

ALKADIENES

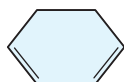
Section - 5

Alkadienes are isomers of alkynes and cycloalkenes. These are classified in three categories.

- (a) Hydrocarbons containing cumulated double bonds are called allenes or cumulated dienes.

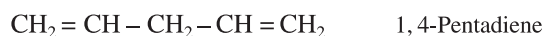


- (b) Those dienes which have an alternate system of double and single bonds are called conjugated dienes.



1, 3-Cyclohexadiene

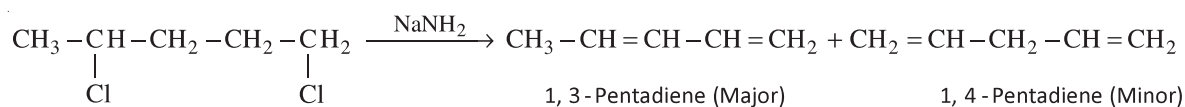
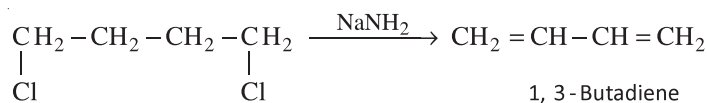
- (c) In case, when one or more sp^3 hybridised carbon atoms come in between the double bonds in dienes, then they are called isolated dienes.



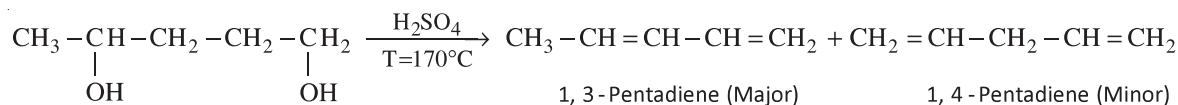
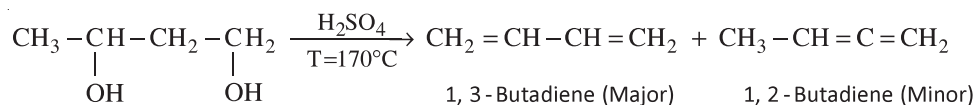
Note : Conjugated dienes are most stable among dienes. They are stabilised due to resonance.

Preparation of Conjugated dienes :

1. From isolated dihalides



2. From isolated diols :



Reactions of Conjugated Dienes :

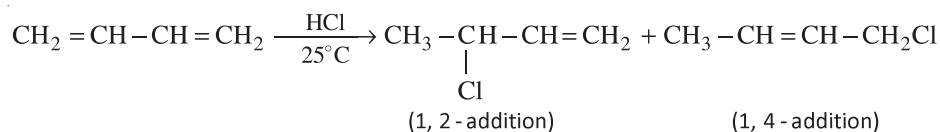
For the discussion of reactions of conjugated dienes we shall take 1, 3-Butadiene as an example.

1. Electrophillic Addition :

1, 3-Butadiene when reacts with HCl show unusual behaviour to give mixture of two products :

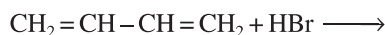
3-Chloro-1-butene (1, 2-addition product) and 1-Chloro-2-butene (1, 4-addition product)

(a) The formation of 1, 4-addition product is interesting.

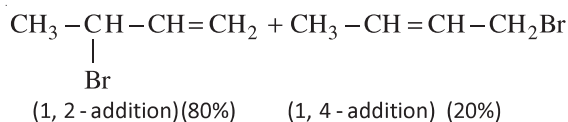


Note: Usually 1,4-addition product is major.

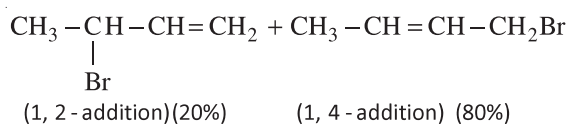
(b) Addition of HBr to 1, 3-Butadiene takes place differently at different temperature to give 1, 2-addition and 1, 4-addition products as follows :



(i) At -80°C (Low temperature) :



(ii) A 40°C (Near room temperature and above) :



Note: At high temperatures, in case of HBr, 1, 2-addition product rearranges to give 1, 4-addition product.

(c) Addition of Br_2 to 1, 3-Butadiene also gives a mixture of 1, 2-addition and 1, 4-addition products.

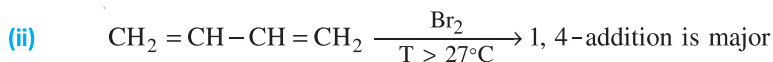
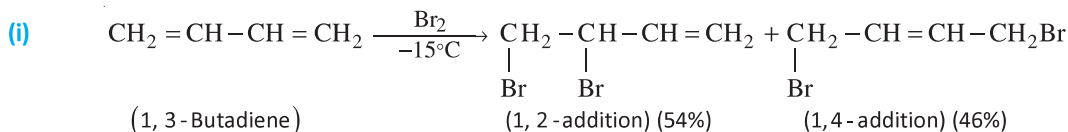


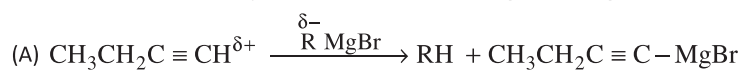
Illustration - 9 Isomers A, B, C, and E have a common molecular formula C_4H_6 . Identify A, B, C..... as per given instructions.

- (a) A reacts with $RMgBr$ to give a hydrocarbon.
 (b) B reacts with Br_2 to give a mixture of two products.
 (c) C, an alicyclic compound, when oxidised by hot acidic $KMnO_4$, gives a dicarboxylic acid whose sodium salt on electrolysis gives an alkene, D. Also identify D.
 (d) E is an alicyclic compound which is oxidized by hot $KMnO_4$ to give 3-Oxo-1-butanoic acid.

SOLUTION :

C_4H_6 : can be alkyne, or alkadiene, or cycloalkene.

- (a) A should be a terminal alkyne as it reacts with Grignard reagent.



- (b) B should be a conjugated diene as it gives a mixture of products.

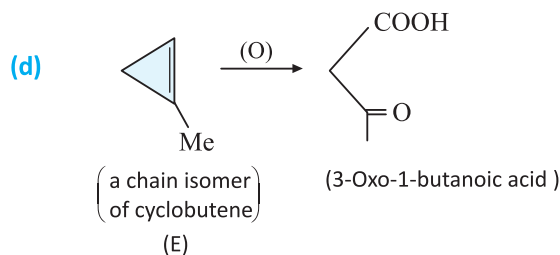
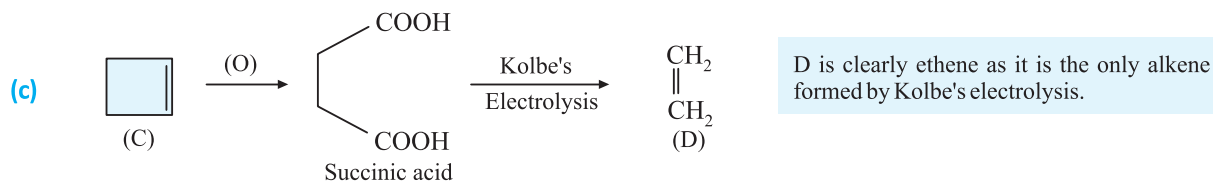
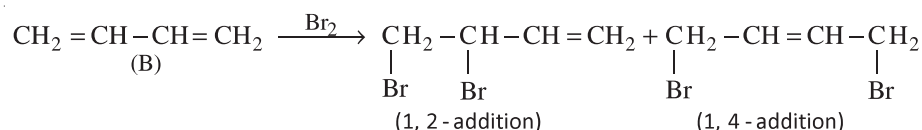
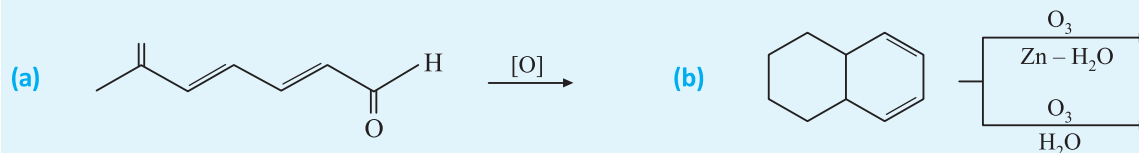
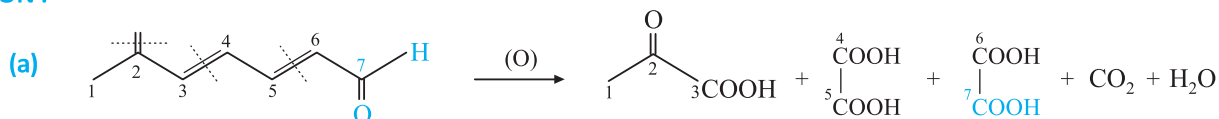


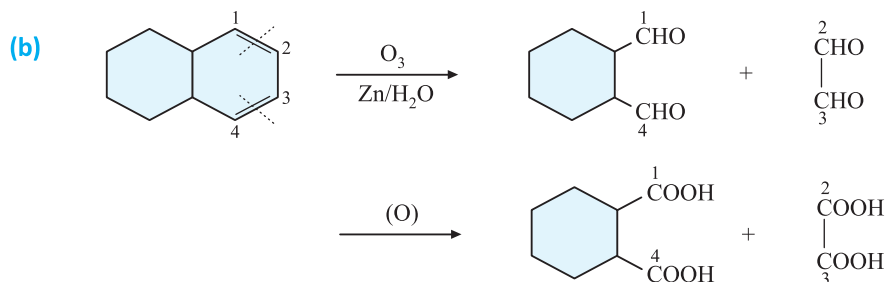
Illustration - 10 Give the products.



SOLUTION :

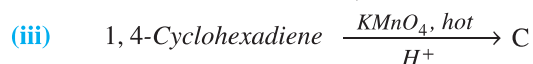
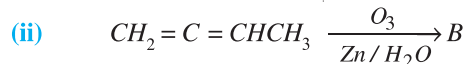
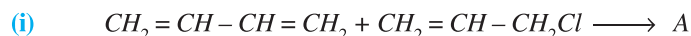


Note that aldehyde group is oxidised to acidic group.



IN-CHAPTER EXERCISE-E

1. Identify the products A, B, C,



2. An organic compound $\text{E}(\text{C}_5\text{H}_8)$ on hydrogenation gives compound $\text{F}(\text{C}_5\text{H}_{12})$. Compound E on ozonolysis gives formaldehyde and 2-ketopropanal. Deduce the structure of compound E and F.

Choose the correct alternative. Only One Choice is Correct. However, questions marked * may have More than One Correct option :

3. (i) In allene (C_3H_4), the type(s) of hybridisation of the carbon atom is(are) :

- (A) sp and sp^3 (B) sp and sp^2 (C) Only sp^3 (D) sp^2 and sp^3

*(ii) 2,3-Pentadiene, $\text{CH}_3\text{CH} = \text{C} = \text{CHCH}_3$ is :

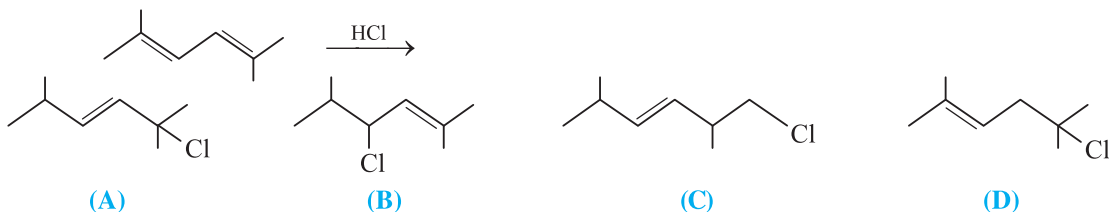
- (A) A planar substance (B) A conjugated diene
(C) An allene (D) A substance capable of cis-trans isomerism

(iii) Hydrogenation of cyclohexene releases 120 kJ/mol of heat. Which of the following most likely represents the observed heat of hydrogenation of 1,3-cyclohexadiene ?

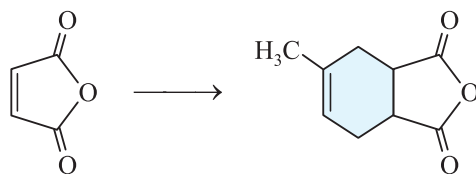
- (A) 232 kJ/mol (B) 247 kJ/mol (C) 240 kJ/mol (D) 120 kJ/mol

- (iv) Which statement best describes the structure of allene molecule, $H_2C = C = CH_2$?
- (A) The C-atoms form an angle of 120° and the H-atoms lie in the same plane as the C-atoms
- (B) The C-atoms form an angle of 120° and the H-atoms lie in a plane perpendicular to that of the C-atoms
- (C) The C-atoms form an angle of 180° and the four H-atoms lie in the same plane
- (D) The C-atoms form angle of 180° and the two CH_2 groups are perpendicular to one another

- (v) What is the product of 1, 4-addition in the reaction shown ?



- (vi) What hydrocarbon reacts with the compound shown (on heating) to give the indicated product ?



- (A) 2-Methyl-1-butene (B) 2-Methyl-2-butene
- (C) 2-Methyl-1, 3-butadiene (D) 1, 3-Pentadiene

4. What two compounds of molecular formula $C_{11}H_{20}$ give 2, 2, 6, 6-tetramethylheptane on catalytic hydrogenation over platinum ?
5. Write structural formulas for all the :
- (i) Conjugated dienes (ii) Isolated dienes
- (iii) Cumulated dienes
- That gives 2, 4-dimethylpentane on catalytic hydrogenation.
6. A monomer of polymer on ozonolysis gives two moles of CH_2O and one mole of CH_3COCHO . Write the structure of monomer and write all 'cis' configuration of polymer chain.