Structural Identification

Introduction

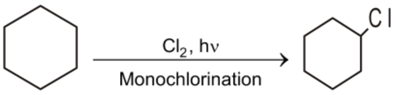
The main objective of an organic chemist is the determination of the structure of a new organic compound which has been obtained in pure state either from a natural source or synthesised in the laboratory.
In order to establish the correct structure of an organic compound, it is necessary to detect skeleton of compound, elements and functional groups present in the organic compound.

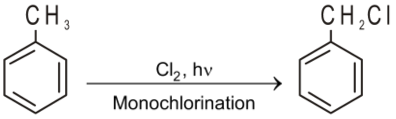
1. Monohalogenation :

When an alkane or a cycloalkane is treated with halogen (Cl_2, Br_2, F_2, I_2), a photochemical reaction takes place, in which a C–H bond cleaves and a C–X bond is formed. In such reactions if one H-atom is substituted by one halogen atom, then this is known as monohalogenation reaction.
Applications : If a molecule has more than one type of H-atoms, then on monochlorination, it forms a mixture of monochloroisomers. **All these products (structures) are position isomers.**
Conclusion : Hence, it can be concluded that the total no. of position isomers (structural) of monochloro compounds is equal to the number of different types of H-atoms present in the reactant. The different type of H-atoms are also known as non-identical Hydrogens or non-equivalent Hydrogens or chemically different Hydrogens.

Note : In aromatic hydrocarbons, the hydrogen atoms of the side-chain are chlorinated, but H-atoms of Benzene ring are stable.

Ex. (i) $CH_4 \xrightarrow[\text{Monochlorination}]{Cl_2,\ h\nu} CH_3Cl + HCl$ ¼1–Monochloroproduct½

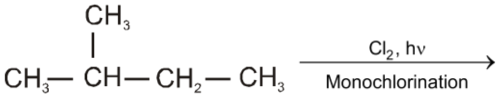
(ii)  + HCl ¼1–Monochloroproduct½

(iii)  ¼1–Monochloroproduct½

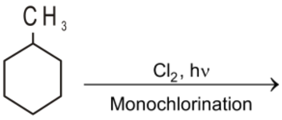
Note : Only one monochloro product is formed because aromatic H atoms are inert towards this reaction.

(iv) $CH_3–CH_2–CH_2–CH_3 \xrightarrow[\text{Monochlorination}]{Cl_2,\ h\nu}$ 2 Products (structure isomers)

(v) $CH_3–CH_2–CH_2–CH_2–CH_3 \xrightarrow[\text{Monochlorination}]{Cl_2,\ h\nu}$ 3 Products (structure isomers)

(vi) 

$CH_3–\overset{\displaystyle CH_3}{\overset{|}{C}H}–CH_2–CH_3 \xrightarrow[\text{Monochlorination}]{Cl_2,\ h\nu}$ 4 Products (structure isomers)

(vii)  5 Products (structure isomers)

2. Catalytic hydrogenation :

Alkenes, Alkynes, polyenes or polyynes can be hydrogenated by using catalysts Ni/Pt/Pd at room temperature.

All Carbon–Carbon π bonds(C=C, C≡C) get hydrogenate. The reaction can't be stopped at any intermediate stage.

Note: **(i)** Aromatic π bonds are stable at room temperature but can be hydrogenated at high temperature.

(ii) It can be concluded that the hydrogenation product of an alkene or alkyne or any unsaturated compound is always a saturated compound.

(iii) The no. of moles of H_2 consumed by 1 mole of compound is equal to the no. of π bonds.

(iv) During catalytic hydrogenation *carbon skelton* does not change.

Application : This reaction gives an information about molecule that the molecule is saturated or unsaturated.

General reaction :

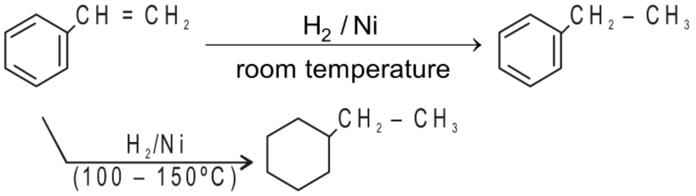
(a) $R–CH=CH–R + H_2 \xrightarrow{Ni} R–CH_2–CH_2–R$

(b)

$$\begin{tikzcd}
R–C≡C–R + 2H_2 \arrow[r, "Ni/Pt/Pd"] \arrow[d, "H_2"] & R–CH_2–CH_2–R \\
\begin{array}{c} R-CH=CH-R \\ \text{(Not isolated)} \end{array} \arrow[r, "H_2"] & R–CH_2–CH_2–R
\end{tikzcd}$$

(c) $CH_2=CH–CH=CH_2 \xrightarrow{2H_2/Ni} CH_3–CH_2–CH_2–CH_3$

(d)



3. Ozonolysis :

Ozonolysis reaction is used to determine the position of C=C, C≡C in a molecule. In this reaction Alkene, Alkyne and polyalkene on ozonolysis undergo oxidative cleavage. It is of two types.

(i) Reductive ozonolysis

Reagents are : (1) O_3 (ozone) (2) Zn or $(CH_3)_2S$ and H_2O or CH_3COOH

The products are carbonyl compounds (aldehydes or ketones).

(ii) Oxidative ozonolysis

Reagents are : (1) O_3 (ozone) (2) H_2O_2 or H_2O

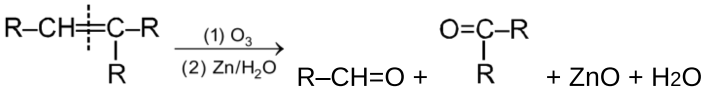
The products are ketones and/or acids.

Note : (i) Ozonolysis does not interfere with other functional groups.

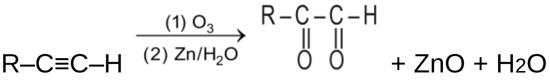
(ii) At higher temperature, the aromatic double bonds can also undergo ozonolysis reaction.

General reaction :

(i) Reductive ozonolysis

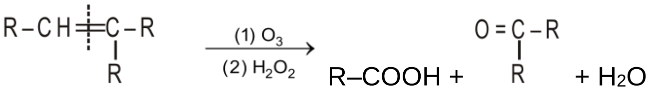


$$R\text{–}CH{=}\underset{R}{C}\text{–}R \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} R\text{–}CH{=}O + O{=}\underset{R}{C}\text{–}R + ZnO + H_2O$$

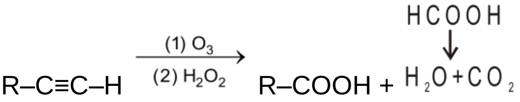


$$R\text{–}C{\equiv}C\text{–}H \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} R\text{–}\underset{O}{\underset{\|}{C}}\text{–}\underset{O}{\underset{\|}{C}}\text{–}H + ZnO + H_2O$$

(ii) Oxidative ozonolysis



$$R\text{–}CH{=}\underset{R}{C}\text{–}R \xrightarrow[(2)\ H_2O_2]{(1)\ O_3} R\text{–}COOH + O{=}\underset{R}{C}\text{–}R + H_2O$$



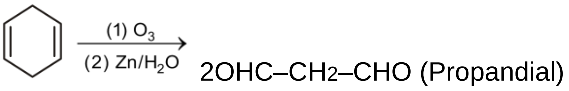
$$R\text{–}C{\equiv}C\text{–}H \xrightarrow[(2)\ H_2O_2]{(1)\ O_3} R\text{–}COOH + \underset{H_2O+CO_2}{\underset{\downarrow}{HCOOH}}$$

Ex. (a) $CH_2{=}CH_2 \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} CH_2{=}O + CH_2{=}O$

(b) $CH_3\text{–}CH_2\text{–}CH{=}CH_2 \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} CH_3\text{–}CH_2\text{–}CH{=}O + O{=}CH_2$

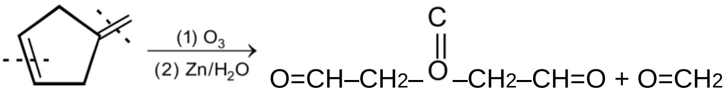
(c) $CH_2{=}CH\text{–}CH_2\text{–}CH{=}CH\text{–}CH_3 \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} CH_2{=}O + O{=}CH\text{–}CH_2\text{–}CH{=}O + O{=}CH\text{–}CH_3$

(d)



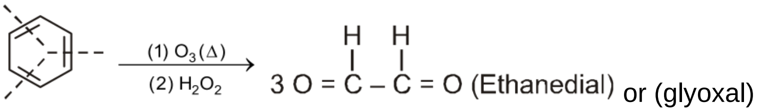
$\xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3}$ 2OHC–CH$_2$–CHO (Propandial)

(e)



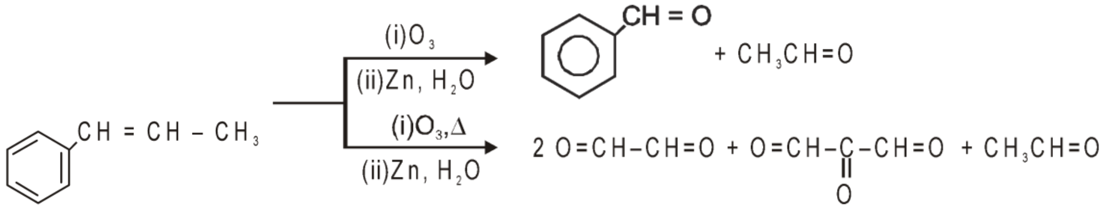
$$\xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} O{=}CH\text{–}CH_2\text{–}\overset{\overset{C}{\|}}{O}\text{–}CH_2\text{–}CH{=}O + O{=}CH_2$$

(f)



$$\xrightarrow[(2)\ H_2O_2]{(1)\ O_3(\Delta)} 3\ O = \overset{H}{\overset{|}{C}} - \overset{H}{\overset{|}{C}} = O$$ (Ethanedial) or (glyoxal)

(g)



$\xrightarrow[(ii)Zn,\ H_2O]{(i)O_3}$ benzaldehyde (CH = O) + $CH_3CH{=}O$

$\xrightarrow[(ii)Zn,\ H_2O]{(i)O_3,\Delta}$ $2\ O{=}CH\text{–}CH{=}O + O{=}CH\text{–}\underset{O}{\underset{\|}{C}}\text{–}CH{=}O + CH_3CH{=}O$