

Carbenes – Generation, Structure, Stability, and Reactions

1. Introduction

Carbenes are divalent carbon intermediates containing a carbon atom with only six valence electrons and two unshared electrons. They are highly reactive and play an important role in many organic reactions, especially in cyclopropanation, rearrangements, and insertions.

2. Structure of Carbenes

Carbenes are represented by the general formula :CH_2 or $\text{R}_2\text{C:}$. They exist in two spin states:

(a) Singlet Carbene

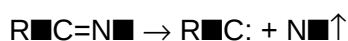
Both nonbonding electrons are paired in the same orbital. The carbon is sp^2 hybridized with a bent geometry (bond angle $\approx 103^\circ$). One empty p-orbital is perpendicular to the plane. Electrophilic in nature. Example: Dichlorocarbene (:CCl_2).

(b) Triplet Carbene

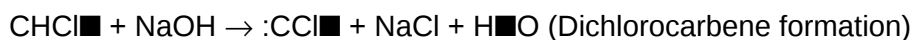
The two nonbonding electrons are unpaired and occupy different orbitals. The carbon is sp hybridized with a linear or nearly linear geometry. Paramagnetic in nature and nucleophilic in character. Example: Methylene (:CH_2) in the gas phase.

3. Methods of Generation of Carbenes

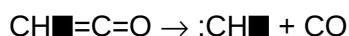
(a) Photolysis or Thermolysis of Diazocompounds



(b) α -Elimination Reactions



(c) Decomposition of Ketene



(d) Metal–Carbene Complex Formation

Transition metals (Cr, Fe, Mo) stabilize carbenes as Fischer or Schrock complexes depending on substituents.

4. Stability of Carbenes

Carbenes are short-lived intermediates. Their stability depends on substituents and spin state.

(a) Nature of Substituents: EDGs stabilize carbenes by +I effect and hyperconjugation; EWGs stabilize singlet carbenes by delocalization.

(b) Type of Carbene: Triplet carbenes are generally more stable than singlet carbenes.

5. Reactions of Carbenes

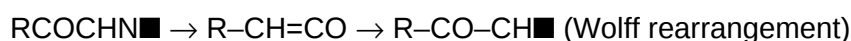
(a) Addition to Alkenes (Cyclopropanation)



(b) Insertion Reactions



(c) Rearrangement Reactions



(d) Metal–Carbene Complexes

Carbenes react with transition metals forming metal–carbene complexes (e.g., olefin metathesis).

6. Example: Dichlorocarbene (:CCl₂)

Generated from chloroform and base. Exists as singlet carbene. Reacts with alkenes to form gem-dichlorocyclopropanes.



Property	Singlet Carbene	Triplet Carbene
Electron pairing	Paired	Unpaired
Geometry	Bent (sp ²)	Linear (sp)
Magnetic property	Diamagnetic	Paramagnetic
Reactivity	Electrophilic	Nucleophilic
Stability	Less stable (except with EWGs)	More stable
Example	:CCl ₂	:CH ₂ (gas phase)

7. Applications

- Synthesis of cyclopropane derivatives
- Formation of organometallic complexes

- Wolff rearrangement in synthesis of carboxylic acids
- Insertion reactions in pharmaceutical intermediates

Suggested Readings

1. S. M. Mukherjee and S. P. Singh – Reaction Mechanism in Organic Chemistry
2. Morrison and Boyd – Organic Chemistry
3. I. L. Finar – Organic Chemistry, Vol. I
4. Graham Solomons – Organic Chemistry