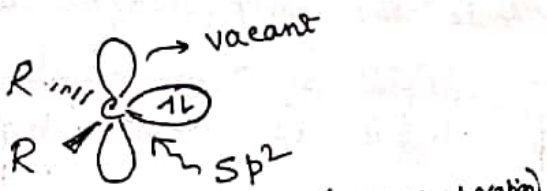
:CARBENES:

H_2C: Methylenes (simple carbene)
R_2C: Dialkyl carbene
Ph_2C: Diphenyl carbene

Carbenes are neutral bivalent carbon intermediates in which a carbon atom is covalently bonded to two atoms or groups of atoms and has two non-bonding orbitals containing two electrons between them. When the two electrons are spin paired the carbene is a singlet (spin multiplicity, M=1), if the spins of the electrons are parallel it is a triplet (spin multiplicity, M = 3).

Structure: A singlet carbene is thought to possess a bent sp^2 hybrid structure in which the paired electrons occupy the vacant sp^2 orbital.



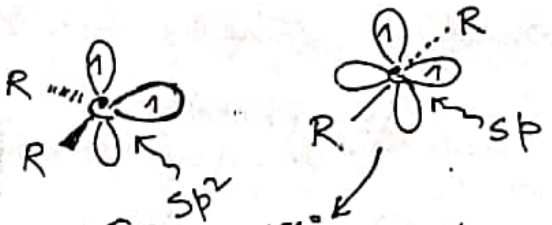
Singlet Carbene (like carbocation)

$[M = 2S+1 = 2(\frac{1}{2}-\frac{1}{2})+1 = 1]$

$R\widehat{-C}-R \simeq (100-110^\circ)$

A distorted triangular planar str.

$H\widehat{-C}-H \times 103^\circ$



$R\widehat{-C}-R \simeq 130-150^\circ$

Triplet Carbene (diradical)

$[M = 2S+1 = 2(\frac{1}{2}+\frac{1}{2})+1 = 3]$

A triplet carbene can be either bent sp^2 hybrid with an electron in each unoccupied orbital, or a linear sp hybrid with an electron in each unoccupied

The existence of two spin states of carbenes has been confirmed by ESR spectroscopy.

A singlet carbene is usually generated in the liquid phase in situ i.e within the reaction medium where carbene is to be reacted with other reagents, by α-elimination and by thermolysis or photolysis.

By the same methods, thermolysis and photolysis, triplet carbenes are formed in the gas phase in the presence of an inert gas like nitrogen, argon etc. which act as a sensitizer. Through collision between the singlet carbene, which form first and the inert gas molecule, triplet carbenes, the ground state carbenes are generated.

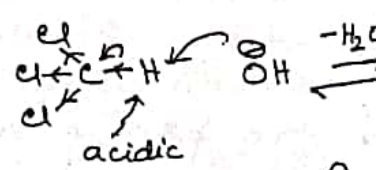
p-orbitals.

Just after generation of carbenes from ch
cal reactions it is in singlet state. e.g :CH_2, :CCl_2;
carbenes with conjugated π-electrons or when gener
in presence of an inert gas ($^-N_2$/Ar), it is trans
med into a stable triplet state. e.g. :CPh_2,

Generation:

(i) By base catalysed α-elimination reaction.

$$CHCl_3 \underset{}{\overset{\ominus OH/\Delta}{\rightleftharpoons}} Cl_3C^{\ominus} \longrightarrow Cl_2C:$$

Mech: 


dichloro carbene.

N.B: A strong organic base can be used instead
water soluble base for the above reaction, be
the protic solvent water generate H^+ that hinder
the generation of carbene by entering into the
position of leaving H^+ ion. Organic base rais
rise the concentration of H^+ in the reaction
medium, thereby facilitate the formation of carb

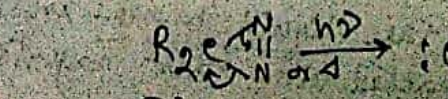
(ii) Photolysis or pyrolysis of compoun
having certain type of double bond

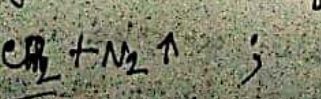
$$CH_2=C=O \xrightarrow{h\nu} :CH_2 + CO$$
(Ketene)

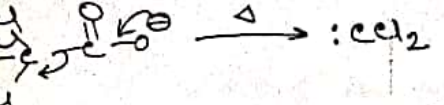
$$CH_2=\overset{\oplus}{N}=\overset{\ominus}{N} \xrightarrow[\text{or } \Delta]{h\nu} :CH_2 + N_2$$
(Diazomethane)

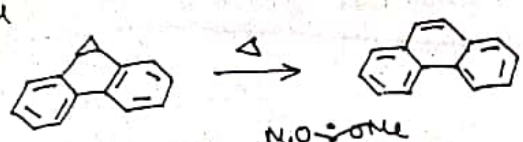
$$\overset{\ominus}{C}H(CO_2Et)-\overset{+}{N}\equiv N \xrightarrow{h\nu \text{ or } \Delta} :CH-CO_2Et + N_2$$
(Diazoacetic ester)

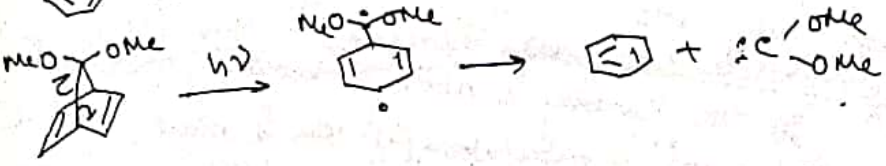
(iii) Three membered ring compounds having oxy
or nitrogen on photolysis yields carbene


Diazirine


oxirane

(IV) 

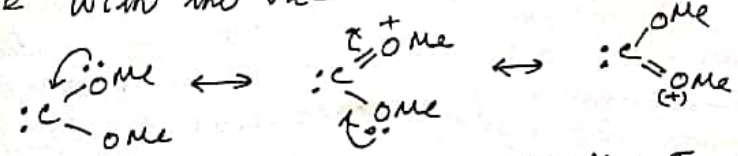
(V) 

(VI) 

Stability :

Carbenes are very unstable (lifetime less than one second) reactive intermediate.

When carbene carbon is attached with an atom or groups with donatable non-bonding electron pair or conjugated π-electrons. The stability of carbene increases. Thus $Ph_2C:$, $:C(\ddot{N}R_2)_2$ & $:C(\ddot{O}Me)_2$ are stabler forms of carbene. Here lone pair (from $\ddot{N}/\ddot{O}$) or π bonded electron can conjugate with the vacant orbitals of carbene carbon.



N·B: (i) Due to above type of conjugation the electron deficiency of the carbene carbon decreases, hence dimethoxy carbene becomes inert towards addition reaction with alkene / alkyne. This is called inert carbene.

(ii) Triplet carbene is more stable than singlet carbene. The repulsion energy between the two electrons in same orbital in singlet carbene is higher than the pairing stabilisation energy due to pairing of two e's in the same hybrid orbital. As a result, a singlet carbene will converted to a triplet one. by breaking the pair and passing one electron to another orbital. (ISC)

[Q] Why dimethoxy carbene is inert towards alkene.

[Q] Diphenyl carbene in singlet state is less stable than triplet state - Explain

N·B: Stability of halocarbenes is in the order -

$:CF_2 > :CCl_2 > :CBr_2 > :CI_2 >> :CH_2$

Since the +R effects of the halogens lie in the order F > Cl > Br > I

The singlet carbene can act as a lewis base by donating its non-bonding electron pair and at the same time it can act also as a lewis acid by using its vacant p-orbital. In fact, singlet carbene can act as a π-acid ligand and it can introduce a metal-carbon double bond character in the carbene complexes.

⊛ Electrophilic carbene:

If the carbene carbon is bonded with strong electron withdrawing groups/atoms (-I) then it react with electron rich alkenes like Ketene, cyclohexene etc. Such type of carbene is called electrophilic carbene.

e.g. $:CCl_2$, $:CF_2$, $:CClF$ etc.

⊛ Nucleophilic carbene: If the carbene carbon is bonded with +I / +R groups, so that the p-orbital is no longer vacant, & behaves as donor carbene. Such type of carbene is called nucleophilic carbene.

e.g $:C(OMe)_2$, $:CPh_2$  etc.

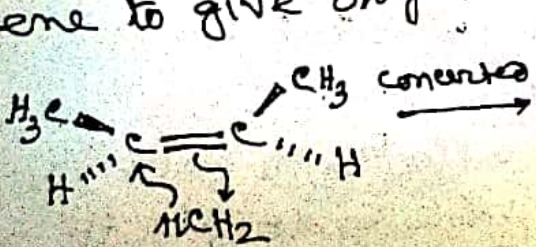
Reactions: carbene undergo four types of reactions.

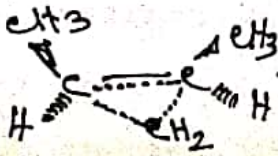
(i) Cycloaddition with an alkene
(ii) Insertion into a σ bond.
(iii) Rearrangements
(iv) Reaction with nucleophiles.

(i) **Cycloaddition with an alkene:**

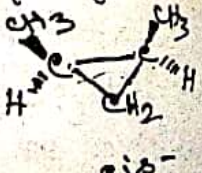
Whether a carbene is singlet or triplet can be determine by its reaction with cis / trans alkene. Both types of carbene adds to alkene to give cyclopropane ~~intermediates~~ derivatives, but show characteristic difference in stereochemistry.

The addition of a singlet carbene to an alkene is an one step concerted process (unshared electron pair in carbene is in favourable spin for simultaneous formation of two σ-bond), therefore the addition is stereospecific and syn. Thus singlet carbene reacts with cis-2-butene to give only cis-1,2-dimethyl cyclopropane and with trans-2-butene to give only trans-1,2-dimethyl cyclopropane.

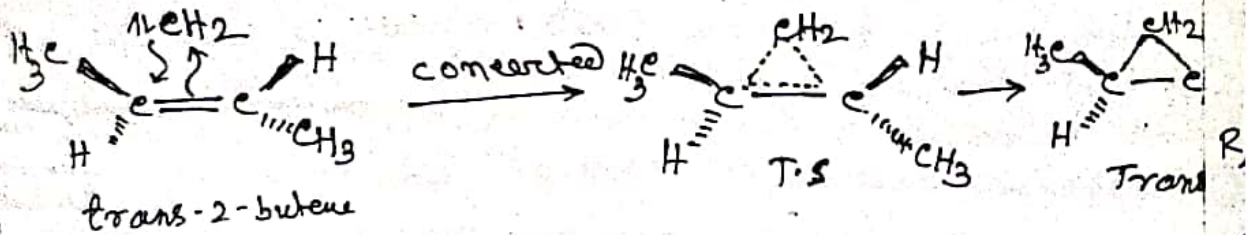




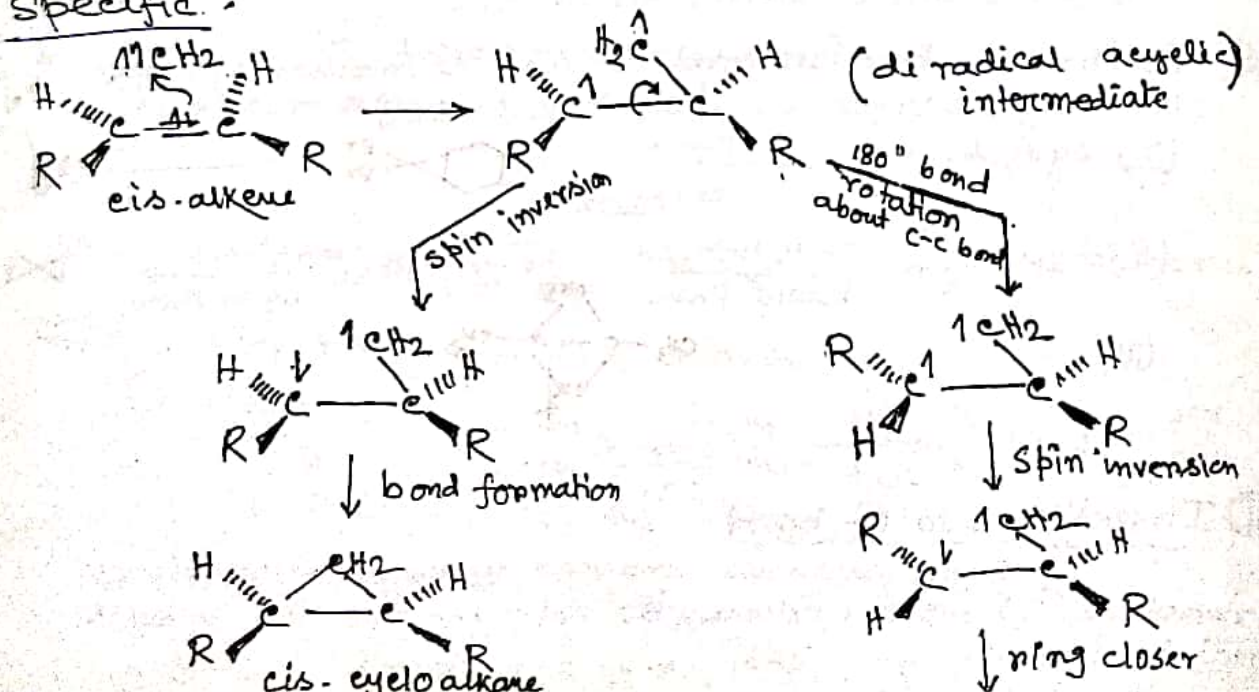
cyclic T.S



cis-1,2-dimethyl cyclopropane



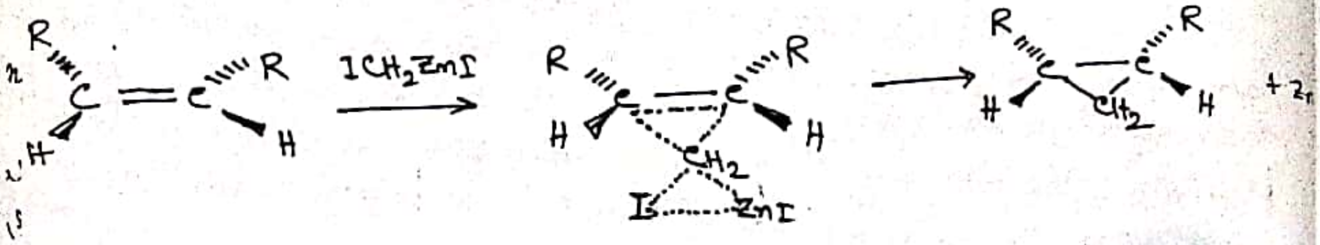
Triplet carbene behaves as a diradical as two unpaired electrons in two separate orbitals having same spin. Therefore it adds to the C–C double bond by two step pathway involving free radical intermediate. (there is a spin restriction for concerted reaction). In the first step, one of the unpaired electrons forms a σ-bond with that π electron which has the opposite spin and results in formation of a diradical. For cyclisation of the diradical spin inversion of one of the electron is required. The diradical undergo spin inversion by some appropriate collisions and then collapse to cyclic product. (only stereoisomer). If before spin inversion of the electron in the diradical, bond rotation takes place, then the other stereoisomeric product is produced with equal probabilities. The reaction is therefore nonstereospecific.



* Trans alkene, by a similar process, gives a mixture of cis and trans cyclopropane derivative

However, in Simmons-Smith reaction a carbene is not directly generated but the reaction proceeds through a carbenoid species (an organozinc compound), adds to alkene. The reaction is stereoselective as well as stereospecific. cyclopropane derivative

$$CH_2I_2 + Zn(Cu) \longrightarrow ICH_2ZnI$$



[Q:] Discuss the outcome of the reactions of singlet and triplet carbene separately with cis-2-butene
C-03

[Q] Reaction of trans-2-butene with methylene obtained from diazomethane occurs in stereospecific manner. What happens when the above reaction is carried out in the presence of nitrogen? Explain.
C-98

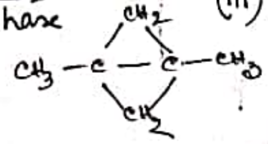
[Q] What are singlet and triplet carbene? Triplet carbene add to E or Z-alkene with loss of stereochemical integrity. Explain with suitable example.
V-00

[Q] Give one example for each of the following:
V-01
(i) Generation of carbene from a neutral molecule.
(ii) Electrophilic behaviour of carbene.

[Q] Predict the product and discuss the mechanism involved in each of the following transformations:-

(i) cyclohexene $\xrightarrow[\text{or } Br_3CH / tBuOK]{CBr_4 / CH_3Li}$

(ii) 2-Butyne $\xrightarrow[\text{Liquid Phase}]{CH_2N_2 / h\nu}$



(iii) Allene $\xrightarrow[\text{Liquid Phase}]{CH_2N_2 / h\nu}$

(iv)

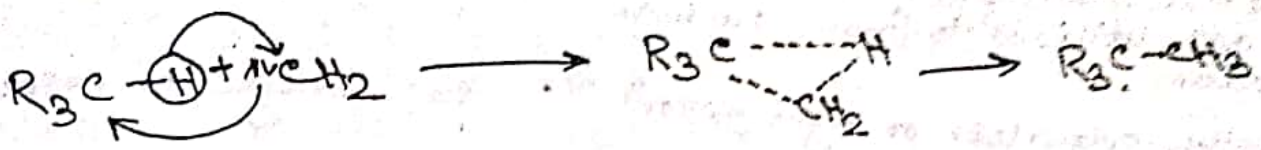
(II) Insertion into σ-bond:

Singlet carbenes undergo unusual insertion reactions but triplet carbenes do not; the reaction occurs mainly in C–H, O–H, C–Cl, N–H, D–H bonds but does not at all occur in a C–C bond. e.g.

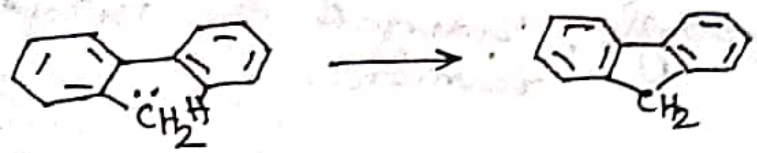
$$3H-CH_2-\overset{O-H}{\underset{CH_3}{C}}-H + 3:CH_2 \longrightarrow CH_3-CH_2-\overset{OH}{\underset{CH_3}{C}}-H + CH_3-\overset{OCH_3}{\underset{CH_3}{C}}-H + CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_3$$

Insertion to all primary, secondary and tertiary C-H bonds are possible. But the rate and also the degree of insertion is p-> s-> t. C-H bond. (Insertion ratio p:s:t = 60:24:16)

Mechanism of insertion:



cyclic T.S

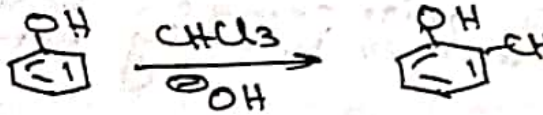


(III) Rearrangements: (Wolf rearrangement)

See rearrangement.

(IV) Reaction with nucleophile:

$R_2C: + R'-OH \longrightarrow R'O-CH(R)(R)$



(Reimer-Tiemann rxn)

[Q] Outline the following conversion:

03 (i) Tetramethylethylene → Tetramethyl allene.

(ii)

Hints (i) $Me_2C=CMe_2 \xrightarrow[aq.\ NaOH]{CHBr_3} Me_2C(CBr_2)-CMe_2 \xrightarrow[ether]{Mg} Me_2C=C=CMe_2$

Mech: $CHBr_3 + NaOH \longrightarrow :CBr_2 + NaBr.$