

## CHAPTER

## 10

## Hydrocarbons

## Section-A

## JEE Advanced/ IIT-JEE

## A Fill in the Blanks

- ..... is most acidic.  
(Ethane, Ethene, Ethyne) (1981 - 1 Mark)
- Acetylene is treated with excess sodium in liquid ammonia. The product is reacted with excess methyl iodide. The final product is ..... (1983 - 1 Mark)
- The starting material for the manufacture of polyvinyl chloride is obtained by reacting HCl with ..... (1983 - 1 Mark)
- Kolbe electrolysis of potassium succinate gives  $\text{CO}_2$  and ..... (1993 - 1 Mark)
- Addition of water to acetylenic compounds is catalyzed by.....and..... (1993 - 1 Mark)
- The bond dissociation energy needed to form the benzyl radical from toluene is.....than the formation of the methyl radical from methane. (1994 - 1 Mark)
- 1, 3-Butadiene with bromine in molar ratio generates predominantly ..... (1997 - 1 Mark)

## B True / False

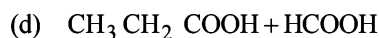
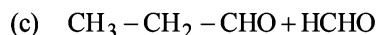
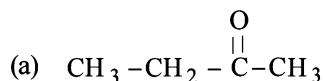
- Moist ethylene can be dried by passing it through concentrated sulphuric acid. (1982 - 1 Mark)
- Photobromination of 2-methylpropane gives a mixture of 1-bromo-2-methylpropane and 2-bromo-2-methylpropane in the ratio of 9: 1. (1993 - 1 Mark)

## C MCQs with One Correct Answer

- Marsh gas mainly contains (1980)
  - $\text{C}_2\text{H}_2$
  - $\text{CH}_4$
  - $\text{H}_2\text{S}$
  - $\text{CO}$
- Which of the following decolourises alkaline  $\text{KMnO}_4$  solution (1980)
  - $\text{C}_3\text{H}_8$
  - $\text{C}_2\text{H}_4$
  - $\text{CH}_4$
  - $\text{CCl}_4$
- The compound with the highest boiling point is (1982 - 1 Mark)
  - n*-hexane
  - n*-pentane
  - 2,2-dimethylpropane
  - 2-methylbutane
- The maximum number of isomers for an alkene with the molecular formula  $\text{C}_4\text{H}_8$  is (1982 - 1 Mark)
  - 2
  - 3
  - 4
  - 5
- When propyne is treated with aqueous  $\text{H}_2\text{SO}_4$  in presence of  $\text{HgSO}_4$  the major product is (1983 - 1 Mark)
  - propanal
  - propyl hydrogensulphate
  - acetone
  - propanol
- Which of the following compounds does not dissolve in conc.  $\text{H}_2\text{SO}_4$  even on warming? (1983 - 1 Mark)
  - ethylene
  - benzene
  - hexane
  - aniline
- Baeyer's reagent is : (1984 - 1 Mark)
  - alkaline permanganate solution
  - acidified permanganate solution
  - neutral permanganate solution
  - aqueous bromine solution
- Acidic hydrogen is present in : (1985 - 1 Mark)
  - ethyne
  - ethene
  - benzene
  - ethane
- Anti*-Markovnikoff addition of  $\text{HBr}$  is not observed in : (1985 - 1 Mark)
  - propene
  - 1-butene
  - but-2-ene
  - pent-2-ene
- The highest boiling point is expected for : (1986 - 1 Mark)
  - iso-octane
  - n*-octane
  - 2,2,3,3-tetramethylbutane
  - n*-butane
- Which of the following will have least hindered rotation about carbon-carbon bond? (1987 - 1 Mark)
  - Ethane
  - Ethylene
  - Acetylene
  - Hexachloroethane

12. When cyclohexane is poured on water, it floats, because:  
 (a) cyclohexane is in 'boat' form (1997 - 1 Mark)  
 (b) cyclohexane is in 'chair' form  
 (c) cyclohexane is in 'crown' form  
 (d) cyclohexane is less dense than water.

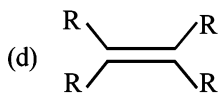
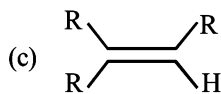
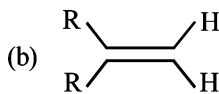
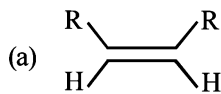
13. The product(s) obtained via oxymercuration ( $\text{HgSO}_4 + \text{H}_2\text{SO}_4$ ) of 1-butyne would be (1999 - 2 Marks)



14. Propyne and propene can be distinguished by (2000S)

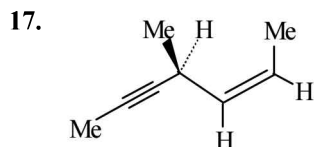
- (a) conc.  $\text{H}_2\text{SO}_4$  (b)  $\text{Br}_2$  in  $\text{CCl}_4$   
 (c) dil.  $\text{KMnO}_4$  (d)  $\text{AgNO}_3$  in ammonia

15. Which one of the following will react fastest with  $\text{H}_2$  under catalytic hydrogenation condition? (2000S)



16. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give *anti*-Markovnikov addition to alkenes because (2001S)

- (a) both are highly ionic  
 (b) one is oxidizing and the other is reducing  
 (c) one of the steps is endothermic in both the cases  
 (d) all the steps are exothermic in both the cases



Hydrogenation of the above compound in the presence of poisoned palladium catalyst gives (2001S)

- (a) an optically active compound  
 (b) an optically inactive compound  
 (c) a racemic mixture  
 (d) a diastereomeric mixture

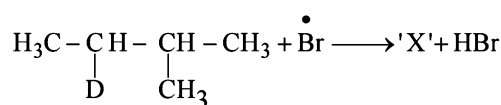
18. The reaction of propene with  $\text{HOCl}$  proceeds via the addition of (2001S)

- (a)  $\text{H}^+$  in the first step  
 (b)  $\text{Cl}^+$  in the first step  
 (c)  $\text{OH}^-$  in the first step  
 (d)  $\text{Cl}^+$  and  $\text{OH}^-$  in a single step

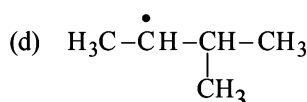
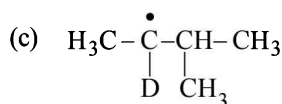
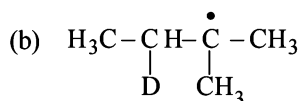
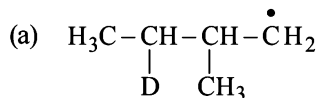
19. The nodal plane in the  $\pi$ -bond of ethene is located in (2002S)

- (a) the molecular plane  
 (b) a plane parallel to the molecular plane  
 (c) a plane perpendicular to the molecular plane which bisects the carbon-carbon  $\sigma$ -bond at right angle  
 (d) a plane perpendicular to the molecular plane which contains the carbon-carbon  $\sigma$ -bond.

20. Consider the following reaction (2002S)



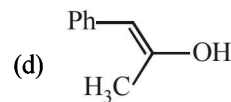
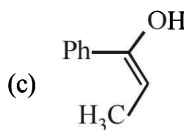
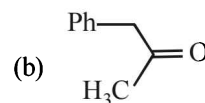
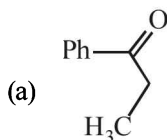
Identify the structure of the major product 'X'



21. Identify the reagent from the following list which can easily distinguish between 1-butyne and 2-butyne (2002S)

- (a) bromine,  $\text{CCl}_4$   
 (b)  $\text{H}_2$ , Lindlar catalyst  
 (c) dilute  $\text{H}_2\text{SO}_4$ ,  $\text{HgSO}_4$   
 (d) ammonical  $\text{Cu}_2\text{Cl}_2$  solution

22.  $\text{Ph}-\text{C}\equiv\text{C}-\text{CH}_3 \xrightarrow{\text{Hg}^{2+}/\text{H}^+} \text{A}$ . A is: (2003S)



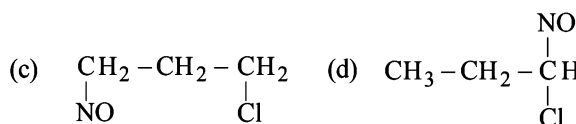
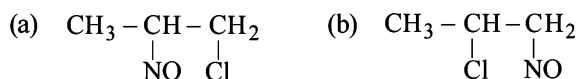
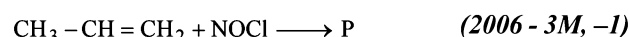
23. Which of the following is used for the conversion of 2-hexyne into *trans*-2-hexene? (2004S)

- (a)  $\text{H}_2/\text{Pd}/\text{BaSO}_4$  (b)  $\text{H}_2$ ,  $\text{PtO}_2$   
 (c)  $\text{NaBH}_4$  (d)  $\text{Li}-\text{NH}_3/\text{C}_2\text{H}_5\text{OH}$

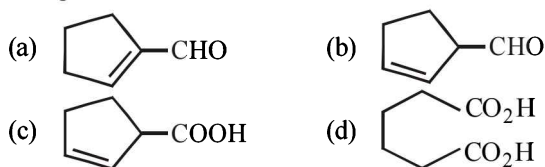
24. On monochlorination of 2-methylbutane, the total number of chiral compounds formed is (2004S)

- (a) 2 (b) 4  
 (c) 6 (d) 8

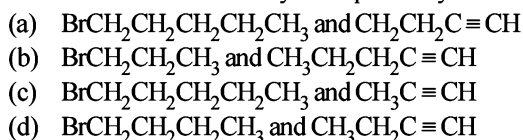
25. Identify the product, P in the following reaction:



26. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound E. Compound E on further treatment with aqueous KOH yields compound F. Compound F is (2007)



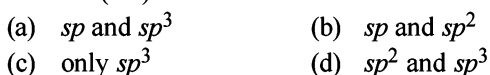
27. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are (2010)



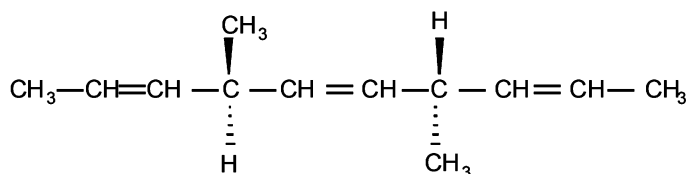
28. The bond energy (in  $\text{kcal mol}^{-1}$ ) of a C–C single bond is approximately (2010)



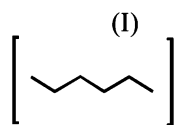
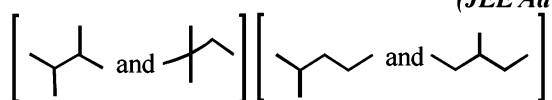
29. In allene ( $\text{C}_3\text{H}_4$ ), the type(s) of hybridisation of the carbon atoms is (are): (2012)



30. The number of optically active products obtained from the complete ozonolysis of the given compound is: (2012)



31. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure. (JEE Adv. 2014)



(III)

The correct order of their boiling point is

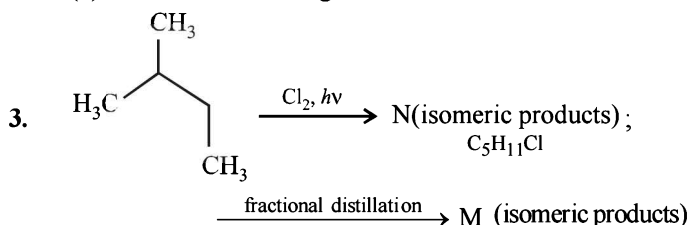
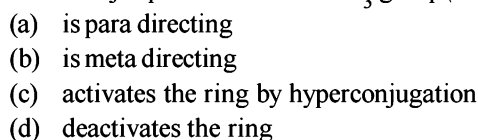


## D MCQs with One or More Than One Correct

1. Which one of the following has the smallest heat of hydrogenation per mole? (1993 - 1 Mark)



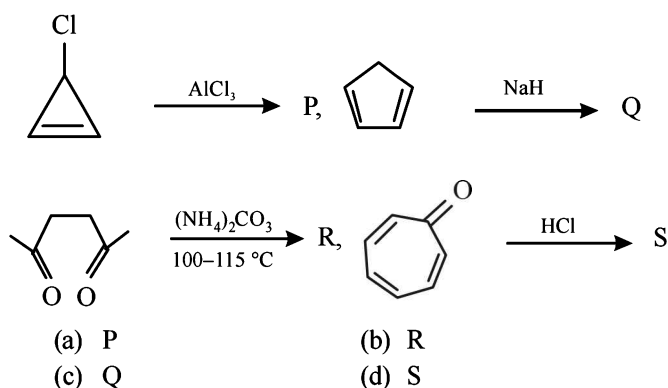
2. Toluene, when treated with  $\text{Br}_2/\text{Fe}$ , gives *p*-bromotoluene as the major product because  $\text{CH}_3$  group (1999 - 3 Marks)



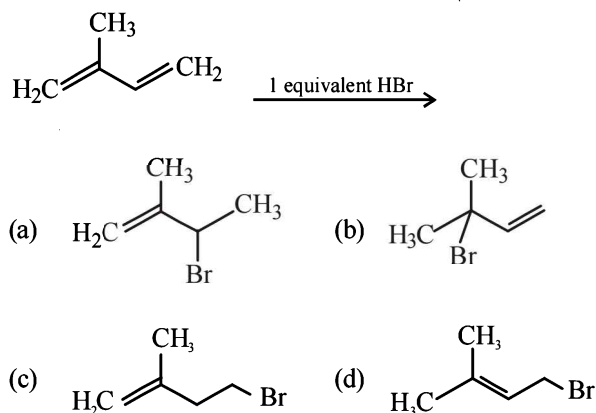
Identify N and M (2006 - 5M, -1)



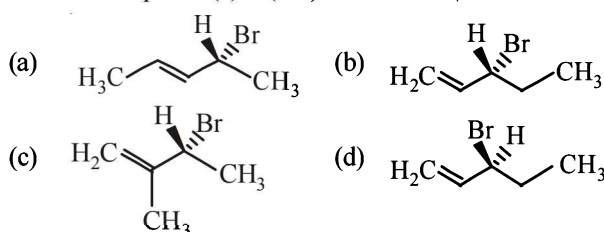
4. Among P, Q, R and S, the aromatic compound(s) is/are (JEE Advanced 2013-I)



5. In the following reaction, the major product is (JEE Adv. 2015)

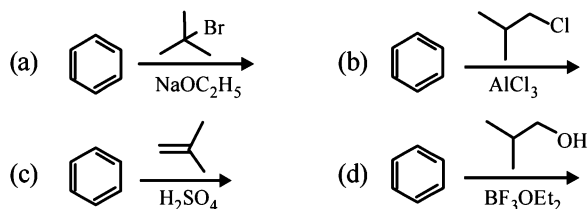


6. Compound(s) that on hydrogenation produce(s) optically inactive compound(s) is (are) (JEE Adv. 2015)



7. Among the following, reaction(s) which gives(give) tert-butyl benzene as the major product is(are)

(JEE Adv. 2016)




## E Subjective Problems

- Give one characteristic test which would distinguish  $\text{CH}_4$  from  $\text{C}_2\text{H}_2$  (1979)
- Write the structural formula of the major product in each of the following cases :

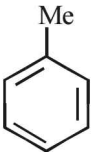
(i) the compound obtained by the hydration of ethyne is treated with dilute alkali (1981 - 1/2 Mark)


(ii) ethene mixed with air is passed under pressure over a silver catalyst at  $250^\circ\text{C}$ . (1981 - 1/2 Mark)

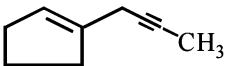
(iii)  +  $(\text{CH}_3)_2\text{CHCH}_2\text{Cl} \xrightarrow{\text{AlCl}_3}$  (1992 - 1 Mark)

(iv)  $\text{C}_6\text{H}_6 + (\text{CH}_3)_2\text{CHCH}_2\text{OH} \xrightarrow{\text{H}_2\text{SO}_4}$  (1994 - 1 Mark)

(v)  $\text{C}_6\text{H}_5\text{C}_2\text{H}_5 \xrightarrow[2. \text{NaCN}]{1. \text{Br}_2, \text{Heat, Light}}$  (1994 - 1 Mark)

(vi)  +  $\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{CH}_2\text{Br}$   
+ Anhyd.  $\text{AlCl}_3 \longrightarrow$  (1997 - 1 Mark)

(vii)  +  $\text{CHBr}_3 + t\text{-BuOK} \longrightarrow$  (1997 - 1 Mark)

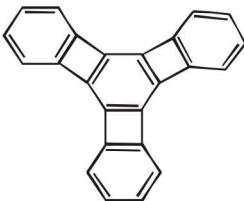
(viii)   $\xrightarrow[\text{Lindlar catalyst}]{\text{H}_2}$  (2000 - 1 Mark)

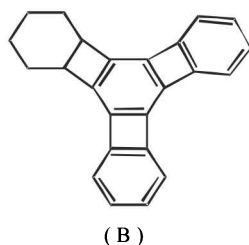
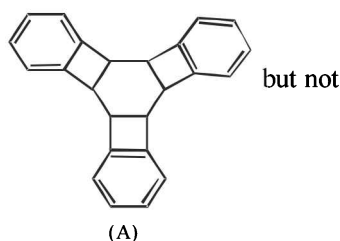
- Outline the reaction sequence for the conversion of ethene to ethyne (the number of steps should not be more than two). (1981 - 1 Mark)
- State with balanced equations, what happens when propene is bubbled through a hot aqueous solution of potassium permanganate. (1982 - 1 Mark)
- Give reasons for the following :
  - Methane does not react with chlorine in the dark. (1983 - 1 Mark)
  - Propene reacts with  $\text{HBr}$  to give isopropyl bromide but does not give n-propyl bromide. (1983 - 1 Mark)
  - Although benzene is highly unsaturated, normally it does not undergo addition reaction. (1983 - 1 Mark)

(iv) Toluene reacts with bromine in the presence of light to give benzyl bromide while in presence of  $\text{FeBr}_3$  it gives p-bromotoluene. Give explanation for the above observations. (1996 - 2 Marks)

(v) The central carbon-carbon bond in 1, 3 - butadiene is shorter than that in n-butane. (1998 - 2 Marks)

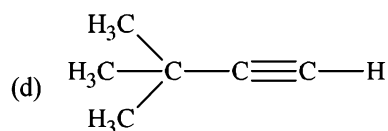
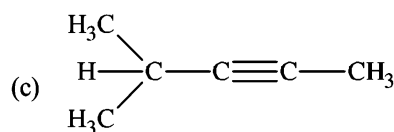
(vi) tert-Butylbenzene does not give benzoic acid on treatment with acidic  $\text{KMnO}_4$ . (2000 - 1 Mark)

(vii)   $\xrightarrow{3\text{H}_2/\text{Pd}}$  (2005 - 1 Mark)

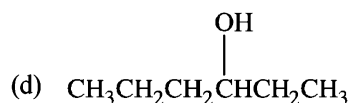
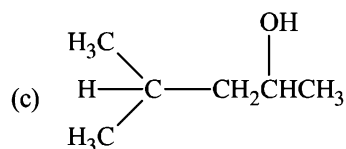
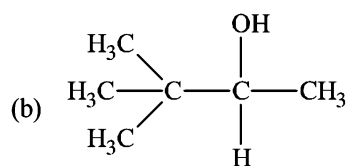
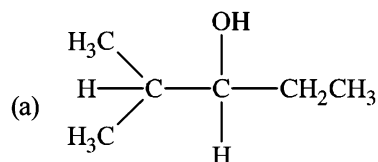


- 2-Methylpropene can be converted into isobutyl bromide by hydrogen bromide, is true under what conditions? (1984 - 1 Mark)
  - 'Ethyne and its derivatives will give white precipitate with ammonical silver nitrate solution', is true under what conditions. (1984 - 1 Mark)
- Write down the reactions involved in the preparation of the following, using the reagents indicated against it in parenthesis.  
Ethylbenzene from benzene [ $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{PCl}_5$ , anhydrous  $\text{AlCl}_3$ ]. (1984 - 2 Marks)
- A certain hydrocarbon A was found to contain 85.7 percent carbon and 14.3 per cent hydrogen. This compound consumes 1 molar equivalent of hydrogen to give a saturated hydrocarbon B. 1.00 g of hydrocarbon A just decolourized 38.05 g of a 5 per cent solution (by weight) of  $\text{Br}_2$  in  $\text{CCl}_4$ . Compound A, on oxidation with concentrated  $\text{KMnO}_4$ , gave compound C (molecular formula  $\text{C}_4\text{H}_8\text{O}$ ) and acetic acid. Compound C could easily be prepared by the action of acidic aqueous mercuric sulphate on 2- butyne. Determine the molecular formula of A and deduce the structure of A, B and C. (1984 - 6 Marks)
- How would you distinguish between
  - 2-butyne and 1-butyne. (1985 - 1 Mark)
  - cyclohexane and cyclohexene. (1988 - 1 Mark)



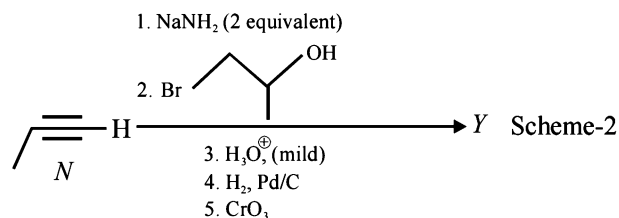
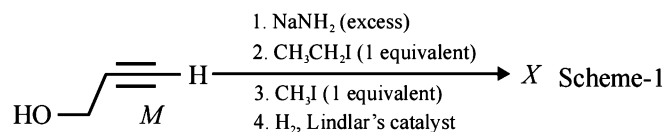


2. The structure of the compound Q is



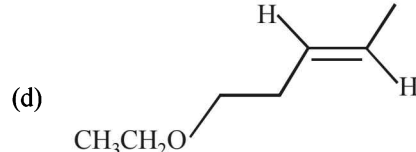
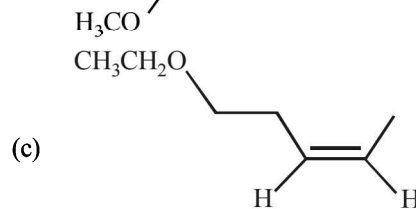
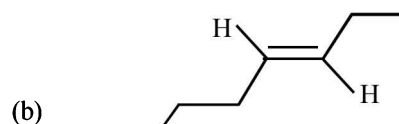
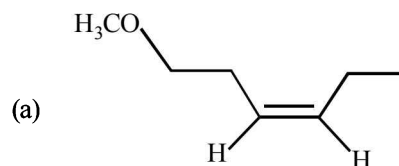
### PASSAGE - II

Schemes 1 and 2 describe sequential transformation of alkynes *M* and *N*. Consider only the major products formed in each step for both the schemes.



3. The product X is

(JEE Adv. 2014)



4. The correct statement with respect to product Y is

(JEE Adv. 2014)

- It gives a positive Tollen's test and is a functional isomer of X
- It gives a positive Tollen's test and is a geometrical isomer of X
- It gives a positive iodoform test and is a functional isomer of X
- It gives a positive iodoform test and is a geometrical isomer of X

### Assertion & Reason Type Questions

Read the following statement (Assertion) and explanation (Reason) and answer each question as per the options given below :

- If both *assertion* and *reason* are correct, and *reason* is the correct explanation of the *assertion*.
- If both *assertion* and *reason* are correct, but *reason* is not the correct explanation of the *assertion*.
- If *assertion* is correct but *reason* is incorrect.
- If *assertion* is incorrect but *reason* is correct.

1. **Assertion :** Addition of  $\text{Br}_2$  to 1-butene gives two optical isomers.

**Reason :** The product contains one asymmetric carbon.

(1998 - 2 Marks)

2. **Assertion :** 1-Butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane.

**Reason :** It involves the formation of a primary radical.

(2000S)

3. **Assertion :** Addition of bromine to *trans*-2-butene yields *meso*-2,3-dibromobutane.

**Reason :** Bromine addition to an alkene is an electrophilic addition.

(2001S)

## Section-B

## JEE Main / AIEEE

- Which of these will not react with acetylene? [2002]  
(a) NaOH (b) ammonical AgNO<sub>3</sub>  
(c) Na (d) HCl.
- What is the product when acetylene reacts with hypochlorous acid? [2002]  
(a) CH<sub>3</sub>COCl (b) ClCH<sub>2</sub>CHO  
(c) Cl<sub>2</sub>CHCHO (d) ClCHCOOH.
- On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane. This alkane could be [2003]  
(a) pentane (b) isopentane  
(c) neopentane (d) propane
- 2-Methylbutane on reacting with bromine in the presence of sunlight gives mainly [2005]  
(a) 1-bromo-3-methylbutane  
(b) 2-bromo-3-methylbutane  
(c) 2-bromo-2-methylbutane  
(d) 1-bromo-2-methylbutane
- Butene-1 may be converted to butane by reaction with [2003]  
(a) Sn-HCl (b) Zn-Hg  
(c) Pd/H<sub>2</sub> (d) Zn-HCl
- Reaction of one molecule of HBr with one molecule of 1, 3-butadiene at 40°C gives predominantly [2005]  
(a) 1-bromo-2-butene under kinetically controlled conditions  
(b) 3-bromobutene under thermodynamically controlled conditions  
(c) 1-bromo-2-butene under thermodynamically controlled conditions  
(d) 3-bromobutene under kinetically controlled conditions
- Of the five isomeric hexanes, the isomer which can give two monochlorinated compounds is [2005]  
(a) 2-methylpentane (b) 2, 2-dimethylbutane  
(c) 2, 3-dimethylbutane (d) n-hexane
- Acid catalyzed hydration of alkenes except ethene leads to the formation of  
(a) mixture of secondary and tertiary alcohols  
(b) mixture of primary and secondary alcohols  
(c) secondary or tertiary alcohol  
(d) primary alcohol
- Which types of isomerism is shown by 2, 3-dichlorobutane? [2005]  
(a) Structural (b) Geometric  
(c) Optical (d) Diastereo
- The compound formed as a result of oxidation of ethyl benzene by KMnO<sub>4</sub> is [2007]  
(a) benzyl alcohol (b) benzophenone  
(c) acetophenone (d) benzoic acid.
- Which of the following reactions will yield 2, 2-dibromopropane? [2007]  
(a) CH<sub>3</sub>-CH=CH<sub>2</sub> + HBr →  
(b) CH<sub>3</sub>-C≡CH + 2HBr →  
(c) CH<sub>3</sub>CH=CHBr + HBr →  
(d) CH≡CH + 2HBr →
- The reaction of toluene with Cl<sub>2</sub> in presence of FeCl<sub>3</sub> gives predominantly [2007]  
(a) m-chlorobenzene  
(b) benzoyl chloride  
(c) benzyl chloride  
(d) o- and p-chlorotoluene.
- Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated with cuprous bromide. The reaction mixture so formed contains [2008]  
(a) mixture of o- and p-bromotoluenes  
(b) mixture of o- and p-dibromobenzenes  
(c) mixture of o- and p-bromoanilines  
(d) mixture of o- and m-bromotoluenes
- In the following sequence of reactions, the alkene affords the compound 'B'  
$$\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3 \xrightarrow{\text{O}_3} \text{A} \xrightarrow[\text{Zn}]{\text{H}_2\text{O}} \text{B}.$$
  
The compound B is [2008]  
(a) CH<sub>3</sub>CH<sub>2</sub>CHO (b) CH<sub>3</sub>COCH<sub>3</sub>  
(c) CH<sub>3</sub>CH<sub>2</sub>COCH<sub>3</sub> (d) CH<sub>3</sub>CHO
- The hydrocarbon which can react with sodium in liquid ammonia is [2008]  
(a) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>C≡CCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>  
(b) CH<sub>3</sub>CH<sub>2</sub>C≡CH  
(c) CH<sub>3</sub>CH=CHCH<sub>3</sub>  
(d) CH<sub>3</sub>CH<sub>2</sub>C≡CCH<sub>2</sub>CH<sub>3</sub>
- The treatment of CH<sub>3</sub>MgX with CH<sub>3</sub>C≡C-H produces [2008]  
(a) CH<sub>3</sub>-CH=CH<sub>2</sub>  
(b) CH<sub>3</sub>C≡C-CH<sub>3</sub>  
(c)  $\text{CH}_3 - \overset{\text{H}}{\underset{|}{\text{C}}} = \overset{\text{H}}{\underset{|}{\text{C}}} - \text{CH}_3$   
(d) CH<sub>4</sub>
- One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is [2010]  
(a) propene (b) 1-butene  
(c) 2-butene (d) ethene

18. Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of :

[2011]

- (a) two ethylenic double bonds
- (b) a vinyl group
- (c) an isopropyl group
- (d) an acetylenic triple bond

19. Which branched chain isomer of the hydrocarbon with molecular mass 72u gives only one isomer of mono substituted alkyl halide ?

[2012]

- (a) Tertiary butyl chloride
- (b) Neopentane
- (c) Isohexane
- (d) Neohexane

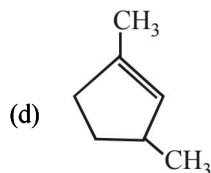
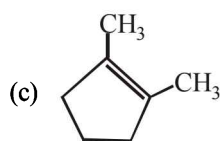
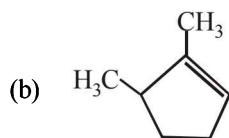
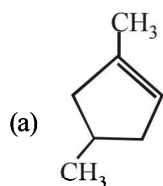
20. 2-Hexyne gives *trans*-2-Hexene on treatment with :

- (a)  $\text{Pt}/\text{H}_2$
- (b)  $\text{Li}/\text{NH}_3$
- (c)  $\text{Pd}/\text{BaSO}_4$
- (d)  $\text{LiAlH}_4$

[2012]

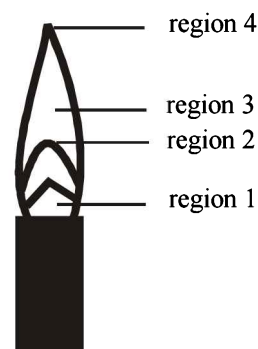
21. Which compound would give 5 - keto - 2 - methylhexanal upon ozonolysis ?

[JEE M 2015]



22. The hottest region of Bunsen flame shown in the figure below is :

[JEE M 2016]



- (a) region 3
- (b) region 4
- (c) region 1
- (d) region 2

23. At 300 K and 1 atm, 15 mL of a gaseous hydrocarbon requires 375 mL air containing 20%  $\text{O}_2$  by volume for complete combustion. After combustion the gases occupy 330 mL. Assuming that the water formed is in liquid form and the volumes were measured at the same temperature and pressure, the formula of the hydrocarbon is:

[JEE M 2016]

- (a)  $\text{C}_4\text{H}_8$
- (b)  $\text{C}_4\text{H}_{10}$
- (c)  $\text{C}_3\text{H}_6$
- (d)  $\text{C}_3\text{H}_8$

24. The reaction of propene with  $\text{HOCl}$  ( $\text{Cl}_2 + \text{H}_2\text{O}$ ) proceeds through the intermediate:

[JEE M 2016]

- (a)  $\text{CH}_3 - \text{CH}(\text{OH}) - \text{CH}_2^+$
- (b)  $\text{CH}_3 - \text{CHCl} - \text{CH}_2^+$
- (c)  $\text{CH}_3 - \text{CH}^+ - \text{CH}_2 - \text{OH}$
- (d)  $\text{CH}_3 - \text{CH}^+ - \text{CH}_2 - \text{Cl}$