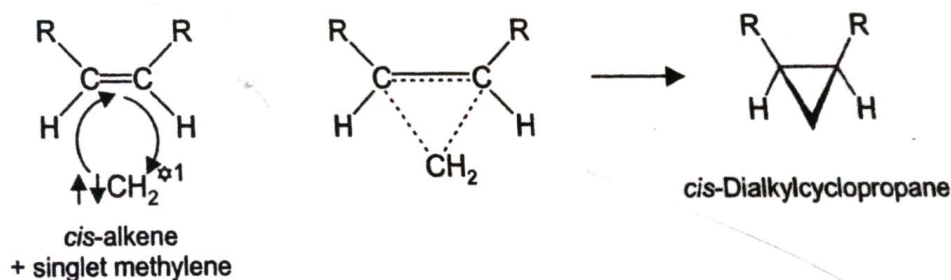


Hg<sup>+</sup>  
Dissociation of mercury from  
the carbocation liberates the  
catalyst and the enol

SCHEME 11.12

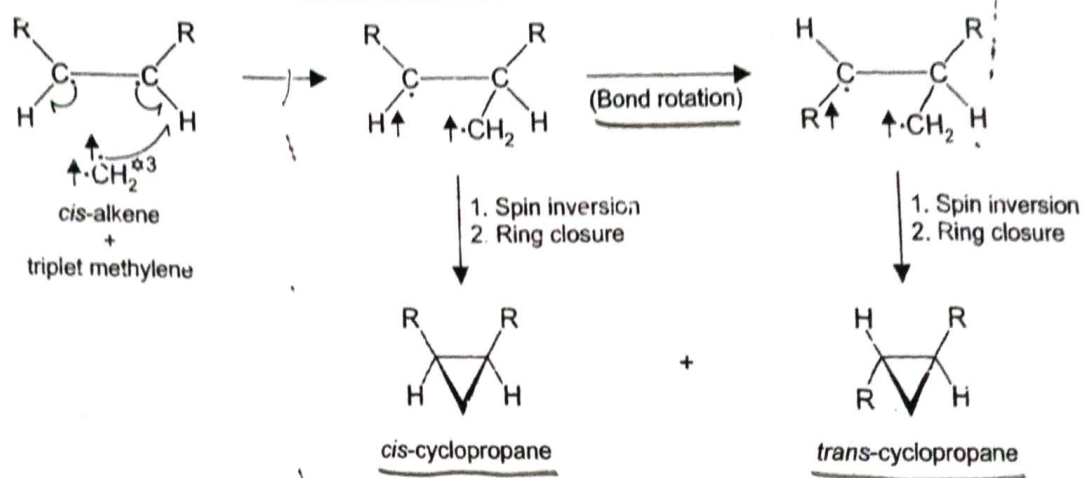
### 11.3 ADDITION OF CARBENES

Carbenes add to alkenes to give cyclopropane derivatives. Singlet methylene *e.g.*, reacts with an alkene is stereospecifically, the addition occurs in one step (concerted addition) and the stereochemistry of the alkene is preserved in the product (Scheme 11.13). The electrons in the



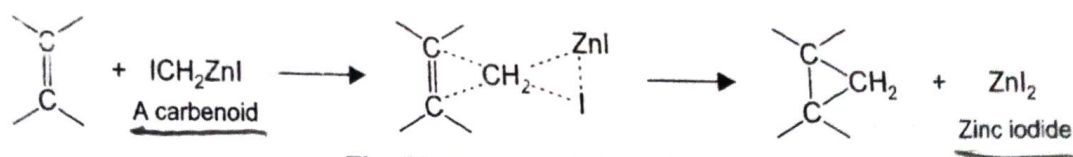
SCHEME 11.13

triplet methylene are not paired and consequently it reacts with an alkene in a stepwise process (Scheme 11.13a). The initial reaction is the formation of a biradical and this has sufficient lifetime to allow rotation. The addition is therefore, non stereospecific.



SCHEME 11.13a

Carbene addition to a double bond is complicated due to too many side products. The Simmons-Smith procedure is superior and leads to same results. The reaction involves reaction of a double bond compound with diiodomethane ( $\text{CH}_2\text{I}_2$ ) and a Zn-Cu couple, the attacking species is an organozinc intermediate ( $\text{ICH}_2\text{ZnI}$ ), a carbene like species called a carbenoid (Scheme 11.13b).



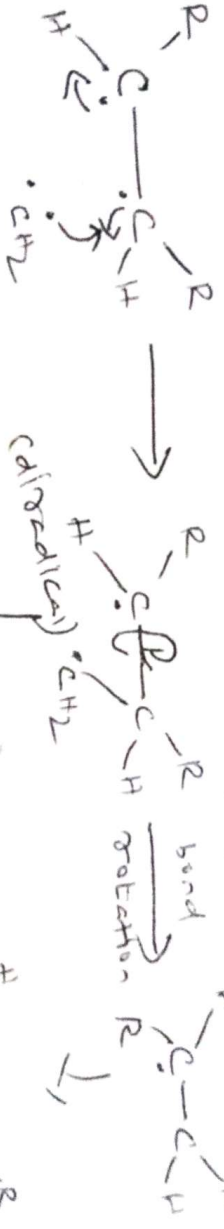
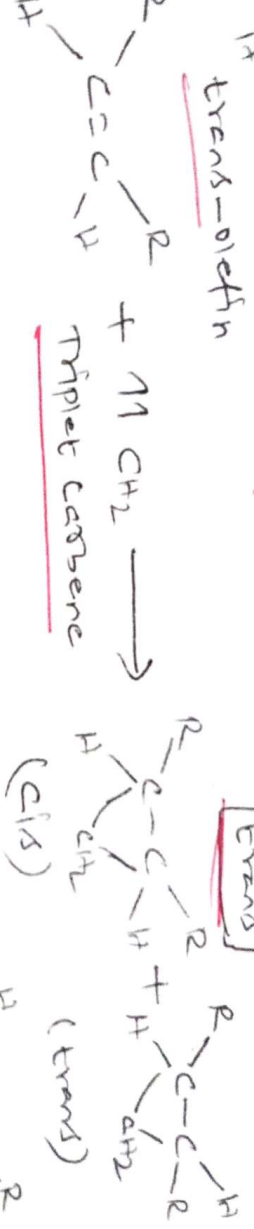
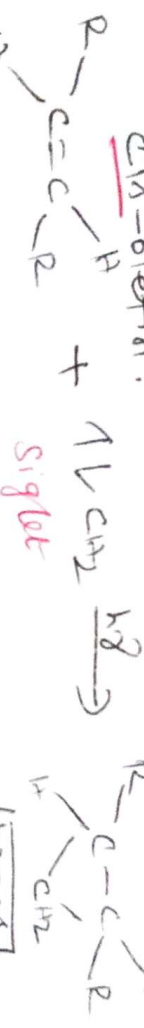
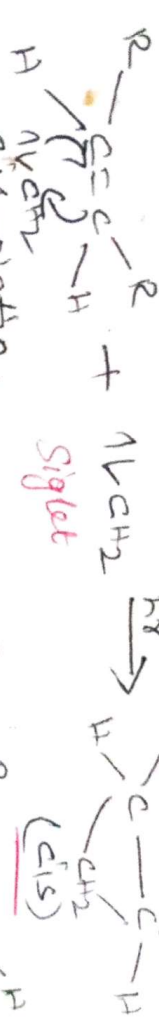
The Simmons-Smith synthesis

SCHEME 11.13b

Reactions of Carbenes :- [4 important reactions]

1) Addition of olefins :-

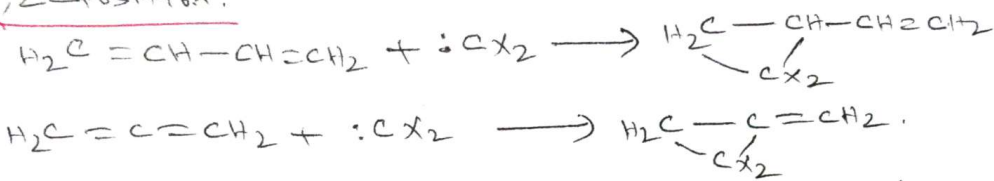
Reaction of an alkene with a single methylene is stereospecific, while with a triplet methylene it is non stereospecific.



selective (cis) non-stereospecific

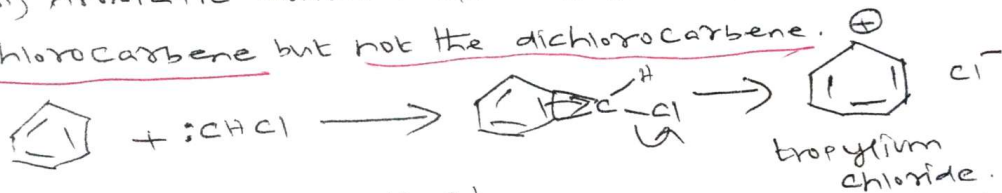
stereospecific

(ii) In case of conjugated (or) cumulative double bond systems, carbenes always add exclusively in 1,2-position.



Carbene + alkenes  
↓  
add only 1,2 position

(iii) Aromatic double bonds add the more reactive chlorocarbene but not the dichlorocarbene.



(B) Ring expansion reactions:- These involve the addition of a halogenocarbene across a double bond followed by rearrangement.

