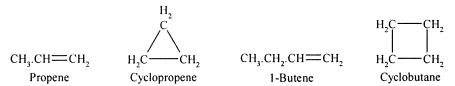
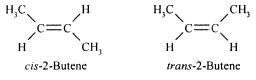
compounds. For example, propene and cyclopropane are the isomeric forms. Similarly, butene is isomeric with cyclobutane.



4. Geometrical isomerism: Except ethene and propene all other alkenes exhibit geometrical isomerism, i.e., they are represented as cis and trans forms in the unsaturated compounds where rotation around the double bond is restricted. For example, two forms of 2-butene are represented as:



(See also chapter on Isomerism).

GENERAL METHODS OF PREPARATION

Alkenes are prepared by the following general methods:

1. **Dehydration of alcohols:** Alkenes can be prepared from an alcohol by dehydration, i.e., elimination of a molecule of water in the presence of an acid at high temperature.

$$CH_3.CH_2.CH_2.CH_2.OH \xrightarrow{75\% H_2SO_4} CH_3.CH_2.CH = CH_2 + H_2O$$
n-Butyl alcohol 1-Butene

The other dehydrating agents are P_2O_5 , H_3PO_4 , Al_2O_3 . The ease of dehydration in case of alcohol is in the order:

Tertiary > Secondary > Primary

The dehydration of secondary and tertiary alcohol is carried out using dilute sulphuric acid, e.g.

$$CH_3.CH_2.CH.OH.CH_3 \xrightarrow{60\% H_2SO_4} CH_3.CH = CH.CH_3$$

sec-Butyl alcohol 2-Butene

$$(CH_3)_2.C.OH.CH_3 \xrightarrow{20\% H_2SO_4} (CH_3)_2.C = CH_2$$

tert-Butyl alcohol Isobutylene

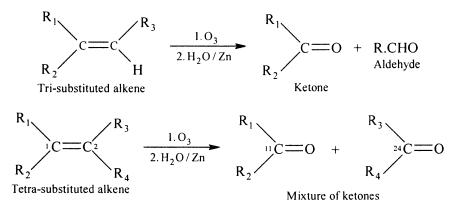
2. **Dehydrohalogenation of alkyl halides:** On heating alkyl halides with alcoholic potassium hydroxide hydrogen halide is eliminated and the alkene is obtained. For example:

$$CH_3.CH_2.CH_2.CI \xrightarrow[-HCl]{alc. KOH} CH_3.CH = CH_2 \xleftarrow[HCl]{alc. KOH} CH_3.CH.CH_3$$

n-Propyl chloride

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The complete process of preparing the ozonide and decomposition is known as **ozonolysis** and is useful for determining the position of double bond in an alkene and to prepare carbonyl compounds. The tri-substituted alkenes give the mixture of the aldehyde and ketone while tetra-substituted alkenes give only ketones on ozonolysis.



10. Addition of hydrogen peroxide: A mixture of hydroperoxide and peroxides is obtained when alkenes are added to hydrogen peroxide in acid catalyst.

 $(CH_3)_2 C = CH_2 + H_2O_2 \xrightarrow{H^+} (CH_3)_3 C - O - O - H \xrightarrow{(CH_3)_2 = CH} (CH_3)_3 C - O - O - (CH_3)_3$ Isobutylene tert-Butylhydroperoxide tert-Butylperoxide

11. Addition of nitrosyl halides: Addition of alkenes to nitrosochloride and nitrosobromide gives crystalline nitrosohalides.

$$CH_{2} = CH_{2} + NO - Br \longrightarrow (CH_{2} - CH_{2}NO) \xrightarrow{Br^{-}} CH_{2} - CH_{2}.NO$$

$$Ethene \qquad Nitroso-bromide \qquad Intermediate carbonium ion \qquad | Br \\ Ethene nitrosobromide \qquad CH_{3}.CH = CH_{2} + NO - CI \longrightarrow (CH_{3}CH.CH_{2}NO) \xrightarrow{CI^{-}} CH_{3}.CHCI.CH_{2}NO$$

Propene nitrosochloride

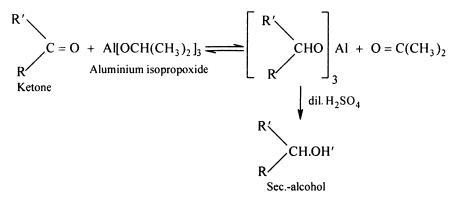
Propene Nitrosochloride

12. Addition of alkene (dimerization): Two molecules of isobutylene are condensed by sulphuric or phosphoric acid to give a mixture of two alkenes of molecular formula C_8H_{16} . Hydrogenation of these products yields an alkane containing the same number of carbon atoms, i.e. 2,2,4-trimethyl pentane, as shown below:

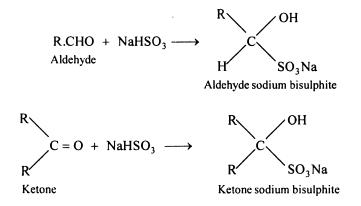
$$2CH_{3} - C = CH_{2} \xrightarrow{H_{2}SO_{4}} \begin{bmatrix} CH_{3} \\ CH_{2} = C.CH_{2}.C.(CH_{3})_{3} \\ 2,4,4-\text{trimethyl-1-pentene} \end{bmatrix} \xrightarrow{H_{2}} (CH_{3})_{2}CH.CH_{2}.C(CH_{3})_{3} \\ 2,2,4-\text{Trimethylpentane} \end{bmatrix}$$

$$(CH_{3})_{2}C = CH.C(CH_{3})_{3} \\ 2,4,4-\text{Trimethyl-2-pentene}$$

A process for reduction of the aldehydes and ketones is the Meerwein-Ponndorf procedure (1925–26) which consists of heating a compound in benzene or toluene with aluminium isopropoxide and distilling the acetone from the mixture so obtained.

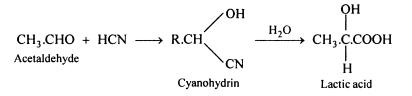


2. Addition of sodium bisulphite: Aldehydes and ketones add on sodium bisulphite to form crystalline bisulphite compounds.



These sulphites are hydroxysulphuric acid salts in which the sulphur is directly attached to the carbon atom. They reproduce the carbonyl compounds when heated with dilute acid or sodium bicarbonate. Hence this reaction is generally used for separating carbonyl compounds from non-carbonyl compounds.

3. Addition of hydrogen cyanide: Aldehydes and ketones add on hydrogen cyanide to yield cyanohydrin products. The reaction is often carried out by adding dilute sulphuric acid into a mixture of carbonyl compound and aqueous sodium cyanide. Cyanohydrins are important compounds in organic synthesis since they are easily converted to α-hydroxy acids.



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Kinetic studies indicate that the rate of reaction depends upon the concentration of acetone and of catalyst used but independent of bromine concentration. In case of bromination of acetone influence of a base catalyst, the following mechanism can be demonstrated. The base abstracts a proton from acetone to form carbanion which then reacts readily to yield bromoacetone.

$$\begin{array}{c} O \\ CH_{3}.C.CH_{3} \\ O \\ CH_{3}.C.CH_{3} \\ CH_{3}.C.CH_{2} \\ Carbanion \\ CH_{3}.C.CH_{2} + Br_{2} \\ CH_{3}.CO.CH_{2}.Br + Br^{-} \end{array}$$

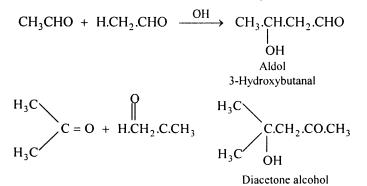
(ii) **Oxidation by selenium dioxide:** Aldehydes and ketones with a methyl or methylene group adjacent to the carbonyl group are oxidized by selenium dioxide at room temperature to dicarbonyl compounds, e.g.:

$$\begin{array}{cccc} CH_3.CHO + SeO_2 & \longrightarrow & OCH.CHO + Se + H_2O \\ Acetaldehyde & & Glyoxal \\ CH_3.CO.CH_3 + SeO_2 & \longrightarrow & CH_3.CO.CHO + Se + H_2O \\ Acetone & & Methyl glyoxal \end{array}$$

10. Schmidt reaction (1924): Carbonyl compounds react with hydrazoic acid in the presence of concentrated sulphuric acid. Aldehydes give a mixture of cyanide and formyl derivatives of primary amines, whereas ketones give amide.

R.CHO + HN₃
$$\xrightarrow{\text{H}_2\text{SO}_4}$$
 R.CN + RNH.CHO + N₂
R.CO.R + HN₃ $\xrightarrow{\text{H}_2\text{SO}_4}$ R.CO.NH.R + N₂

11. Aldol condensation: Two molecules of an aldehyde or ketone may combine to afford a β -hydroxyaldehyde or β -hydroxyketone with or without the elimination of water under the influence of dilute acids or bases. This reaction is called the aldol condensation. In every product the α -carbon of the first is attached to the carbonyl carbon of the second.



On heating, these products eliminate water to form unsaturated compounds, e.g.: