Classifications and reactions involving carbon radicals

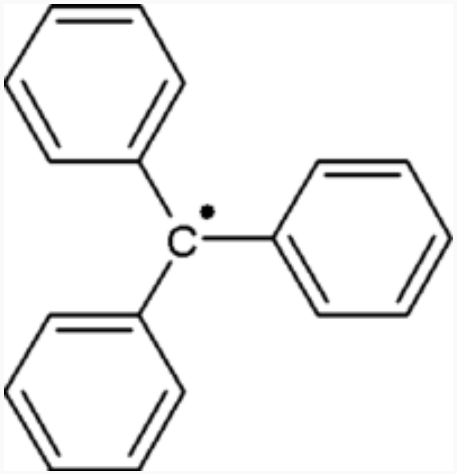
Key words: radicals, stability, addition, cyclization reactions, polymerization

Introduction

In this module an overview of carbon radicals are given. Some preliminary examples of their structure, properties and reactions are provided. Since this topic is expected to be part of physical organic and other domains, only a brief account is presented.

Carbon radicals

The first organic free radical identified was triphenylmethyl radical formed by abstraction of chlorine by silver metal .

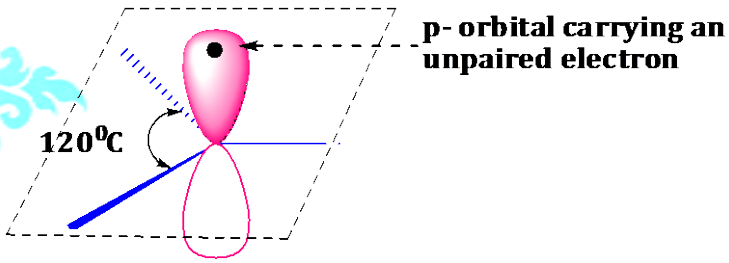


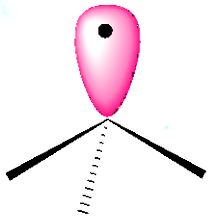
This species was discovered by Moses Gomberg in 1900 at the University of Michigan USA.

- A radical is a reactive intermediate with a single unpaired electron, having very short lifetime .
- Radical reaction are non-ionic reactions judged by the frontier molecular orbital approach (and not the nucleophilicity or electrophilicity concept).
- It is generated by homolysis of a covalent bond.
- Radial is represented by atom with one dot.
- Electronic movements involving radicals are represented using half headed fishhook arrows.
- Carbon radical is a neutral carbon species with three single bonds and one unpaired electron.

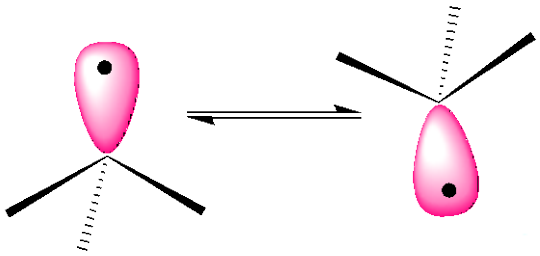
STRUCTURE OF RADICAL

- A carbon radical is *sp2* hybridized with an unpaired single electron occupying an unhybridised p-orbital, having trigonal pyramidal or planar geometry possessing an angle of 120^0.





sp_2 Hybridised carbon having rigid pyrimidal geometry.

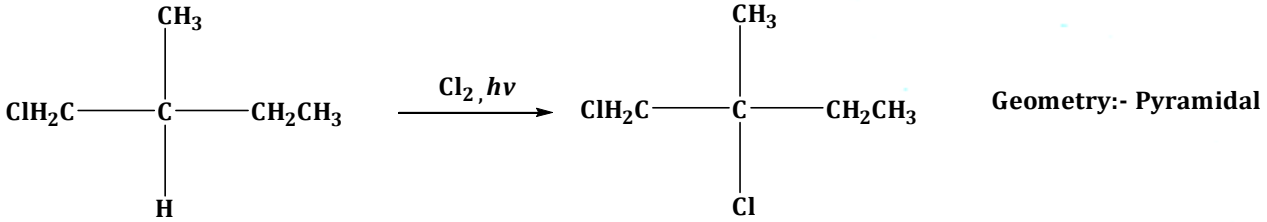


Flexible pyrimidal geometry

- In most of the cases the pyramidal geometry is observed, especially when heteroatom's are π electron donating substituent or electronegative groups like flourine or oxygen are present. However, some of the lower group of alkyl class like methyl posses planer geometry, t-butyl show pyramidal geometry with a slight characteristics of planer geometry.
- The energy required to invert the geometry is very low in the case of flexible pyramidal geometry.

Prediction of geometries.

- Geometries can be very well predicted from the product stereochemistry.
- Rigid pyramidal geometry of structure give product with retention of configuration .
- Planar or rapidly inverting radical will give racemerised product.
- Examples :-1.

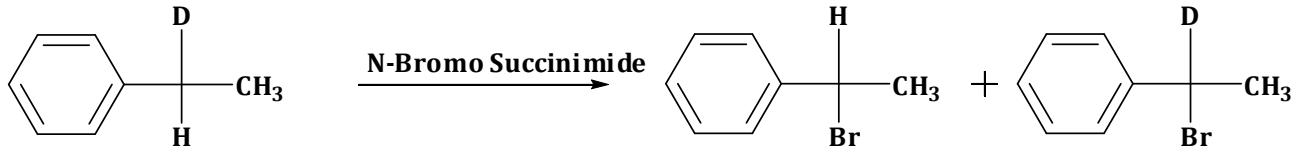


Geometry:- Pyramidal

(+)-1-Chloro-2-methyl butane.

(±)-1,2-dichloro-2-methyl butane.

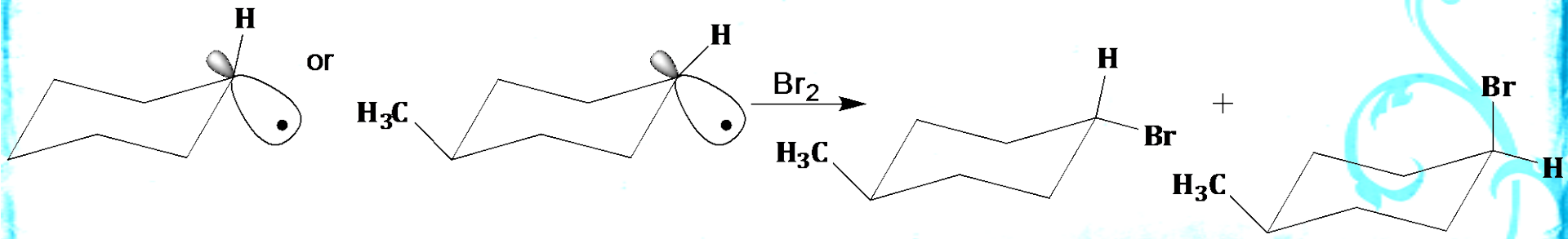
2.



99.7 % racemization

Geometry:- Pyramidal

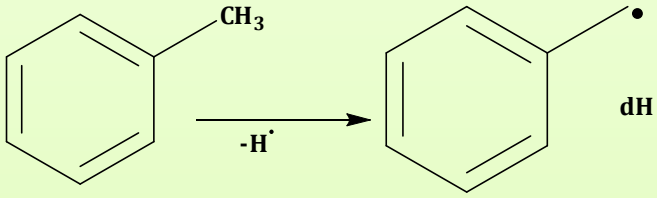
However in case of cyclic compound the stereochemistry is not retained. Cis and trans isomers both independently give cis or trans isomer .



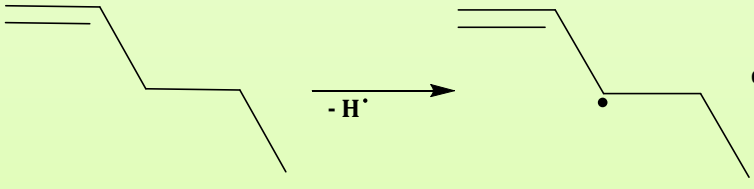
Stability of radical

Radicals are produced by heat or light or by the action of peroxide. Once a radical is produced, it will attack another species and would try to abstract a hydrogen radical or bind with another radical or with a π electron, forming σ bond in all the cases,
Radicals are formed when they are exposed to sufficiently high energy (in the form of heat or light) to break the bond between the two atoms.

The increased substitution will improve the stability of radical formed, and lesser will be the energy required for its formation.



dH = 355 kJ mol^{-1}



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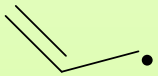
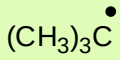
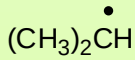


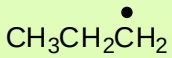
Allyl radical
dH= 369 kJ mol^{-1}



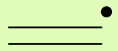
Tertiary
butyl radical
dH = 400 kJ mol^{-1}



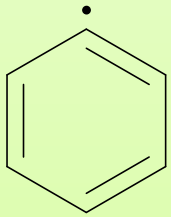
Secondary
radical
dH = 431 kJ mol^{-1}



Primary
radical
dH = 423 kJ mol^{-1}



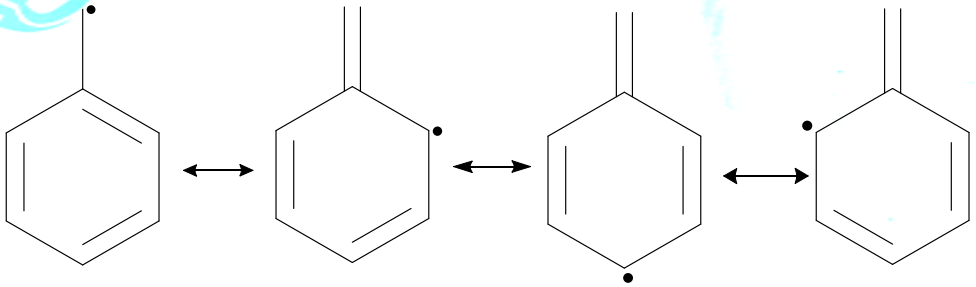
Vinyl
radical
dH = 465 kJ mol^{-1}

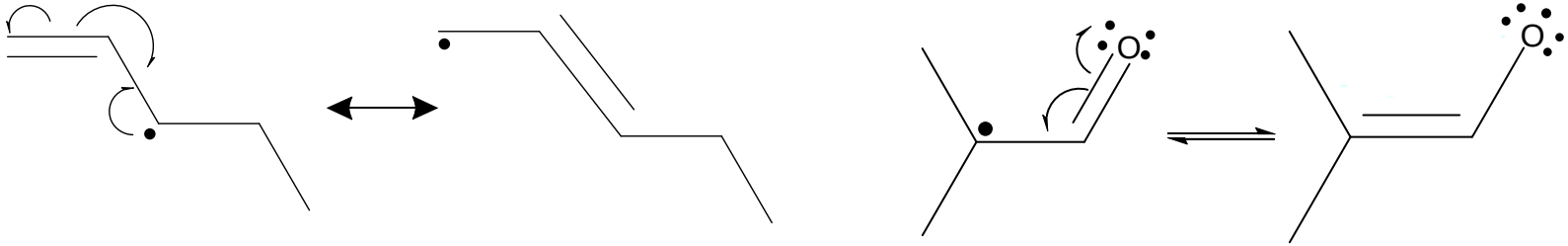


dH = 460.55 kJ mol^{-1}

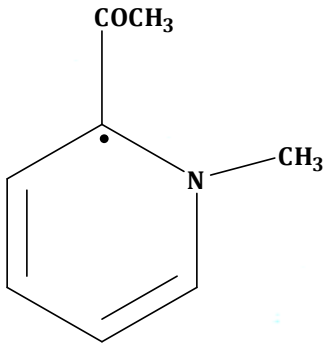
Hence stability decreases form allylic and benzylic radical to vinylic and phenyl radical.

- The higher stability of radical in the case of benzyl and allyl through resonance stabilization. This type of stabilization is not present in case of phenyl or vinyl radical.

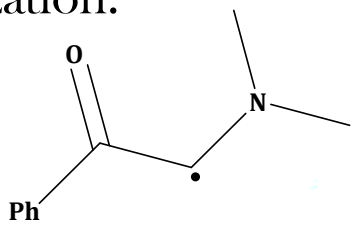




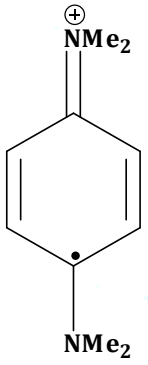
- When both electron donating and withdrawing groups are present in the same molecule, with a suitable separation between them, it can provide additional stabilization know as capto-dative stabilization.



J.Hermolin , M. Levin, JAC 1991 103: 4795



F. M. Welle , H.D. Beckhaus & G.Ruchardt
liebigs Ann 1997: 155



Wruster's salt

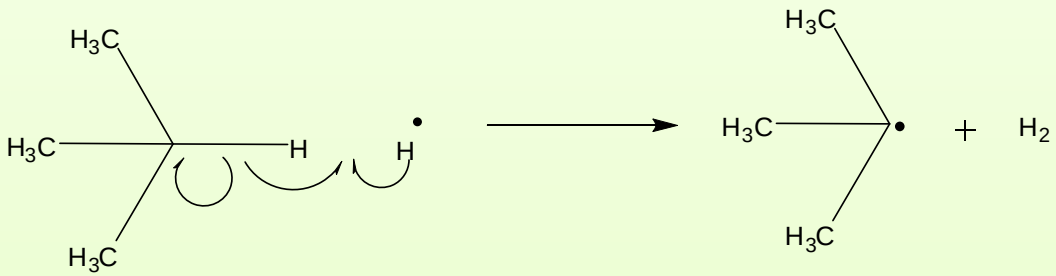
Carbocation

- Carbocation are electron deficient species with 6 electrons accounting for a lower stability and higher energy state.
- The stability is supported by alkyl group, pi bonding electron or lone pair .
- In a chemical reaction when carbocation MO or AOs interact with filled MO or AOs the electrons are placed in lower energy bonding orbital .

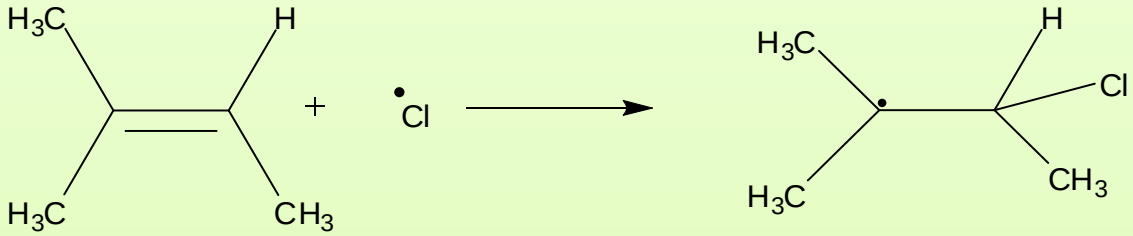
Radical

- Radicals posses 7 electrons with a better stability due to lesser energy compared with carbocation hence lower member of radical are existent.
- Stability resulting from alkyl pi bonding or lone pair is relatively negligible, however there is assisted stability in case of benzylic radical.
- When a radical interact the two electrons are placed one in lower energy and one in higher energy antibonding orbital.

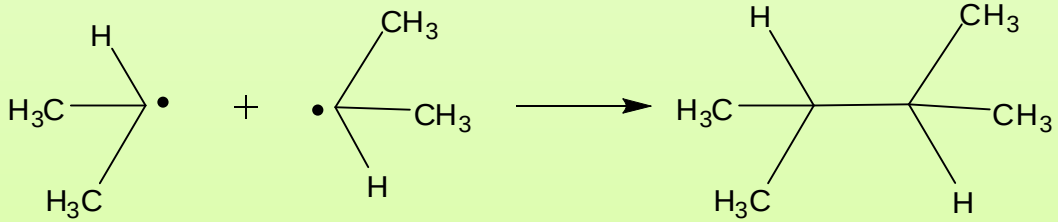
- **Reactions of free radicals**
- Consider a radical **R** undergoing a reaction.



- The addition to alkene result in radical initiation step where the molecule of reactant alkene form a radical which then attack another similar molecule resulting in a polymer.



- Radical combination leading to termination



Classification of radical reactions

- Radical are generally very reactive species with a short lifetime. If the reaction rate can be controlled, selectivity of radical reactions can be improved. Radicals can undergo,

1. **Substitution**
2. **Addition**
3. **Rearrangement**
4. **Auto-oxidation**
5. **Single electron transfer (SET).**

Substitution Reactions: This radical reaction involves substitution of smaller molecules, (e.g., chlorination of methane). The reaction function as a chain substitution reaction

•This radical reaction involve substitution of smaller molecules , the well known evident reaction is chlorination of methane. The reaction function as a chain substitution reaction.