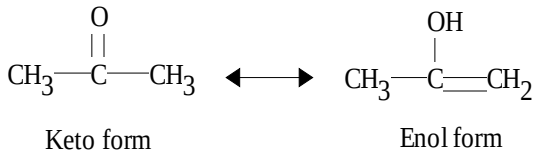
(Fig: 11.21)

415. (d) Neutral compounds or compounds with very nill basic characteristics would not be able to form salt with diluted H_2SO_4. Among the given choices, only propanamide falls into this category. Ammonia, ethyl amine and sodium bicarbonate are mild to moderate bases, and form salts with an acid such as diluted H_2SO_4.

416. (c) Urine is a liquid waste product of the body secreted by the kidneys by a process of filtration from blood and excreted through the urethra. Cellular metabolism generates numerous waste compounds, many rich in nitrogen, that require elimination from the bloodstream. This waste is eventually expelled from the body in a process known as urination, the primary method for excreting water-soluble chemicals from the body. Urine is a transparent solution that can range from colorless to amber but is usually a pale yellow. It is an aqueous solution of metabolic wastes such as urea, uric acid, dissolved salts such as sodium chloride, and dissolved organic compounds. Albumin is a serum protein that cannot be filtered by the kidneys; and hence is not found in normal adult urine.

417. (c) In organic chemistry, keto-enol tautomerism refers to a chemical equilibrium between a keto form (a ketone) and an enol (an aldehyde form). The enol and keto forms are said to be tautomers of each other. The interconversion of the two forms involves the movement of a proton and the shifting of bonding electrons; hence, the isomerism qualifies as tautomerism.

Acetone Isomers:



418. (b) Hydrogenation is the chemical reaction that results in the addition of hydrogen (H_2). The process is usually employed to a reduced or saturated organic compound. The process typically constitutes the addition of pairs of hydrogen atoms to a molecule.

The hydrogenation of an oil to a fat is called hardening. Hydrogenation is widely applied to the processing of vegetable oils and fats. Complete hydrogenation converts unsaturated fatty acids to saturated ones. Hydrogenation results in the conversion of liquid vegetable oils to solid or semi-solid fats, such as those present in margarine. Changing the degree of saturation of the fat changes some important physical properties such as the melting point, which is why liquid oils become semi-solid.

419. (b) Saponification is the hydrolysis of an ester under basic conditions to form an alcohol and the salt of a carboxylic acid. Saponification value or saponification number represents the number of milligrams of potassium hydroxide or sodium hydroxide required to saponify 1g of a fat or oil. In the saponification reaction, one mole of a fat reacts with three moles of KOH or NaOH since the fat has three ester groups.

$$\text{Saponification number of fat} = \frac{168000}{\text{MW of fat}}$$

A lower saponification number indicates high- molecular-weight fatty acid residues in the given fat, whereas a higher saponification number indicates the low molecular weight fatty acid residues.

420. (a) The Iodine value or number is defined as the number of grams of iodine that are consumed by carbon-carbon double bonds (C=C) present in 100 grams of the fat or oil. The iodine number is used to determine the amount of unsaturation contained in fatty acids. The higher the iodine number, the more unsaturated fatty acid bonds are present in a fat. Since saturated fatty acids have no double bonds, its iodine number is zero.

421. (c) A fatty acid is a carboxylic acid often with a long unbranched aliphatic tail (chain), which is either saturated or unsaturated. Carboxylic acids as short as butyric acid (4 carbon atoms) are considered to be fatty acids, whereas fatty acids derived from natural fats and oils may be assumed to have at least 8 carbon atoms, e.g. caprylic acid or octanoic acid. Fatty acids are produced by the hydrolysis of the ester linkages in a fat or biological oil with the removal of glycerol.

422. (c) Soap is a surfactant cleaning compound, used for personal or minor cleaning. It is a mixture of salts of fatty acids. Detergent is defined as a cleaning compound with soap-like property.

423. (d) Triglyceride is a glyceride in which the glycerol is esterified with three fatty acids. It is the main constituent of vegetable oil and animal fats. Triglycerides are formed from a single molecule of glycerol, combined with three fatty acids on each of the OH groups, and make up most of fats digested by humans. Ester bonds form between each fatty acid and the glycerol molecule. This is where the enzyme pancreatic lipase acts, hydrolyzing the bond and "releasing" the fatty acid. In triglyceride form, lipids cannot be absorbed by the duodenum. Fatty acids, monoglycerides (one glycerol, one fatty acid) and some diglycerides are absorbed by the duodenum, once the triglycerides have been broken down. In the human body, high levels of triglycerides in the blood

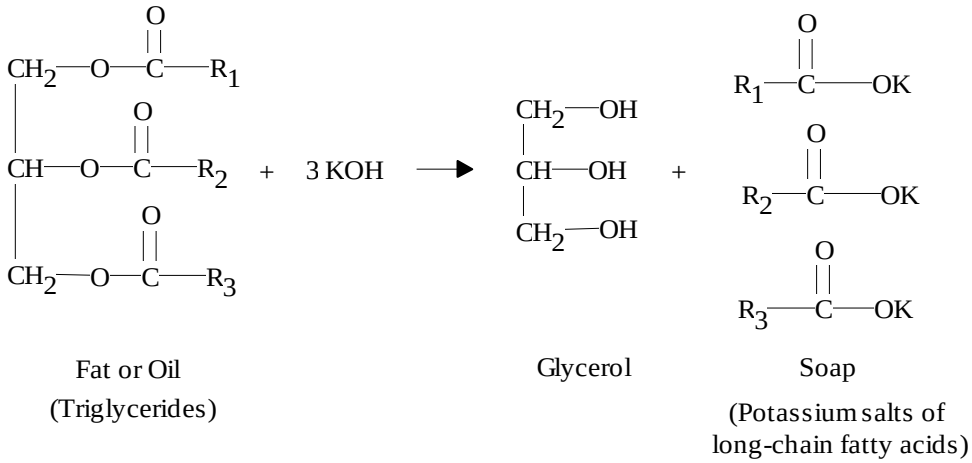


Fig: 11.22

stream have been linked to atherosclerosis, and by extension, the risk of heart disease and stroke. According to the American Heart Association, the normal range for serum triglycerides is less than 160 mg/dL.

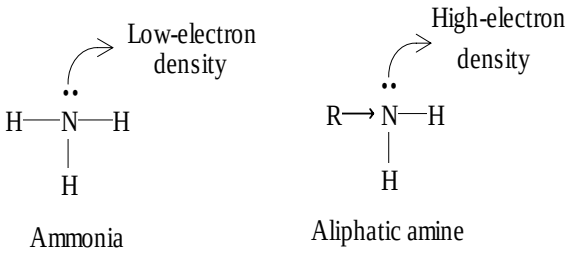
424. (b) When a high proportion of saturated fatty acids is used to manufacture the soap, the resultant soap would be defined as hard soap. In contrast when the soap is manufactured by using a high proportion of unsaturated fatty acids, it yields soft soap.

425. (b) I and II only. Soaps are potassium or sodium salts of fatty acids.

426. (b) I and II only. Saponification (alkaline hydrolysis) of a fat yields soaps (sodium or potassium salts of fatty acids) and propane-1,2,3-triol (also known as glycerol or glycerine).

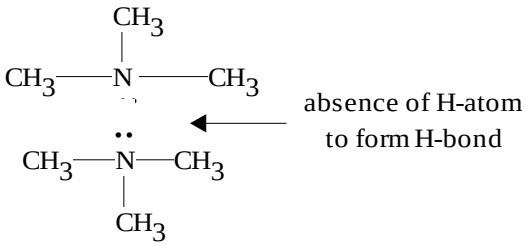
427. (c) In chemistry, a base is most commonly thought of as an aqueous substance that can accept protons. A base is also often referred to as an alkali (only if OH- ions are involved). Alternate definitions of bases include electron pair donors (Lewis), as sources of hydroxide anions (Arrhenius) and can be thought of as any chemical compound that, when dissolved in water, gives a solution with a pH higher than 7.0. The base dissociation constant or Kb is a measure of basicity. pKb is the negative log of Kb and related to the pKa by the simple relationship pKa + pKb = 14.

Aliphatic amines are a stronger base than ammonia due to the presence of the electron-donating alkyl group.



In this regard, methyl amine should be more basic than ammonia, dimethyl amine should be more basic than methyl amine, and trimethyl amine should be more basic than dimethylamine. However, surprisingly Kb value for trimethyl amine is 6.7×10^{-5} compared to the Kb value of dimethyl amine, which is 54×10^{-5}. This low Kb value or basicity of trimethyl amine is due to the crowding of three methyl groups. These three methyl groups block the path to donate electrons by trimethylamine to an acid. Therefore, the correct answer should be dimethyl amine.

428. (d) An absence of hydrogen bonding in trimethylamine is responsible for the lower boiling point than dimethylamine, even though the molecular weight of trimethylamine is higher than the molecular weight of dimethylamine.



Trimethylamine

429. (c) Amines are organic compounds and functional groups that contain a basic nitrogen atom with a lone pair. Amines are derivatives of ammonia, wherein one or more hydrogen atoms are replaced by organic substituents such as alkyl and aryl groups. Primary amines arise when one of three hydrogen atoms in ammonia is replaced by an organic substituent. Secondary amines have two organic substituents bound to N together with one H. In tertiary amines all three hydrogen atoms are replaced by organic substituents. Since tertiary amines do not have any hydrogen atom, they cannot form intramolecular hydrogen bonding. Among the given choices, only triethylamine is a tertiary amine. Therefore, the correct answer should be "c."

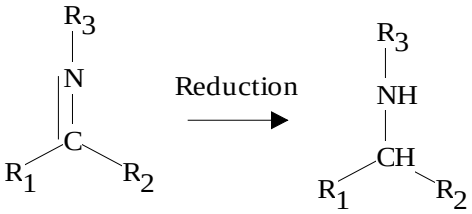
430. (d) Primary, secondary and tertiary amines are water soluble since they form a hydrogen bond with water molecules. Tertiary amines in water may form a hydrogen bond with water molecules (intermolecular hydrogen bond); however, they will not be able to form an intramolecular hydrogen bond.

431. (b) When we compared different compounds with the same molecular weights and side chain, among the given choices an alcohol will possess the highest boiling point due to its ability to form extensive hydrogen bonding. Therefore, the correct choice would be "b" or propanol. Please review the following chart to answer boiling point related questions:

Boiling point in increasing order:

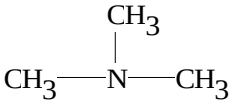
Alkenes < Alkynes < Alkanes, Ethers < Alkyl halides < Aldehydes < Ketones, Esters < Thiols , Amines < Alcohols < Polyhydric alcohols < Carboxylic acids < Hydroxy acids < Amides

432. (b) An imine is a functional group or chemical compound containing a carbon–nitrogen double bond. An imine can be reduced to an amine via hydrogenation.



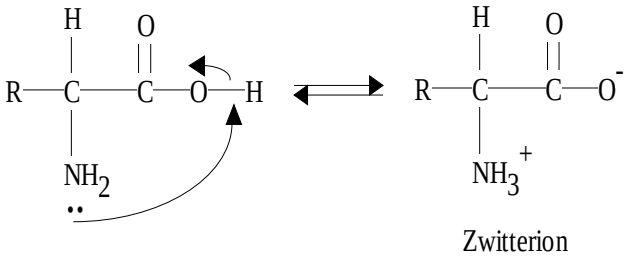
Imine Amine

433. (c) Amines are normally prepared by heating an alkyl halide with alcoholic ammonia. In the above reaction, tertiary amine or 3° amine known as trimethylamine has been obtained.



Trimethyl amine

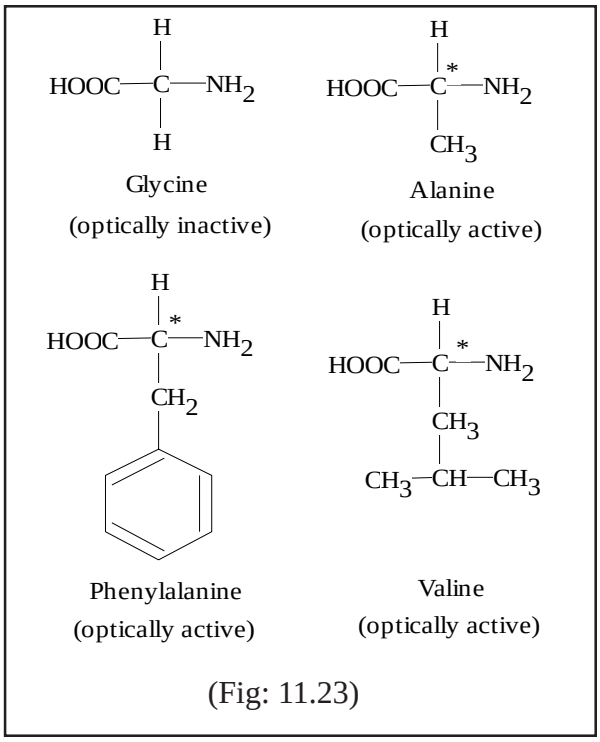
434. (b) A zwitterion is a chemical compound that carries a total net charge of zero, thus is electrically neutral but carries formal positive and negative charges on different atoms. Zwitterions are polar and are usually very water-soluble, but poorly soluble in most organic solvents. Most amino acids at a physiological pH are for the most part zwitterionic.



Zwitterion

435. (b) The isoelectric point (pI) is the pH at which a particular molecule or surface carries no net electrical charge. Amphoteric molecules called zwitterions contain both positive and negative charges depending on the functional groups present in the molecule. They are affected by the pH of their surrounding environment and can become more positively or negatively charged due to the loss or gain of protons (H^+). For example, in acidic solution amino acids exist as a positive ion and migrate toward negative charged electrodes called cathodes. In contrast, the basic solution of amino acids exists as negative ions and migrates toward positively charged electrodes called anodes. However, at particular pH amino acids exist as zwitterions. Since zwitterions contain both a positive and a negative charge, they are neutral and hence do not migrate towards either electrode. This particular pH is known as isoelectric point.

436. (c) Except for glycine, all α-amino acids possess an asymmetric carbon atom or a chiral carbon and are optically active, (fig:11.23).



(Fig: 11.23)

437. (d) Alpha-amino acids are the building blocks of proteins. Amino acids have both an amine and a carboxylic acid functional group and are therefore both acids and bases at the same time. At a certain compound-specific pH known as the isoelectric point, the number of protonated ammonium groups with a positive charge and deprotonated carboxylate groups with a negative charge are equal, resulting in a net neutral charge. They have very high melting point. They are freely soluble in polar solvents such as water but insoluble in non-polar solvents such as alkane, benzene and ethanol. Their aqueous solutions are neutral to litmus test due to formation of zwitterions.

438. (c) A peptide bond is a chemical bond formed between two molecules (preferably amino acids) when the carboxyl group of one amino acid reacts with the amino group of the other amino acid, thereby releasing a molecule of water (H_2O). This is a dehydration reaction. The resulting CO-NH bond is called a peptide bond, and the resulting molecule is a dipeptide. The four-atom functional group -C(=O)NH- is called an amide group or (in the context of proteins) a peptide group. Polypeptides and proteins are chains of amino acids held together by these peptide bonds. A peptide bond can be broken by amide hydrolysis (the adding of water).

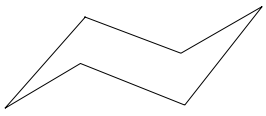
439. (a) Proteins are large organic compounds made of α amino acids arranged in a linear chain and joined together by peptide bonds between the carboxyl and amino groups of adjacent

amino acid residues. The sequence of α amino acids in a protein is defined by the sequence of a gene, which is encoded in the genetic code.

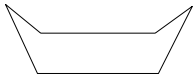
440. (d) Denaturation is a process in which proteins or nucleic acids lose their structure (tertiary structure) by application of some external stress or compound, for example, treatment of proteins with strong acids or bases, high concentrations of inorganic salts, organic solvents (e.g. alcohol or chloroform), or heat. If proteins in a living cell are denatured, this results in disruption of cell activity and possibly cell death.

A classic example of denaturing in proteins comes from egg whites, which are largely egg albumins in water. Fresh from the eggs, egg whites are transparent and liquid. Cooking the thermally unstable whites turns them opaque, forming an interconnected solid mass. The same transformation can be effected with a denaturing chemical. Pouring egg whites into a beaker of acetone will also turn egg whites opaque and solid.

441. (a) Cyclohexane conformation is a much studied topic in organic chemistry because of the complex interrelationship between the different conformers of cyclohexane and its derivatives. Different conformers may have differing properties, including stability and chemical reactivity. The Chair form of cyclohexane has the lowest energy, and hence is the most stable among the given choices. At any given time more than 99.9% molecules of cyclohexane exhibit chair form.



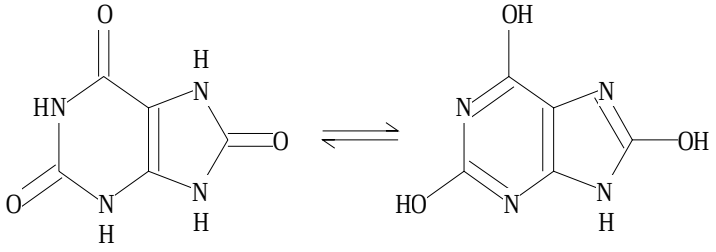
Chair Form Cyclohexane
(most stable)



Boat form Cyclohexane
(least stable)

442. (d) In organic chemistry, keto-enol tautomerism refers to a chemical equilibrium between a keto form (a ketone) and an enol (an aldehyde) form. The enol and keto forms are said to be tautomers of each other. The interconversion of the two forms involves the movement of a proton and the shifting of bonding electrons; hence, the isomerism qualifies as tautomerism.

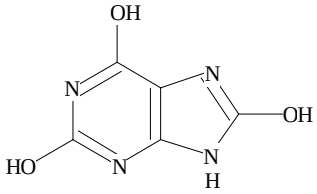
Purine Tautomeric Forms:



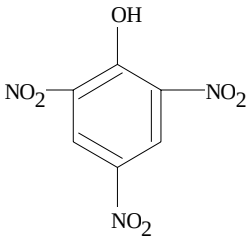
2,6,8-Purinetrione
(Keto Tautomer)

2,6,8-Trihydroxypurine
(Uric acid)
(Enol Tautomer)

443. (b) I and II only. Picric and uric acids are two acids that do not contain any carboxylic groups in their structure.



2,6,8-Trihydroxypurine
(Uric acid)

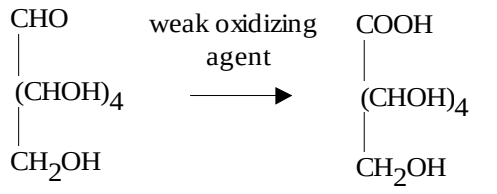


2,4,6 Trinitrophenol
(Picric acid)

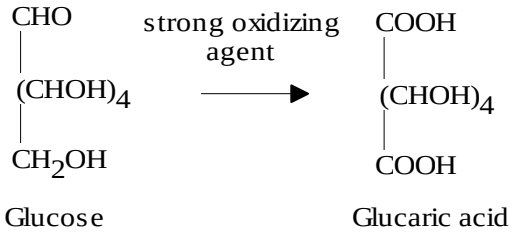
444. (d) Allantoin is a chemical compound with the formula $C_4H_6N_4O_3$. It is also called 5-ureidohydantoin or glyoxyldiureide. It is a diureide of glyoxylic acid. It is a product of oxidation of uric acid by purine catabolism. The hydrolysis of allantoin gives two molecules of urea and one molecule of glyoxylic acid, (fig: 11.24, page 188).

445. (b) Gluconic acid is an organic compound with the molecular formula $C_6H_{12}O_7$. In an

aqueous solution at a neutral pH, gluconic acid forms the gluconate ion. The salts of gluconic acid are known as "gluconates." Gluconic acid and gluconate salts occur widely in nature because such species arise from the oxidation of glucose. Gluconate esters can also be formed, such as quinine gluconate, which is used for intramuscular injection in the treatment of malaria. Gluconic acid occurs naturally in fruit, honey, kombucha tea and wine.

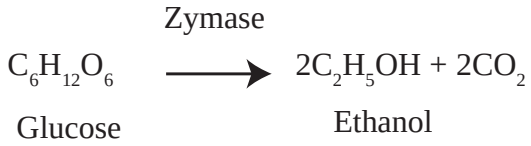


446. (c) A strong oxidizing agent such as HNO_3 oxidizes glucose to glucaric acid or saccharic acid by oxidizing both the CHO and CH_2OH groups.



447. (b) Sorbitol, also known as glucitol, is a sugar alcohol that the body metabolizes slowly. It is obtained by reduction of glucose changing the aldehyde group to an additional hydroxyl group hence the name sugar alcohol. Sorbitol is used in "sugar-free" mints and various cough syrups and is usually listed under the inactive ingredients. Sorbitol is a sugar substitute often used in diet foods (including diet drinks and ice cream) and sugar-free chewing gum. Mannitol, used as an osmotic diuretic agent and a weak renal vasodilator, is a stereoisomer of sorbitol, (fig:11.35, page 187)

448. (c) II and III only. A glucose solution fermented in the presence of the enzyme zymase in anaerobic condition would yield ethanol and carbon dioxide.



449. (a) Monosaccharides (from the Greek monos: single, sacchar: sugar) are the most basic unit of carbohydrates. They consist of one sugar and are usually colorless, water-soluble, crystalline solids. Examples of monosaccharides include glucose or dextrose, fructose, galactose, xylose and ribose.

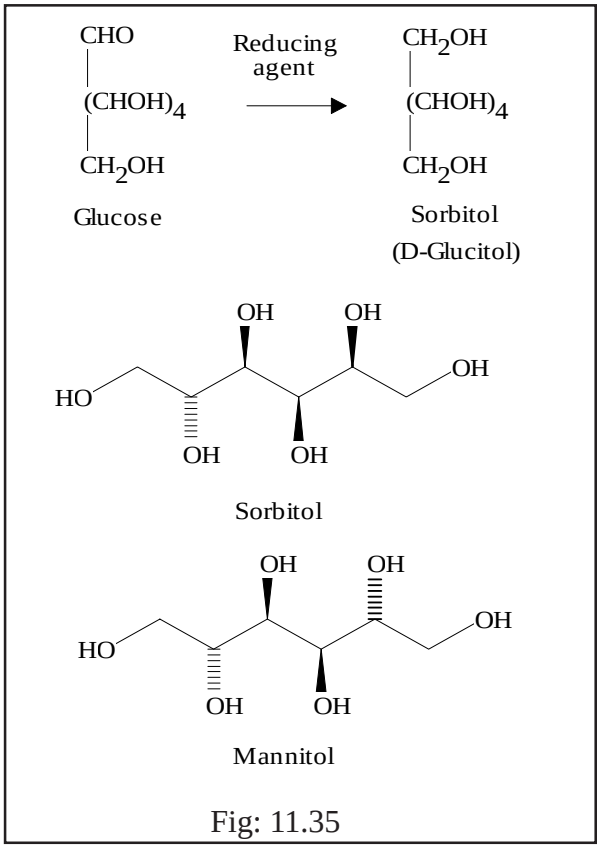
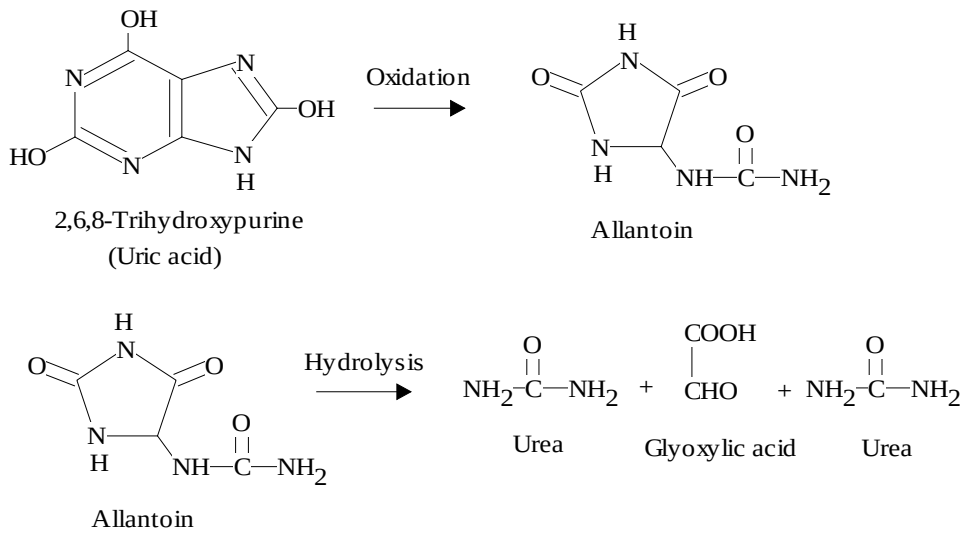


Fig: 11.35

450. (a) I only. A disaccharide is a sugar composed of two monosaccharides. It is formed when two monosaccharides are joined together and a molecule of water is removed. The hydrolysis of maltose would yield two molecules



(Fig:11.24)

of glucose. The hydrolysis of sucrose would yield a molecule of glucose and fructose whereas the hydrolysis of lactose would yield glucose and galactose.

451. (b) Raffinose is a trisaccharide composed of three saccharides called galactose, fructose, and glucose. It can be found in beans, cabbage, brussel sprouts, broccoli, asparagus, other vegetables, and whole grains.

452. (b) Common table sugar or sucrose is classified as a disaccharide. Upon hydrolysis it yields one molecule of glucose and one molecule of fructose.

453. (c) The solution of α-glucose has a specific rotation of 112°, whereas the solution of β-glucose has the specific rotation 19°. When either α-glucose or β-glucose is dissolved in water and allowed to stand, a gradual change in specific rotation occurs. The specific rotation of α-glucose falls from 112° whereas the specific rotation of β-glucose rises from 19° until a constant value of 53° is achieved. This change in optical rotation of a solution of either α-glucose or β-glucose until a constant value is obtained is called mutarotation.

454. (c) Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand linked D-glucose units. Cellulose is the structural component of the primary cell wall of green plants and many forms of algae.

Starch, chemical formula $(C_6H_{10}O_5)_n$, is a polysaccharide carbohydrate consisting of a large number of glucose monosaccharide units joined together by glycosidic bonds. All plant seeds and tubers contain starch, which is predominantly present as amylose and amylopectin. Depending on the plant, starch generally contains 20 to 25 percent amylose and 75 to 80 percent amylopectin.

455. (d) To answer this type of question, students should know the effects of various substituents on the reactivity of benzene. As a rule of thumb, substituents that release or donate electrons to an aromatic ring increase the activity of the ring whereas the substituents that withdraw or pull electrons from an aromatic ring decrease the activity of the ring. In phenol, the -OH group is an electron-donor therefore activates the ring the most. The -Cl and NO_2 groups are electron-withdrawer, hence deactivate the ring.

Therefore the correct order should be:

Phenol > Benzene > Chlorobenzene > Nitrobenzene

Please remember the following chart to answer this type of question:

Strongly activating substituents:

-OH, -OR, -NH_2, -NHR, -NR_2

Moderate or weakly activating substituents:

-CH_3, -C_2H_5, -R (any alkyl group)

Deactivating substituents:

-F, -Cl, -Br, -I

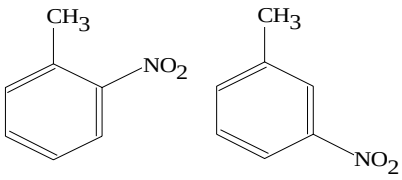
Strongly deactivating substituents:

-NO_2, -CHO, -COR, -SO_3H, -CN, -COOH

456. (a) Among the given choices, aniline should undergo substitution reactions faster than benzene (same logic as the answer 455).

457. (c) Since the alkyl group activates the ring toward electronic substitution, ethylbenzene will undergo the nitration most rapidly among the given choices.

458. (b) In a simple definition, isomers are compounds with the same molecular formula but different structural formulae. The structural formula for nitrotoluene can be shown three different ways:

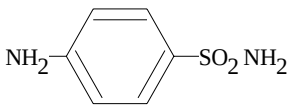


o-Nitrotoluene m-Nitrotoluene p-Nitrotoluene

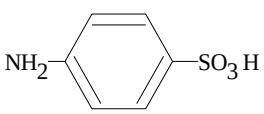
459. (a) In difluorobenzene, the fluorine atom is highly electronegative compared to carbon. Since fluorine has a strong electron withdrawing power it pulls out electrons from the carbon atom, and makes it positively charged where itself possesses a negative charge. This difference in charge on both ends of a bond make the bond polarized, and hence induces dipole moment. The magnitude of dipole moment depends on the distance between two atoms, an electron withdrawing power of an atom and the direction of dipole moment. In para position, dipole moment induced by both fluorine atoms cancel out each other's effects. Compared to a meta position, an ortho position provides synergistic dipole effects induced by two fluorine atoms. Therefore, o-difluorobenzene would have the most dipole moment whereas p-difluorobenzene would have the least dipole moment.

460. (b) Saccharin is an artificial sweetener. The basic substance, benzoic sulfinide, has effectively no food energy and is much sweeter than sucrose (about 500 times), but has an unpleasant bitter or metallic aftertaste, especially at high concentrations. Saccharin is used to sweeten products such as drinks, candies, medicines and toothpaste. It is widely marketed as a soluble sodium salt of saccharin.

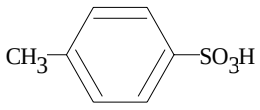
461. (a) Sulfanilamide is an antibacterial drug. It is the compound from which other sulfa drugs are derived. Sulfanilamide and its derivatives are also known as sulpha drugs. Most sulpha drugs are structurally related to sulfanilamide.



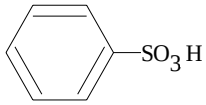
Sulfanilamide



Sulfanilic acid



p-Toluenesulfonic acid



Benzenesulfonic acid

462. (d) The basicity of any given compound can be determined by its ability to accept protons or donate electrons. When comparing aniline with aliphatic amine, the latter one is more basic than the former one. This is because a lone pair of electrons on nitrogen atoms is delocalized into the benzene ring by resonance in aniline, whereas in aliphatic amine this pair of electrons is fully localized on the nitrogen atom. As we have discussed previously, any group or atom that increases electron density on nitrogen atoms will make the compound more basic, whereas any group or atom that reduces electron density on nitrogen atoms will make the compound less basic.

In the case of o-nitroaniline, the electron withdrawing $-NO_2$ group reduces the electron density on nitrogen atoms makes the compound less basic compared to aniline, whereas in the case of o-toluidine, the electron releasing $-CH_3$ group enhances the electron density on nitrogen atoms makes the compound more basic than aniline. Arrangement in order of decreasing basicity: ethyl amine > o-toluidine > aniline > o-nitroaniline.

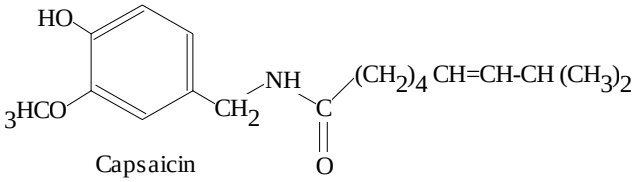
463. (d) Aromatic amine (P) is a weaker base compared to nonaromatic cyclic amine (Q) due to delocalization of a lone pair of electrons of nitrogen in the aromatic ring. The option R would be the least basic due to the presence of the electron withdrawing group -Cl. The option (S) would be the most basic among the given choices since a lone pair of electrons are localized on the nitrogen atom and not into the aromatic ring; hence, it acts as a primary aliphatic amine ($-CH_2-NH_2$).

464. (d) Electron withdrawing group substitution such as $-NO_2$, -X, -CHO, -COOH make compounds more acidic. These groups withdraw electrons from the aromatic ring, which in turn pulls electrons from the phenoxy oxygen. This makes phenoxy hydrogen easily available and hence results in a stronger acid.

Electron donating groups such as $-CH_3$, $-OCH_3$, and $-NH_2$ release electrons and make phenoxy oxygen highly negative. This result in a firm holding of the phenoxy hydrogen by the phenoxy oxygen, and hence results in a weaker acid.

The relative acid-strength: p-Nitrophenol > p-Chlorophenol > Phenol > p-Cresol.

465. (b) Capsaicin is the active component of chili peppers, which are plants belonging to the genus Capsicum. It is an irritant for mammals, including humans, and produces a sensation of burning in any tissue with which it comes into contact. Capsaicin and several related compounds are called capsaicinoids. It is also used in topical ointments to relieve arthritis pain.



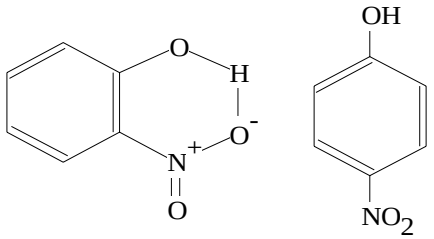
Capsaicin

466. (d) Phenol, also known as carbolic acid, has antiseptic properties. It is also the active ingredient in some oral anesthetics such as Chloraseptic spray. It is also used in the production of certain pharmaceutical drugs as starting material. It is also used in the preparation of cosmetics including sunscreens, hair dyes, and skin lightening preparations.

467. (b) A hydrogen bond results from a dipole-dipole force with a hydrogen atom bonded to nitrogen, oxygen or fluorine, thus the name "hydrogen bond," which must not be confused with a covalent bond to hydrogen. The energy of a hydrogen bond (typically 5 to 30 kJ/mole) is comparable to that of weak covalent bonds (155 kJ/mol), and a typical covalent bond is only 20 times stronger than an intermolecular hydrogen bond. These bonds can occur between molecules (intermolecularly), or within different

parts of a single molecule (intramolecularly), as we see in o-nitrophenol. The hydrogen bond is a very strong fixed dipole-dipole van der Waals-Keesom force, but weaker than covalent, ionic and metallic bonds. The hydrogen bond is somewhere between a covalent bond and an electrostatic intermolecular attraction. Intermolecular hydrogen bonding is responsible for the high boiling point of water (100 °C).

468. (c) II and III only. The major difference between o-nitrophenol and p-nitrophenol is that the former one is able to form an intramolecular hydrogen bond, whereas the latter one cannot.



o-Nitrophenol p-Nitrophenol

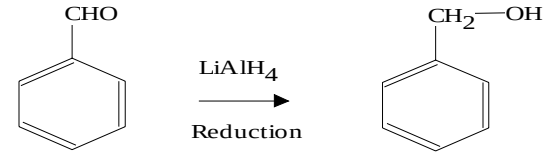
Similarly, p-nitrophenol is able to form an intermolecular hydrogen bond with water molecules whereas o-nitrophenol cannot due to unavailability of its phenoxy group (since it forms intramolecular H-bond). These differences change the physical properties of both isomers. For example, since p-nitrophenol is able to form an intermolecular H-bond with water molecules, its solubility as well as boiling points are higher compared to o-nitrophenol. Also, due to the low solubility and low boiling point of o-nitrophenol, it makes it possible to readily separate from p-nitrophenol by steam distillation.

469. (c) Phenol is the most capable of forming hydrogen bond with water compared to the other choices. The reason behind this is the presence of an aromatic ring in phenol structure. The ring, which is always in search of electrons, pulls electrons from phenoxy oxygen. This leads to loss of a phenoxy hydrogen. Electron-deficit phenoxy oxygen is then able to form strong hydrogen bonds with water molecules. This also explains the higher boiling point of phenols compared to the boiling points of alcohols with comparable molecular weights.

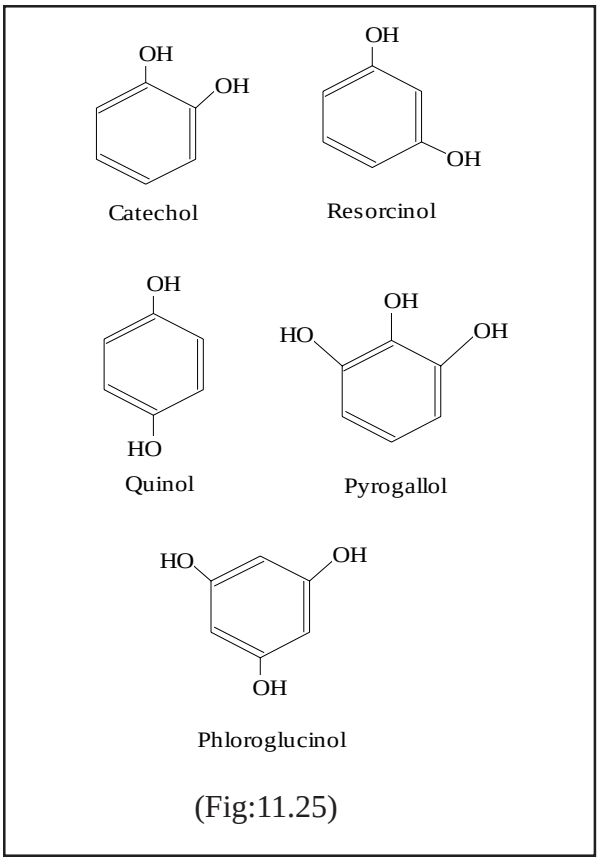
470. (a) The boiling point of any given compound is highly dependant on its ability to form a hydrogen bond with water molecules. The compound more capable of forming hydrogen bonds with water molecules tends to have a higher boiling point compared to the compound incapable or weekly capable for forming hydrogen bonds. The option (B) would have the highest boiling point due to the presence of two hydroxy groups. The option (D) would have the lowest boiling point among the given choices due to absence of the hydroxy group. Between option (A) and (C), phenol would have the higher boiling point. This is because the electron releasing -CH_3 group in option (C) reduces the ability of a compound to form a hydrogen bond with water molecules.

471. (d) Phenol, also known as a carbolic acid, is a toxic, colorless crystalline solid with a sweet tarry odor, commonly referred to as a "hospital smell." Its chemical formula is C_6H_5OH and its structure is that of a hydroxyl group (-OH) bonded to a phenyl ring; it is thus an aromatic compound. Dihydric phenols contain two hydroxy groups attached to a phenyl ring, whereas trihydric phenols contain three hydroxy groups attached to a phenyl ring. Pyrogallol is a trihydric phenol, (fig:11.25, page 192).

472. (a) Benzaldehyde undergoes reduction reaction in the presence of $LiAlH_4$ to form benzyl alcohol.

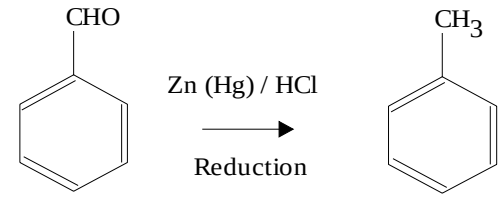


Benzaldehyde Benzyl alcohol

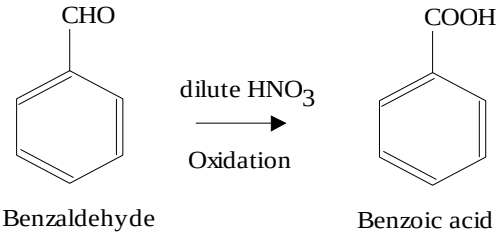


(Fig:11.25)

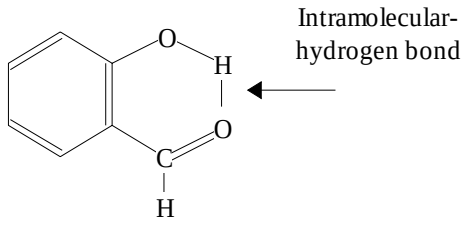
473. (b) Benzaldehyde undergoes reduction reaction in the presence of Zinc amalgam and concentrated HCl to form methylbenzene, also known as toluene. This reaction is known in organic chemistry as Clemmensen reduction.



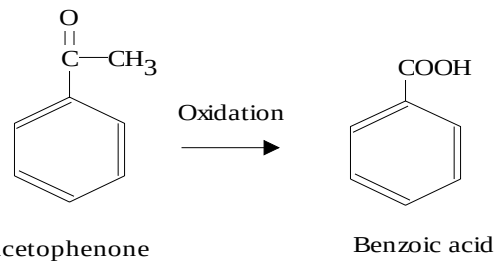
474. (c) Under the presence of oxidizing agents such as acidic potassium dichromate ($K_2Cr_2O_7$), acidic potassium permanganate ($KMnO_4$) or dilute nitric acid (HNO_3), benzaldehyde readily undergoes oxidation to form benzoic acid.



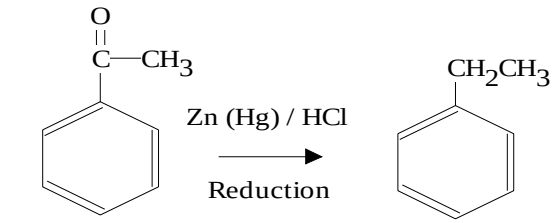
475. (b) Salicylaldehyde, or 2-hydroxybenzaldehyde, is the chemical compound with the formula C_6H_4CHO-2-OH. This colorless oily liquid has a bitter almond odor at a higher concentration and a characteristic buckwheat aroma at a lower concentration. Salicylaldehyde is a key precursor to a variety of chelating agents, some of which are commercially important. It can be prepared from phenol and chloroform by heating with sodium hydroxide. It forms intramolecular hydrogen bonding. This also explains why salicylaldehyde has a low water solubility because the -OH group of salicylaldehyde is tied up with the -CHO group by forming intramolecular hydrogen bonding that prevents hydrogen bond formation of salicylaldehyde with water molecules.



476. (b) Acetophenone in the presence of an oxidizing agent -acidic potassium permanganate oxidizes to benzoic acid.

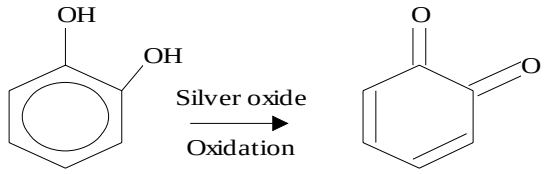


477. (c) Acetophenone undergoes reduction reaction in the presence of Zinc amalgam and is concentrated HCl to form ethylbenzene. This reaction is known in organic chemistry as Clemmensen reduction.



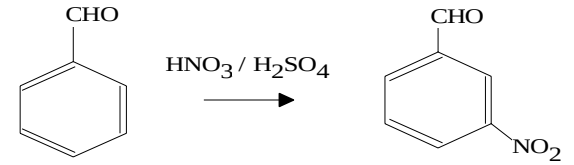
Acetophenone Ethyl benzene

478. (c) o-Benzoquinone, also known as o-quinone, can be prepared by the oxidation of catechol in the presence of silver oxide.



Catechol o-Benzoquinone

479. (a) I only. In benzaldehyde, the -CHO group is a meta-director therefore nitration of benzaldehyde would result in m-nitrobenzaldehyde as a major product.



Benzaldehyde m-Nitrobenzaldehyde

480. (b) Tollens' reagent is an ammoniacal silver nitrate ($Ag(NH_3)_2OH$) solution. It was named after Bernhard Tollens. The diamminesilver complex ($Ag(NH_3)_2OH$) is an oxidizing agent, which is itself reduced to silver metal, which in a clean glass reaction vessel forms a "silver mirror." This feature is used as a test for aldehydes, which are oxidized to carboxylic acids. It should be noted that the actual oxidation product is the carboxylate ion, which on acidification gives the corresponding carboxylic acid.

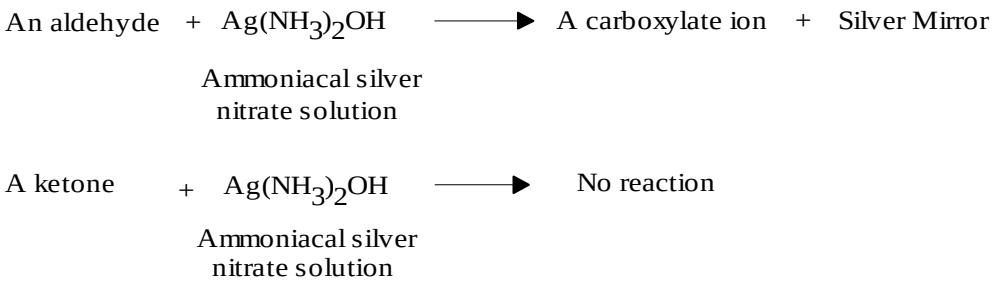
Tollens' reagent is also used to distinguish an aldehyde from a ketone (except alpha-hydroxy ketone, which gives a positive Tollens' test). A test can be performed by adding the aldehyde or ketone to Tollens' reagent and then putting the test tube in a warm water bath. If the reactant under the test is an aldehyde, the Tollens' test results in a silver mirror. If the reactant is a ketone (except alpha-hydroxy ketone), it will not react because a ketone cannot be oxidized easily. A ketone has no available hydrogen atom on the carbonyl carbon that can be oxidized, unlike an aldehyde, which has this hydrogen atom, (fig: 11.26, page 194).

481. (d) All. The haloform reaction is a chemical reaction where a haloform (CHX_3, where X is a halogen) is produced by the exhaustive halogenation of a methyl ketone (a molecule containing the R-CO-CH_3 group) in the presence of a base. R may be H, alkyl or aryl. The reaction can be used to produce $CHCl_3$, $CHBr_3$ or CHI_3. Since chloroform ($CHCl_3$) and bromoform ($CHBr_3$) are liquid at room temperature whereas iodoform (CHI_3) is solid at room temperature, an iodine solution is commonly used.

The haloform reaction is used as a diagnostic test for the presence of the -$COCH_3$ group. The test can be performed by the addition of a solution of iodine to an unknown compound in the presence of aqueous alkali (NaOH). A presence of yellow precipitates of iodoform indicates a positive iodoform test.

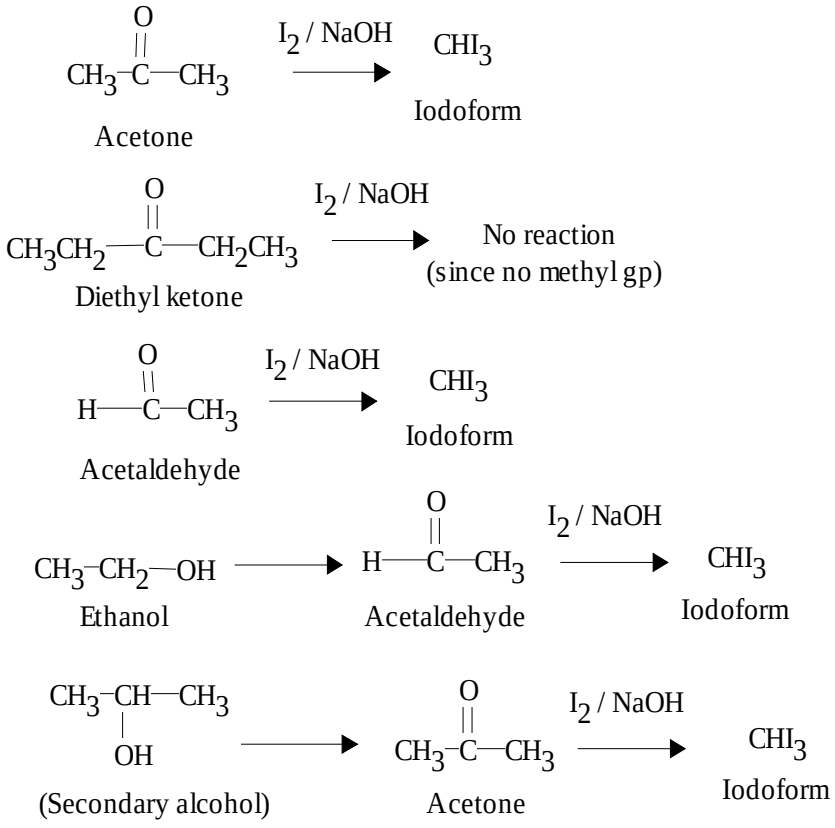
This test is positive with the following compounds:

1. Methyl ketone
2. Acetaldehyde
3. Ethanol
4. Secondary alcohol



(Fig: 11.26)

Iodoform Tests:



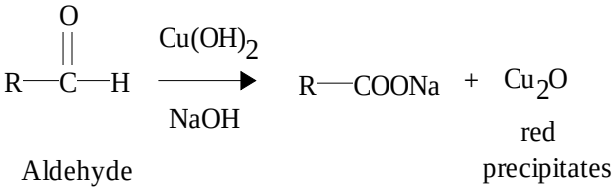
(Fig: 11.27)

This is because ethanol is subsequently oxidized to acetaldehyde and secondary alcohols are oxidized to methyl ketones under the condition used for the test. The test is also used to distinguish ethanol from methanol since the latter one does not give a positive iodoform test. The test is also used to distinguish methyl ketone from other ketones, (fig: 11.27).

482. (b) With an alkaline solution of iodine, acetaldehyde forms yellow precipitates of iodoform whereas formaldehyde does not react.

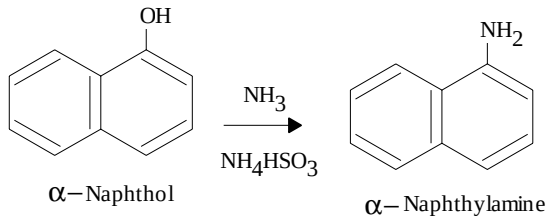
483. (d) Fehling's solution is a solution used to distinguish aldehyde from the ketone functional groups, although ketose monosaccharides (such as fructose) will also test positive, due to con-

version to aldoses by the base in the reagent. It is an alkaline solution of cupric ion complexed with sodium potassium tartrate ions. An aldehyde reduces the complex cupric ion (deep blue) to cuprous oxide, and itself get oxidized. The presence of red precipitates of cuprous oxide indicates that an unknown compound contains an aldehyde group in the molecule. Benedict's solution is an alkaline solution of cupric ion complexed with citrate ions used and reacted the same way as Fehling's solution.

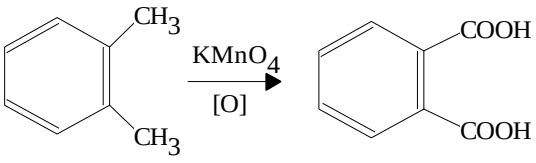


484. (d) All. Ketones (except alpha-hydroxy ketones) do not react with Tollens' reagent, Fehling's solution and Benedict's solution. These tests help in distinguishing aldehydes from ketones.

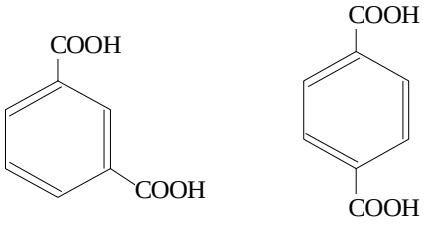
485. (c) When α-naphthol reacts with ammonia in the presence of ammonium bisulfite, it yields 1-Naphthylamine or α-naphthylamine.



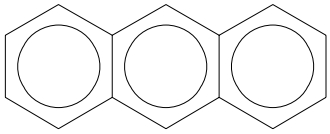
486. (c) Phthalic acid (benzene-1,2-dicarboxylic acid) is an aromatic dicarboxylic acid, with the formula $C_6H_4(COOH)_2$. It is an isomer of isophthalic acid and terephthalic acid. Phthalic acid is used mainly in the form of the anhydride to produce other chemicals such as dyes, perfumes, saccharin, phthalates and many others.



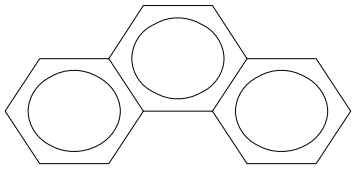
Other Isomers:



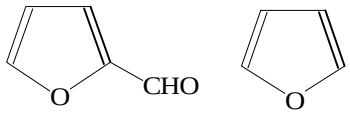
487. (b) Anthracene is a solid polycyclic aromatic hydrocarbon consisting of three fused benzene rings derived from coal-tar. Anthracene is used in the artificial production of the red dye alizarin. It is also used in wood preservatives, insecticides, and coating materials.


Anthracene

Phenanthrene is another compound from this family. The name phenanthrene is a composite of phenyl and anthracene. It provides the framework for the steroids.

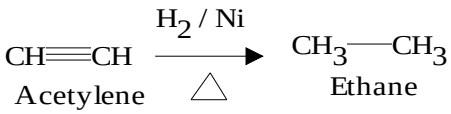

Phenanthrene

488. (c) Furfural is an aromatic aldehyde as well as cyclic ether. Its chemical formula is $C_5H_4O_2$. In its pure state, it is a colorless oily liquid with the odor of almonds, but upon exposure to air it quickly becomes yellow. It is widely used as a selective solvent in petroleum refining and in the preparation of furan and furan derivatives.



Furfural Furan

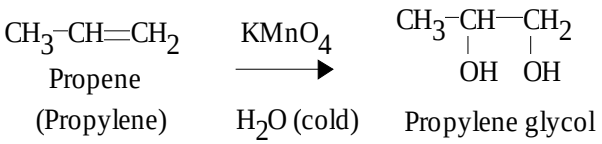
489. (b) The reduction of acetylene in presence of nickel would yield ethane.

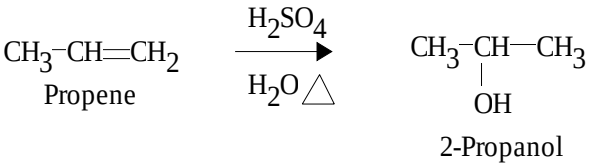


490. (d) All. Cracking is the process whereby complex organic molecules such as kerogens or heavy hydrocarbons are broken down into simpler molecules (e.g. light hydrocarbons) by the breaking of carbon-carbon bonds in the precursors. The rate of cracking and the end products are strongly dependent on the temperature and presence of any catalysts. Cracking, also referred to as pyrolysis, is the breakdown of a large alkane into smaller, more useful alkenes and an alkane.

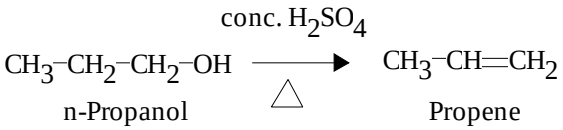
The cracking of n-Butane would yield 1-butene, 2-butene, propene and ethylene, (fig: 11.28, page 197).

491. (c) The hydrolysis of propene in presence of $KMnO_4$ and cold water would yield propylene glycol. However, in the presence of H_2SO_4 and heat, the hydrolysis of propene would yield 2-propanol (Markovnikov rule is followed).

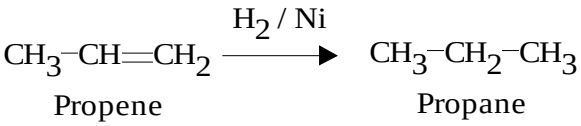




492. (a) Propene and propane are formed during the reaction. The first reaction is called dehydration reaction where a molecule of water is eliminated from propanol to form propene.

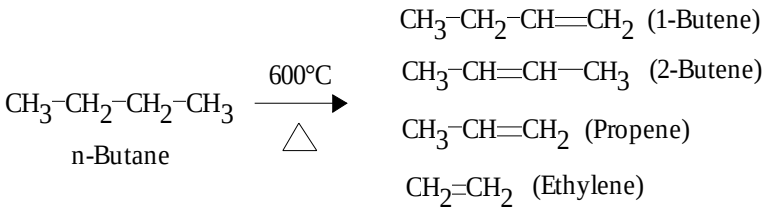


The second reaction is called reduction reaction. In the presence of nickel, an alkene is reduced to an alkane.



493. (a) The Williamson ether synthesis was developed by Alexander Williamson in 1850. Typically it involves the reaction of an alkoxide ion with a primary alkyl halide via an SN_2 reaction. This reaction is important in the history of organic chemistry because it helped prove the structure of ethers. For example, the reaction of ethyl chloride with sodium ethoxide will yield diethyl ether, (fig: 11.29, page 197).

494. (b) Baeyer's test is used to detect the presence of a double bond. Baeyer's reagent, named after the German organic chemist Adolf von Baeyer, is used in organic chemistry as a qualitative test for the presence of unsaturation, such as double bonds. The bromine test is also able to determine the presence of unsaturation.

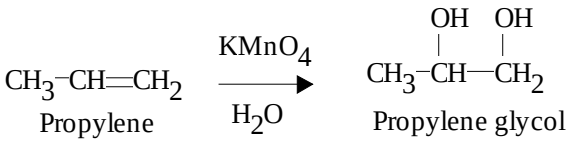


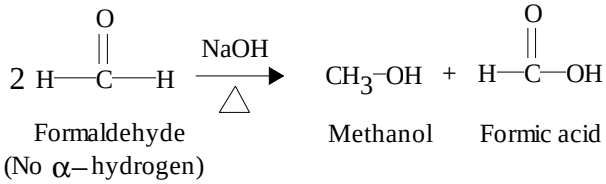
(Fig: 11.28)

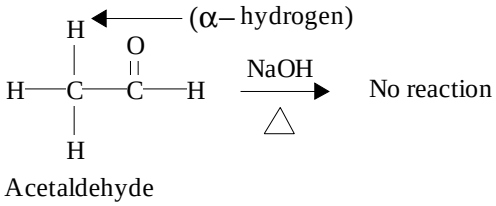


(Fig: 11.29)

Baeyer's reagent is an alkaline solution of potassium permanganate, which is a powerful oxidant. Reaction with double or triple bonds in an organic material causes the color to fade from purplish-pink to brown. For example, the reaction of propylene with potassium permanganate would yield propylene glycol and the purple color of $KMnO_4$ is removed by the reaction.







undergo Cannizzaro reaction whereas acetaldehyde wouldn't react.

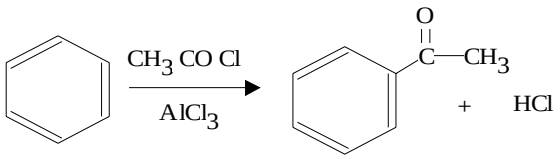
495. (a) The Cannizzaro reaction, named after its discoverer Stanislao Cannizzaro, is a chemical reaction that involves the base-induced disproportionation of an aldehyde lacking a α-hydrogen. When heated with concentrated NaOH, one half of the aldehyde molecules are oxidized to carboxylic acid and the other half are reduced to an alcohol. Aldehydes with α-hydrogens do NOT undergo this reaction; instead they undergo aldol condensation.

A carbon atom next to the carbonyl group is called an α-carbon. A hydrogen attached to an α-carbon is known as an α-hydrogen. Therefore, formaldehyde would

496. (d) As we learned previously, Cannizzaro reaction is when 2 molecules of formaldehyde are heated in the presence of NaOH, methanol and formic acid are formed. However, when we select two different aldehydes, each lacking α-hydrogen, and they heated in the presence of NaOH, the reaction is called a Crossed Cannizzaro reaction. For example, when benzaldehyde and formaldehyde (two different aldehydes) are heated in the presence of NaOH, benzyl alcohol and formic acid are formed.

497. (c) The Friedel-Crafts reactions are a set of reactions developed by Charles Friedel and James Crafts in 1877. There are two main types of Friedel-Crafts reactions: alkylation reactions and acylation reactions. Here we will discuss Friedel-Crafts acylation.

Friedel-Crafts acylation is the acylation of aromatic rings (benzene) with an acyl chloride (CH_3COCl) using a strong Lewis acid catalyst ($AlCl_3$). Friedel-Crafts acylation is also possible with acid anhydrides. This reaction has several advantages over the alkylation reaction. Due to the electron-withdrawing effect of the carbonyl group, the ketone (acetophenone) produced under the reaction is always less reactive than the original molecule (benzene), so multiple acylations do not occur.



Benzene Acetophenone

498. (b) Organometallic compounds are those compounds that contain at least one carbon-metal bond where metals can be Mg, Li, Pb, Zn, etc, for example, ethyllithium (C_2H_5Li). Organomagnesium halides are known as Grignard reagents. They are named after the French chemist François Auguste Victor Grignard who discovered them. The general formula for Grignard reagents can be written as RMgX where R is the alkyl or aryl group and X is the Cl, Br or I. Grignard reagents are highly reactive and used in the synthesis of alkanes, alkenes, alcohols, aldehydes, ketones and carboxylic acids.

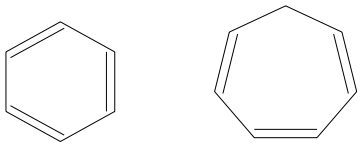
499. (d) In organic chemistry, aromatic compounds usually contain alternate single and double bonds in a cyclic structure and resemble benzene in chemical behavior. This characteristic behavior of the compound is called aromaticity. Aromaticity is defined as a property of the sp_2 hybridized planar ring in which the p orbitals allow cyclic delocalization of π electrons. There are few important criteria to be remembered to determine whether the compound is aromatic or non-aromatic.

1. A compound should be cyclic and planar.

2. Each atom in an aromatic ring should have a p-orbital. These p orbitals must be parallel so that a continuous overlap is possible around the ring.

3. The cyclic π molecular orbital formed by the overlap of p orbitals must contain $(4n + 2)\ \pi$ electrons, where n is equal to integer 0, 1, 2 etc. This is known as Huckel Rule.

In order for a compound to be an aromatic, these three rules must be followed. Let's discuss benzene and cycloheptatriene to get a better idea.



Benzene Cycloheptatriene

Both benzene and cycloheptatriene are cyclic and planar compounds. Both have three double bonds and 6 π electrons, in accordance with the Huckel Rule.

$4n + 2 = 6$, hence $n = 1$

However, benzene possesses aromaticity whereas cycloheptatriene does not since the latter one does not follow criteria 2 of the aromaticity rules. In cycloheptatriene, in addition to three double bonds there is one saturated carbon that does not possess any p-orbital. Because of this, continuous overlap around the ring is not possible, and hence cycloheptatriene is non-aromatic.

500. (c) Gasoline is a complex mixture of hydrocarbons. The branched-chain alkanes give a relatively smooth performance when burnt in the internal combustion engine of motor cars, hence they are excellent fuels for cars. In contrast, normal alkanes detonate and cause knocking of the engine, and are bad fuels. The knock property of various gasolines is stated in terms of octane number or octane rating. Isooctane, which has no tendency to knock, is assigned an octane number of 100 and heptane, which causes great knocking, is assigned the octane number 0.

The octane number of a particular gasoline is the percentage of isooctane in a mixture of isooctane and heptane, which gives equivalent knock performances. For example, the knock performance of an unknown sample of a gasoline is found to be the same as that of a mixture of 65% isooctane and 35% of heptane. The unknown compound should have an octane number of 65.

PREPARATION

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