



Cyclic Aliphatic

Introduction

In the cyclic compounds, the carbon atoms are arranged to form rings. Cycloalkane for example, is an alkane, and in general acts like one. But the cyclic nature of some of these compounds confers very special properties on them.

The formula does not fit the general one, a cyclic compound must necessarily contain two hydrogen atoms fewer than its corresponding straight-chain compound.

The cyclic alkanes tend to boil at slightly higher temperature than their straight-chain counterparts.

Nomenclature

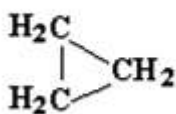
Cyclic aliphatic hydrocarbons are named by prefixing **cyclo-** to the name of the corresponding open-chain hydrocarbon having the same number of carbons as the rings. For example:



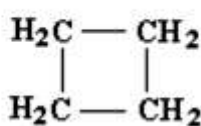
Cyclopentane



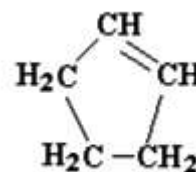
Cyclohexane



Cyclopropane

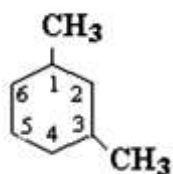


Cyclobutane

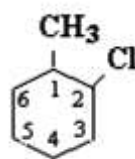


Cyclopentene

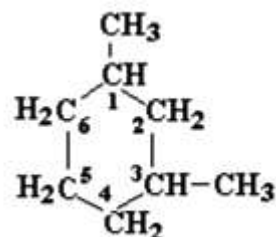
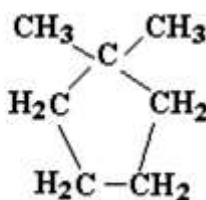
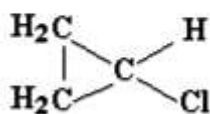
Substituents on the ring, alkyl groups, halogens, are named and their positions are indicated by numbers. We assign position 1 to a particular carbon and then number either clockwise or counterclockwise around the ring; we do all this in such a way to give the lowest combination of numbers. For example:



1,3-Dimethylcyclohexane

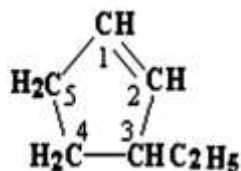


2-Chloro-1-methylcyclohexane

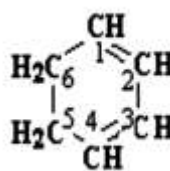


Chlorocyclopropane 1,1-Dimethylcyclopentane 1,3-Dimethylcyclohexane

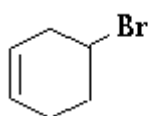
In simple cycloalkenes and cycloalkynes, the doubly and triply bonded carbons are considered to occupy positions 1 and 2. For example:



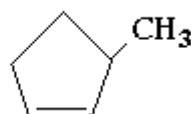
3-Ethylcyclopentene



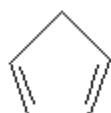
1,3-cyclohexadiene



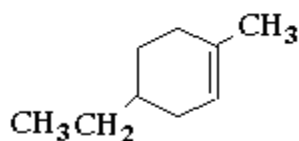
4-Bromocyclohexene



3-Methylcyclopentene



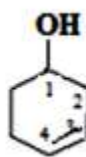
1,3-Cyclopentadiene



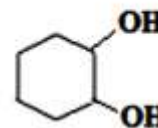
4-Ethyl-1-methylcyclohexene



Cyclopentanol



3-Cyclohexenol



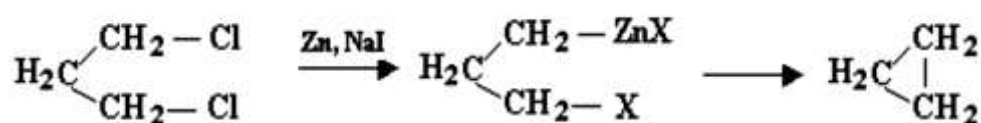
1,2-Cyclohexanediol

Preparation of Cyclic Hydrocarbons

Preparation of alicyclic compounds from other aliphatic compounds generally involves two stages: (a) conversion of some open-chain compound or compounds into a compound that contains a ring, a process called cyclization; (b) conversion of the cyclic compound thus obtained into the kind of compound that we want: for example, conversion of a cyclic alcohol into a cyclic alkyl halide, or a cyclic alkene into a cyclic alkane.

1- Cyclization

A dihalides can bring about coupling between two alkyl groups that are part of the same molecule.

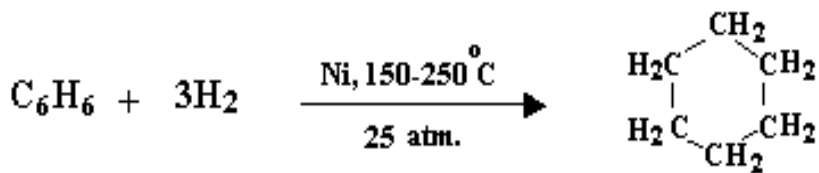


1,3-Dichloropropane

Cyclopropane

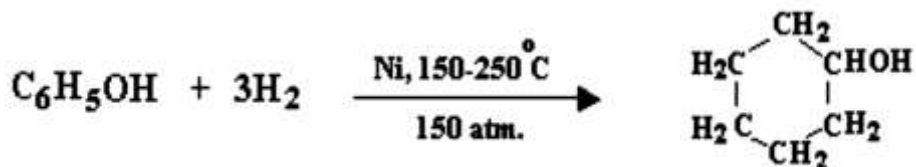
2- Hydrogenation (Industrial source)

Addition of hydrogen to aromatic compounds yields cyclic aliphatic compounds, specifically cyclohexane derivatives. An important example of this is the hydrogenation of benzene to yield pure cyclohexane.



Benzene

Cyclohexane



Phenol

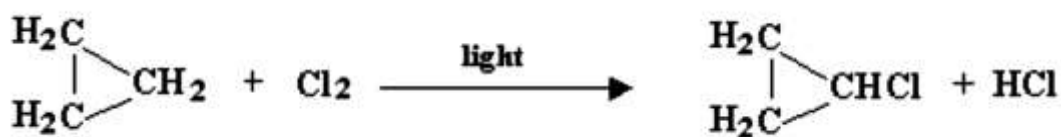
Cyclohexanol

Reactions of Cyclic Hydrocarbons

Cyclic hydrocarbons show similar chemical properties to the open-chain compounds of the same structure. Cycloalkanes, like alkanes are quite unreactive toward most reagents.

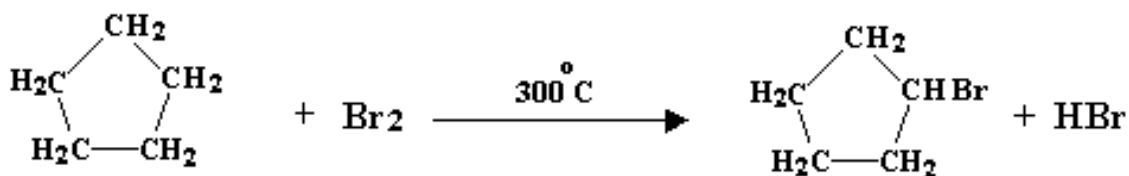
1- Substitution reaction

Cycloalkanes undergo chiefly free-radical substitution reaction.



Cyclopropane

Chlorocyclopropane



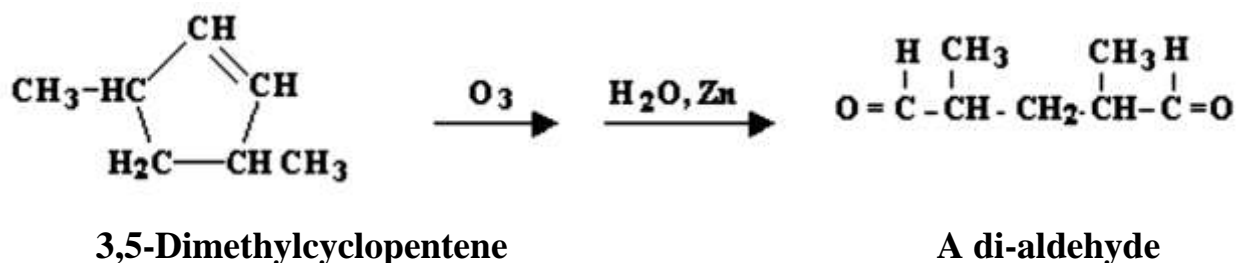
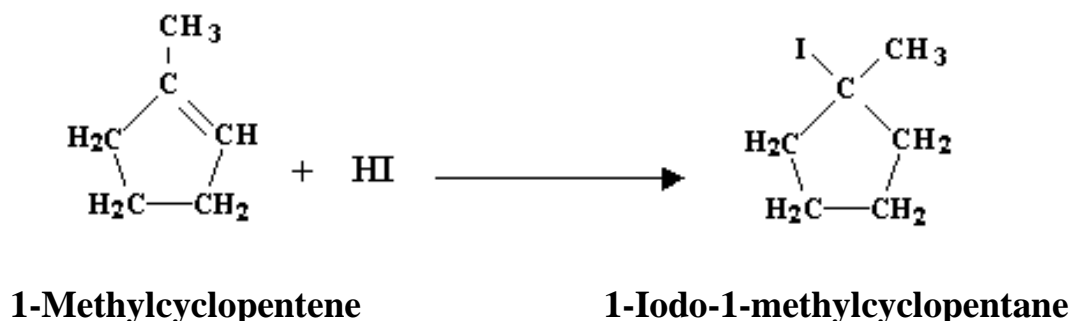
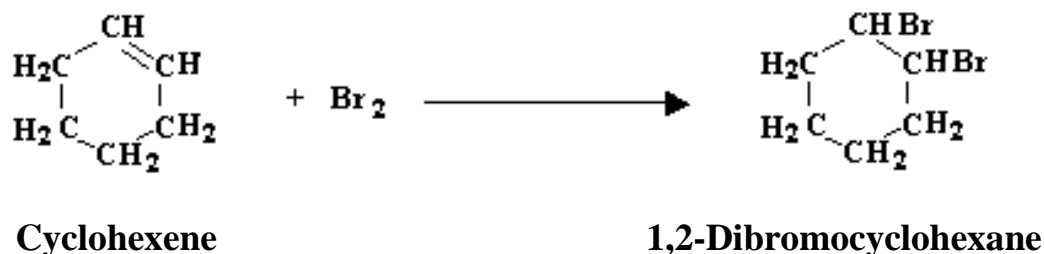
Cyclopentane

Bromocyclopentane



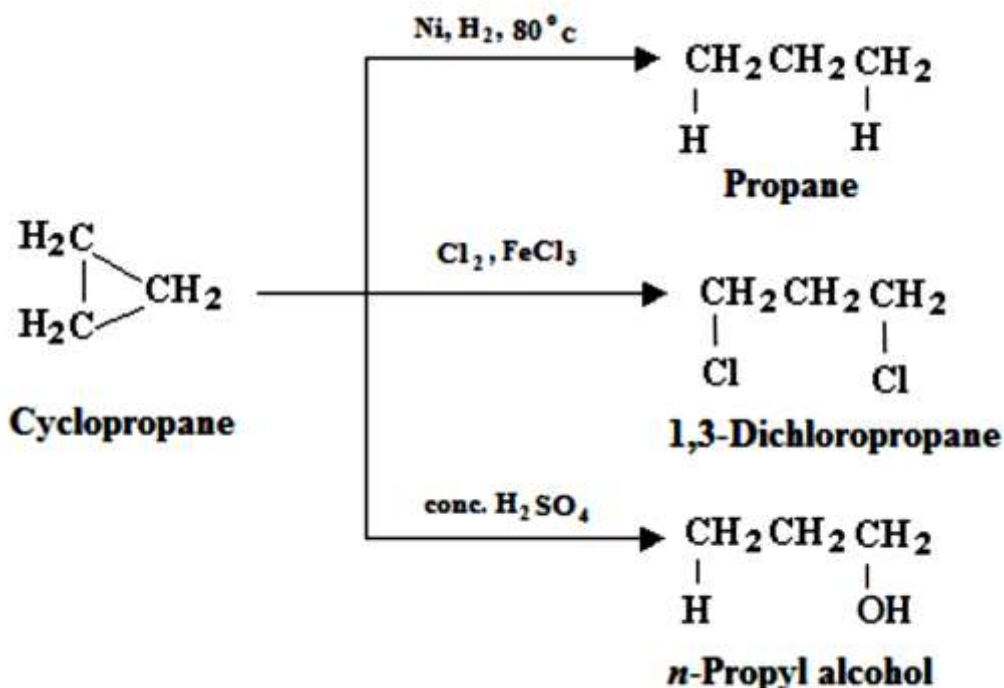
2- Addition and cleavage reactions

Cycloalkenes undergo chiefly addition reactions, both electrophilic and free-radical; like other alkenes, they can also undergo cleavage and allylic substitution.

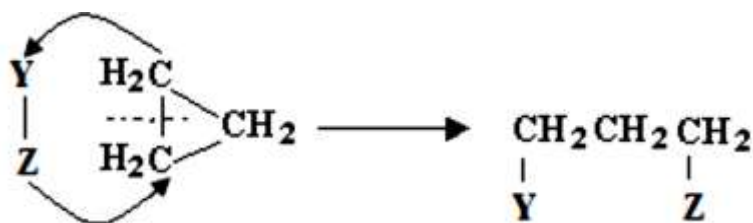


Reactions of small-ring compounds. Cyclopropane and cyclobutane

Besides the free-radical substitution reactions that are characteristic of cycloalkanes and of alkanes in general, cyclopropane and cyclobutane undergo certain addition reactions. These addition reactions destroy the cyclopropane and cyclobutane ring system, and yield open-chain products.

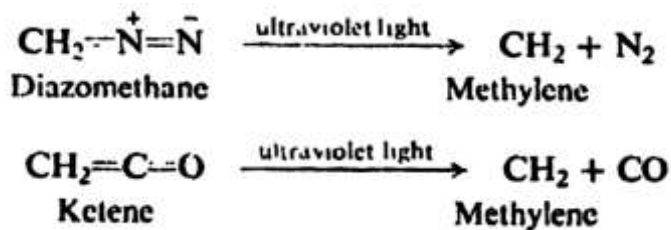


In each of these reactions a carbon-carbon bond is broken, and the two atoms of the reagent appear at the ends of the propane chain:

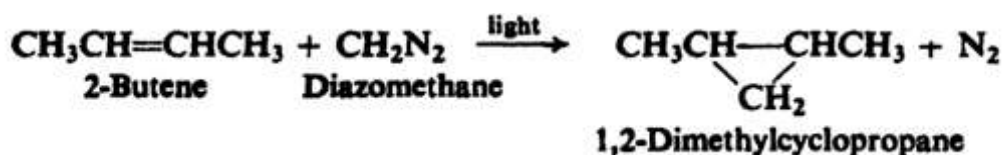


Carbenes. Methylene:

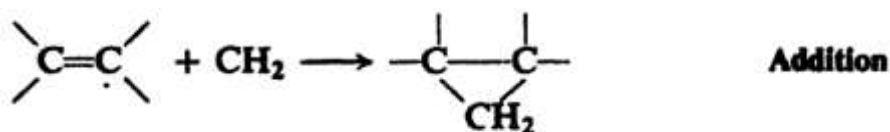
Methylene is formed by the photolysis of either diazomethane, CH_2N_2 , or ketene, $\text{CH}_2=\text{C}=\text{O}$.



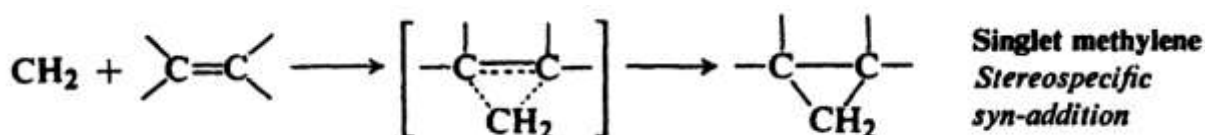
When methylene is generated in the presence of alkenes, there are obtained cyclopropanes. For example:



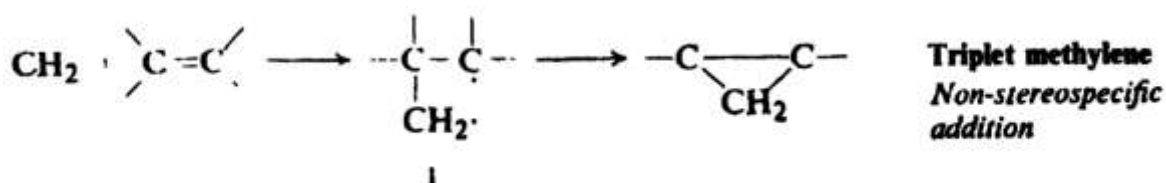
This is an example of the most important reaction of methylene and other carbenes: addition to the carbon-carbon double bond. Its most striking feature is that it can occur with two different kinds of stereochemistry.



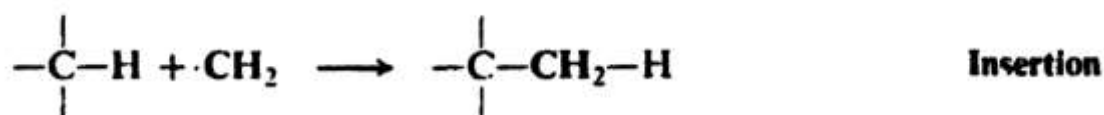
It is singlet methylene that undergoes the stereospecific addition.



It is triplet methylene that undergoes the non-stereospecific addition.

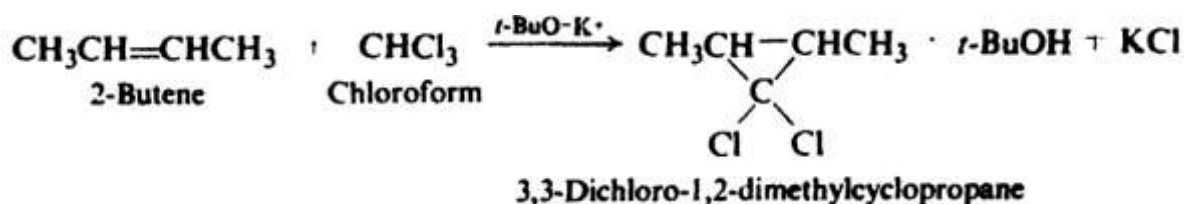


Besides addition, methylene undergoes another reaction which, quite literally, belongs in a class by itself: insertion.

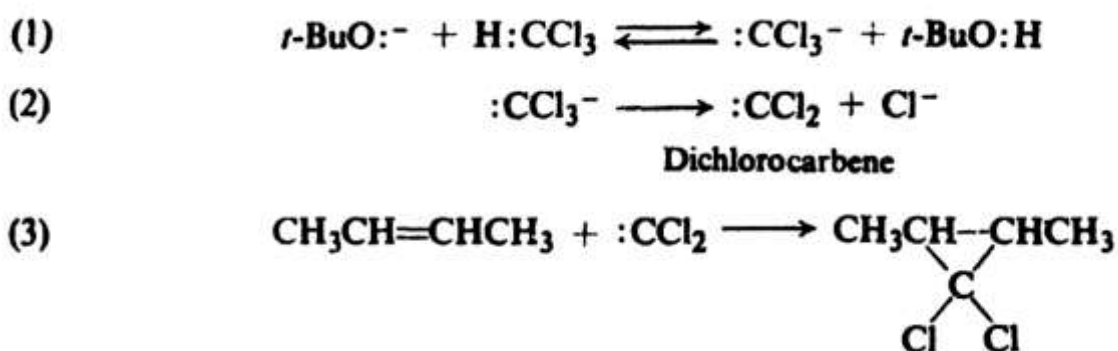


Substituted carbenes. α -Elimination:

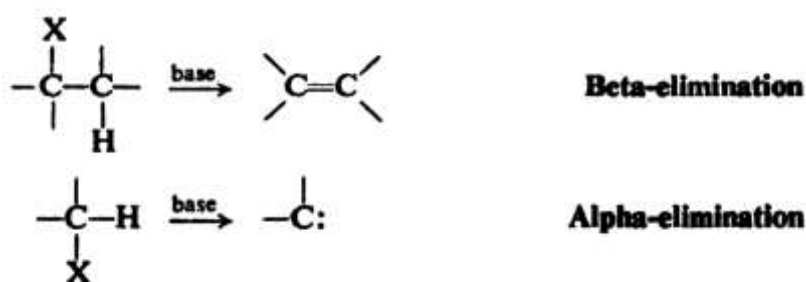
A more generally useful way of making cyclopropanes is illustrated by the reaction of 2-butene with chloroform in the presence of potassium tert-butoxide (t-Bu = tert-butyl):



Here, too, reaction involves a divalent carbon compound, a derivative of methylene: dichlorocarbene, CCl_2 . It is generated in two steps, initiated by attack on chloroform by the very strong base, tert-butoxide ion, and then adds to the alkene.



In dehydrohalogenation of alkyl halides, we have already encountered a reaction in which hydrogen ion and halide ion are eliminated from a molecule by the action of base; there -H and -X were lost from adjacent carbons, and so the process is called β -elimination.



In some cases, at least, it seems clear that no free carbene is actually an intermediate; instead, a carbenoid (carbene-like) reagent transfers a carbene unit directly to a double bond. For example, in the extremely useful Simmons-Smith reaction the carbenoid is an organozinc compound which delivers methylene stereo specifically to the double bond.

