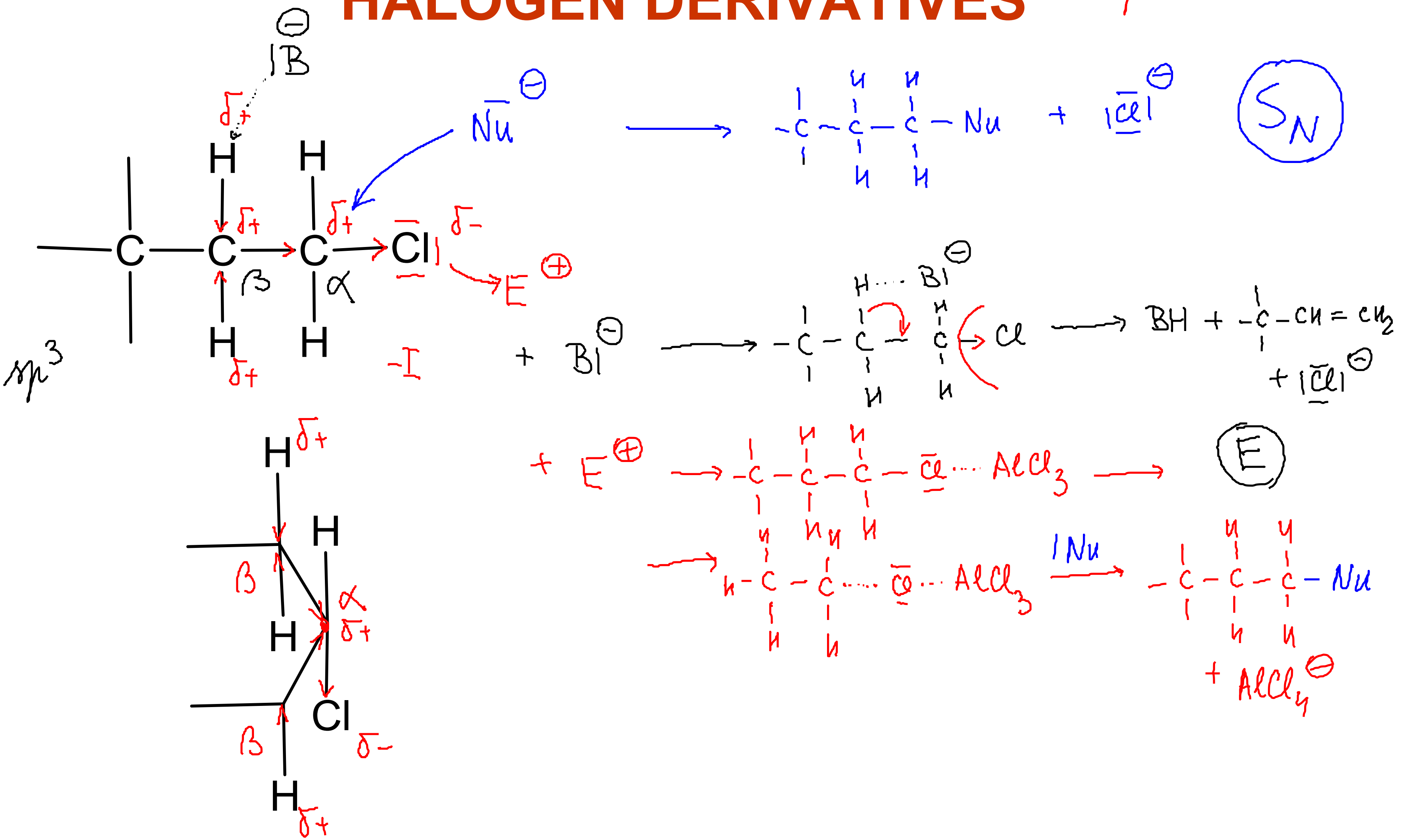
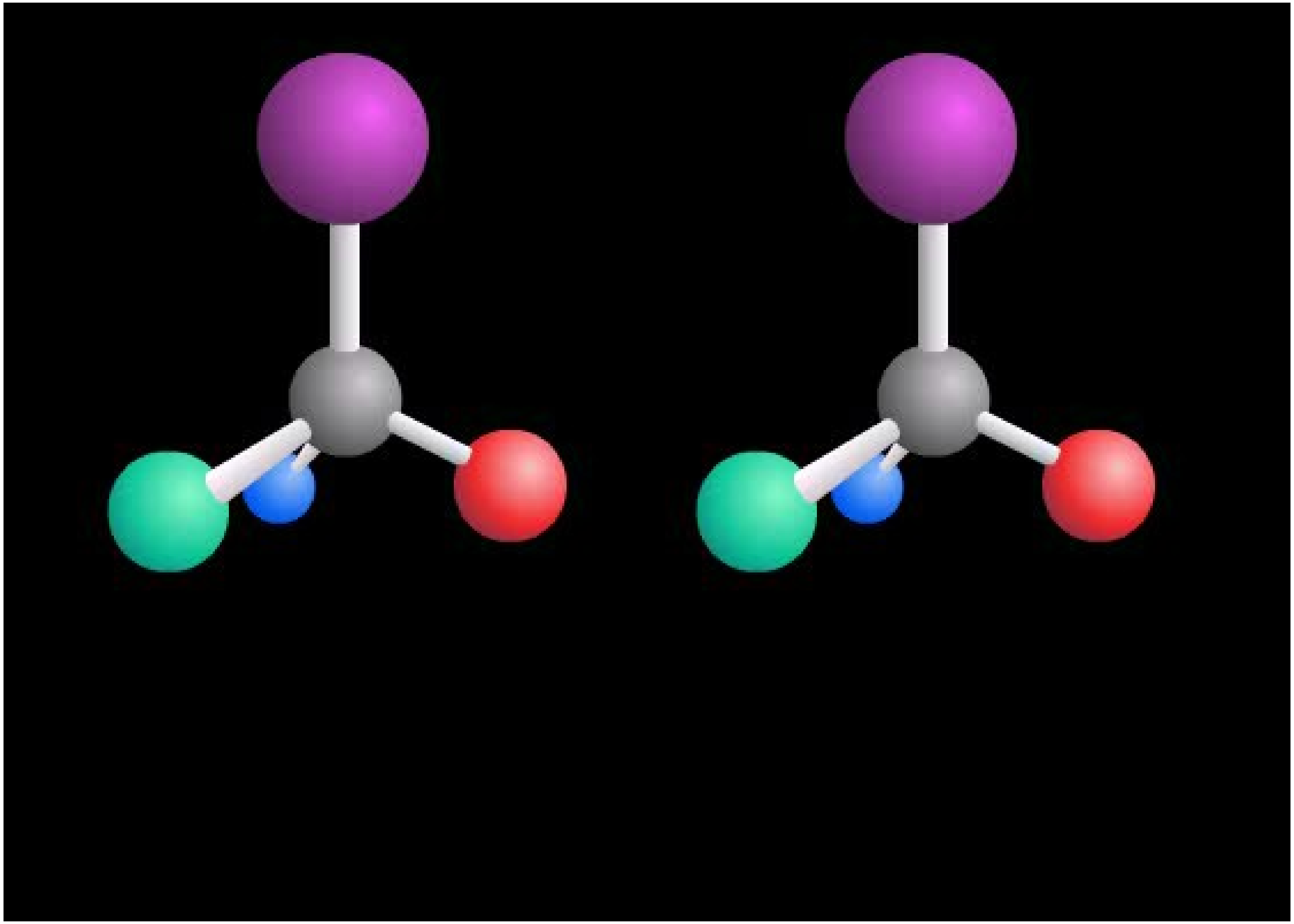
HALOGEN DERIVATIVES

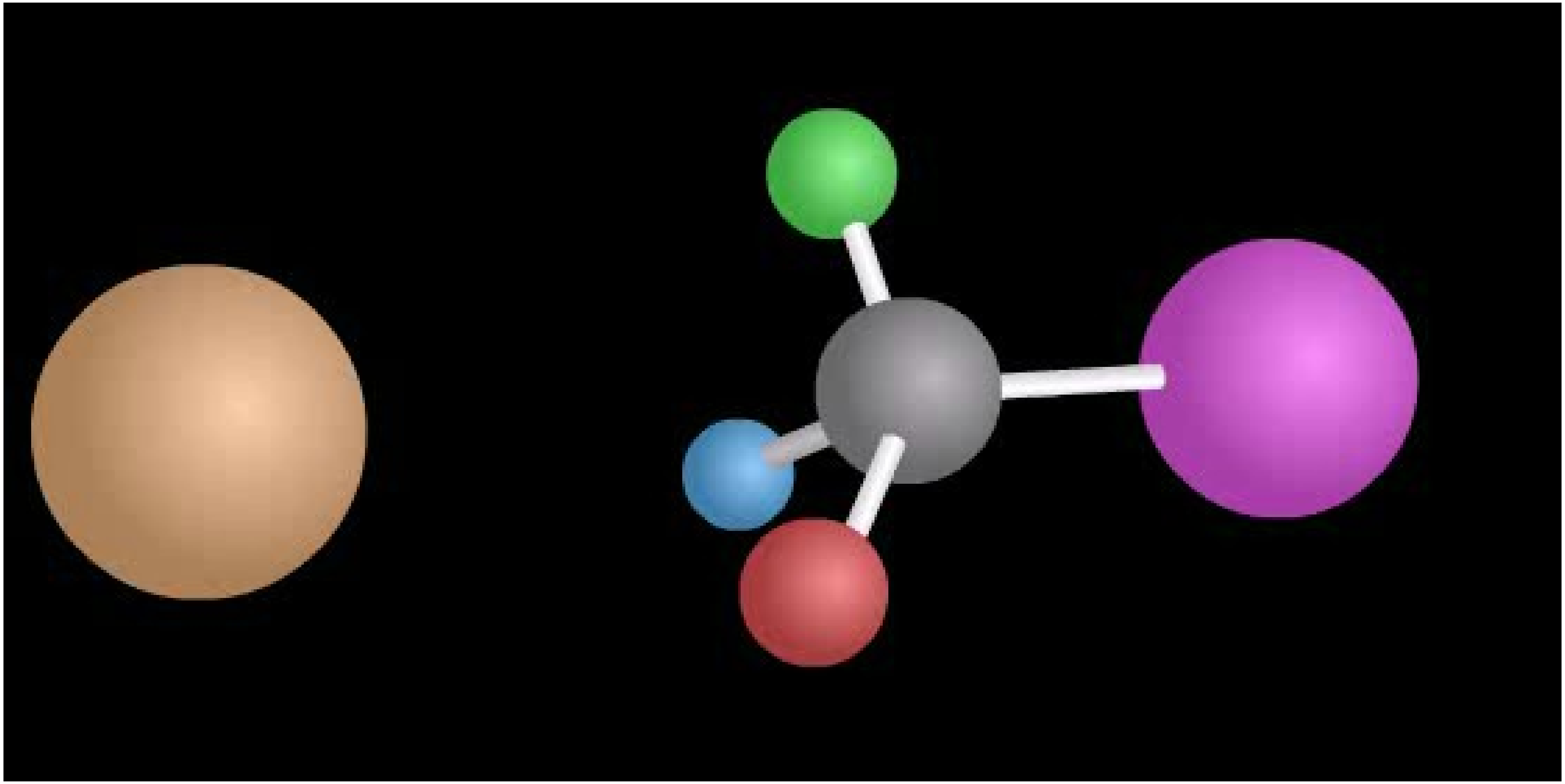
C_{sp^3}



S_N1 substitution

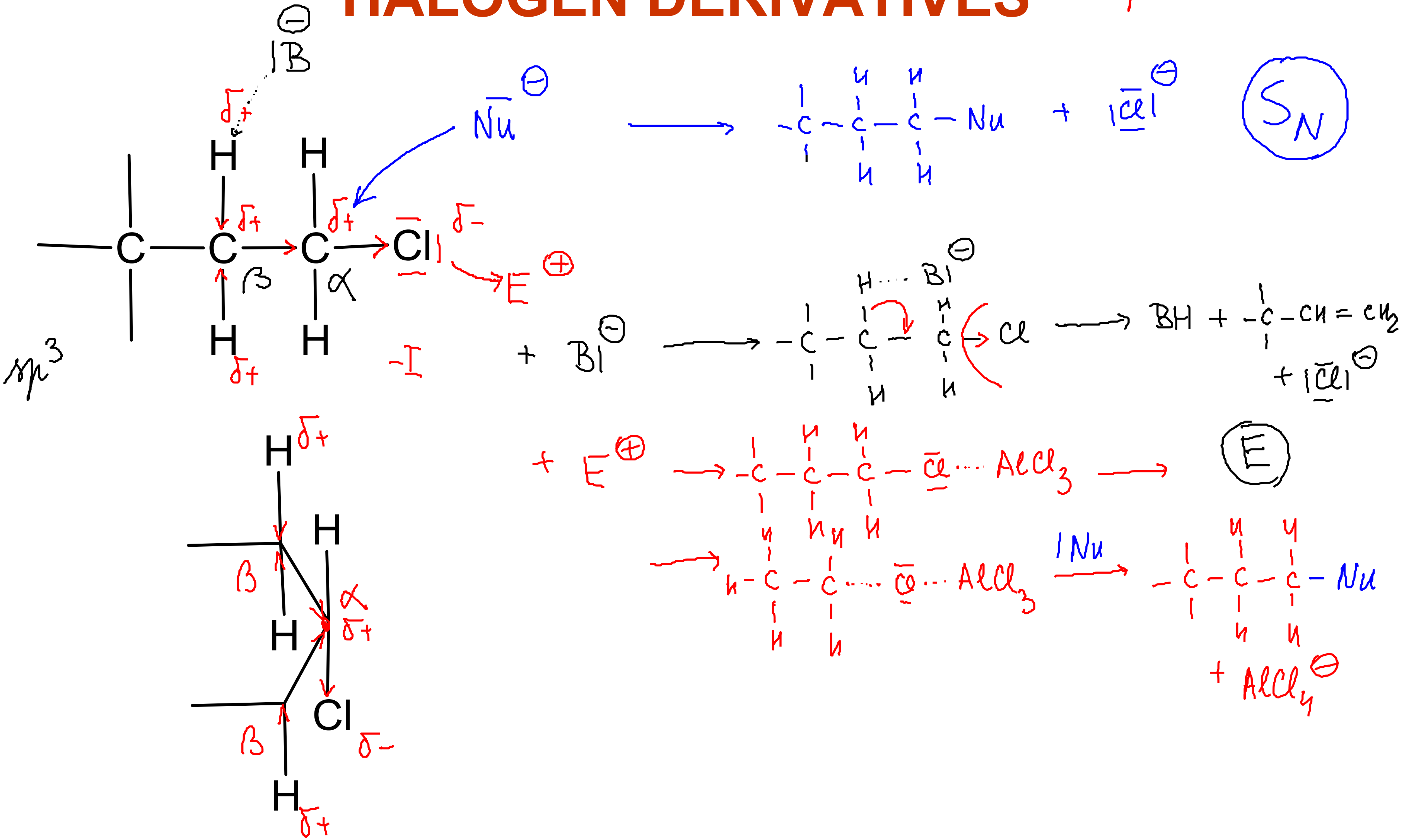


S_N2 substitution

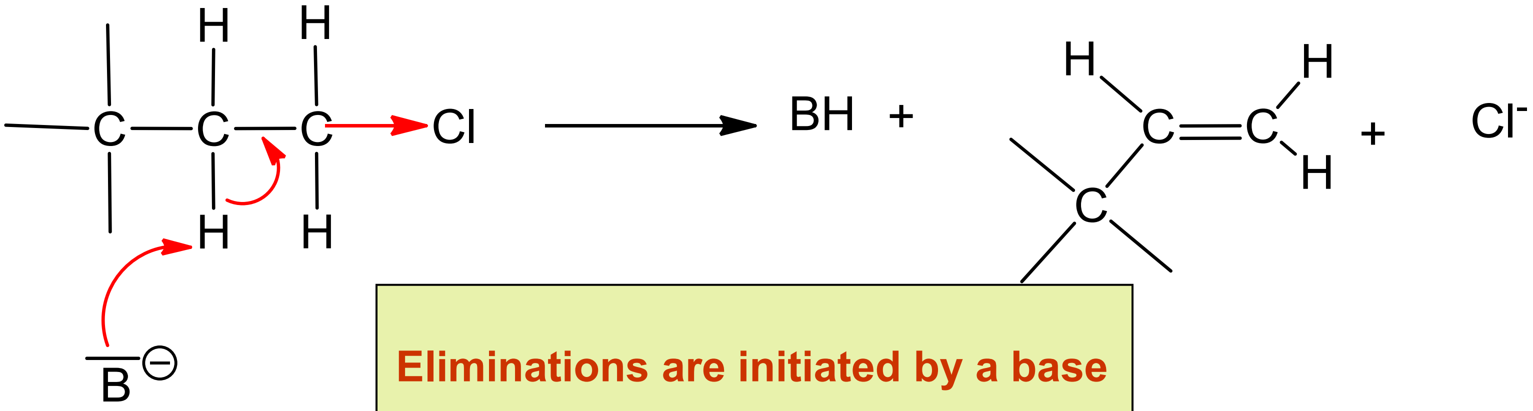


HALOGEN DERIVATIVES

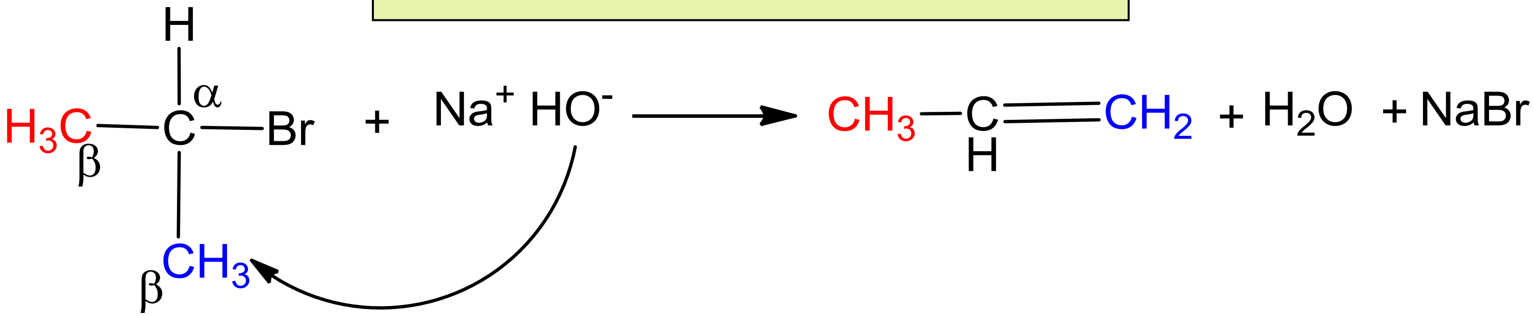
C_{sp^3}



Elimination



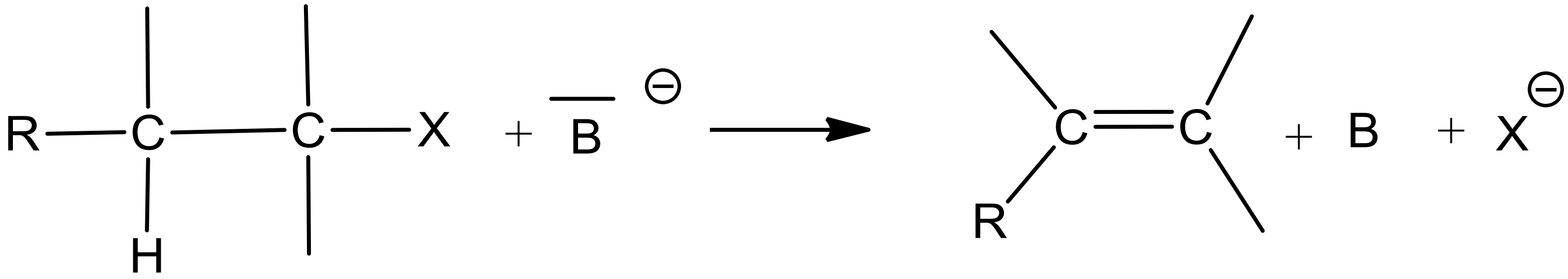
Eliminations are initiated by a base



during elimination **halogen** and **hydrogen atom** at β-C atom are split off

Eliminations proceeds by monomolekular (E1) or bimolekular(E2) mechanism

E1 elimination



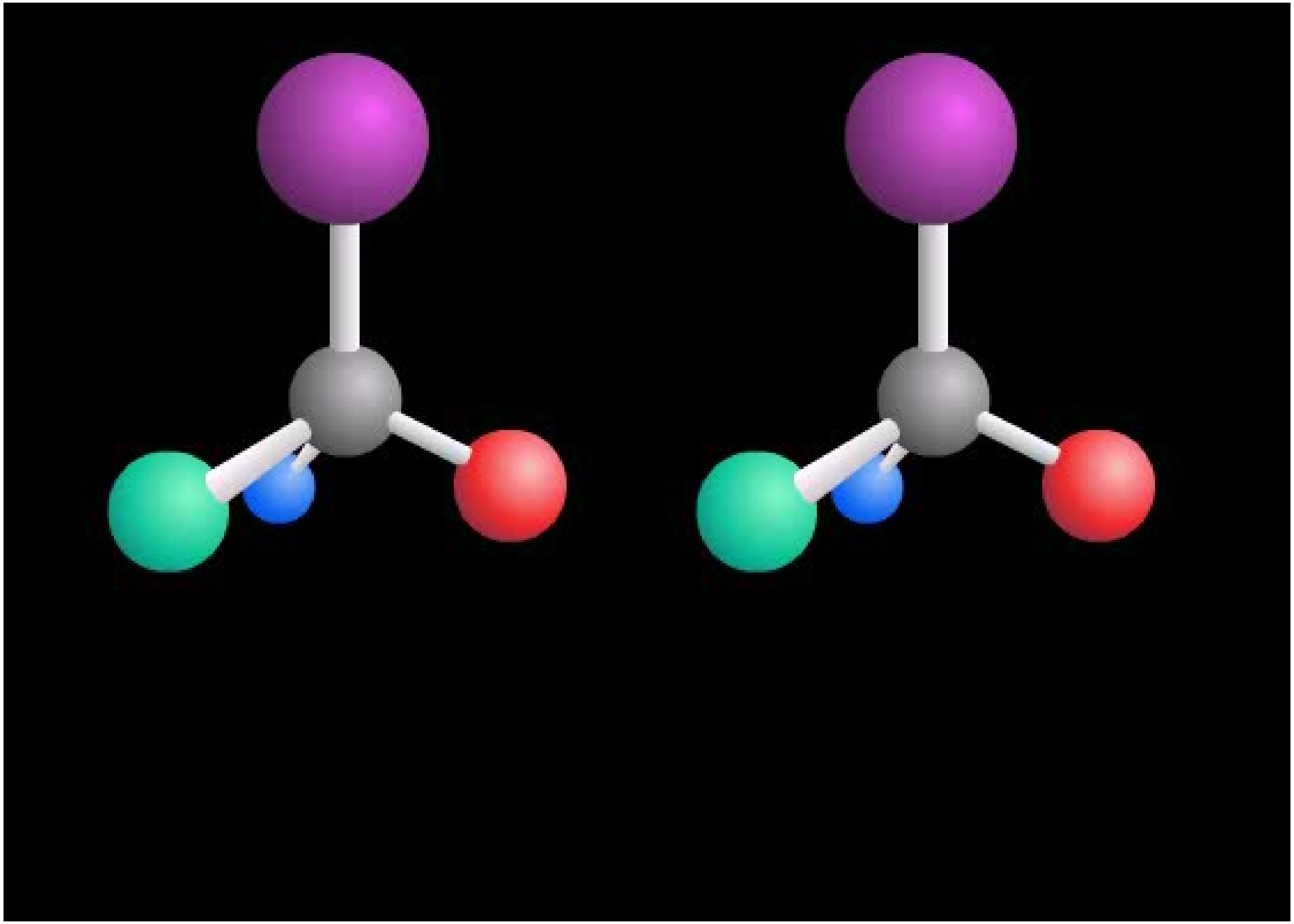
$$v = k \cdot [\,RX] = -\frac{d[RX]}{dt} = +\frac{d[alken]}{dt}$$

reaction is monomolecular - elimination E1

reaction is characteristic for branched halogen derivatives

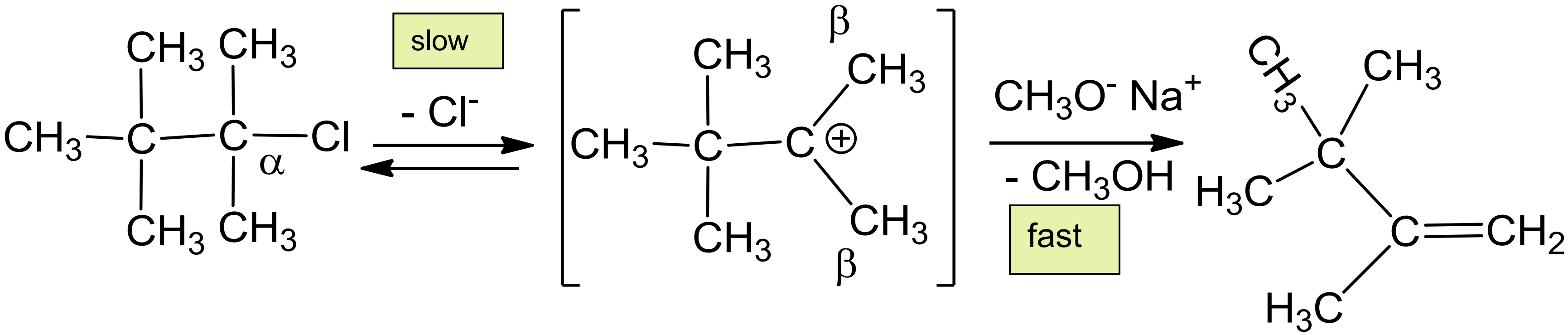
Reaction coordinate

Substituce S_N1 substitution and similarity with E1



Elimination E1

Elimination E1 begins as S_N1 reaction by formation of carbonium ion and is therefore typical for tertiary halogen derivatives



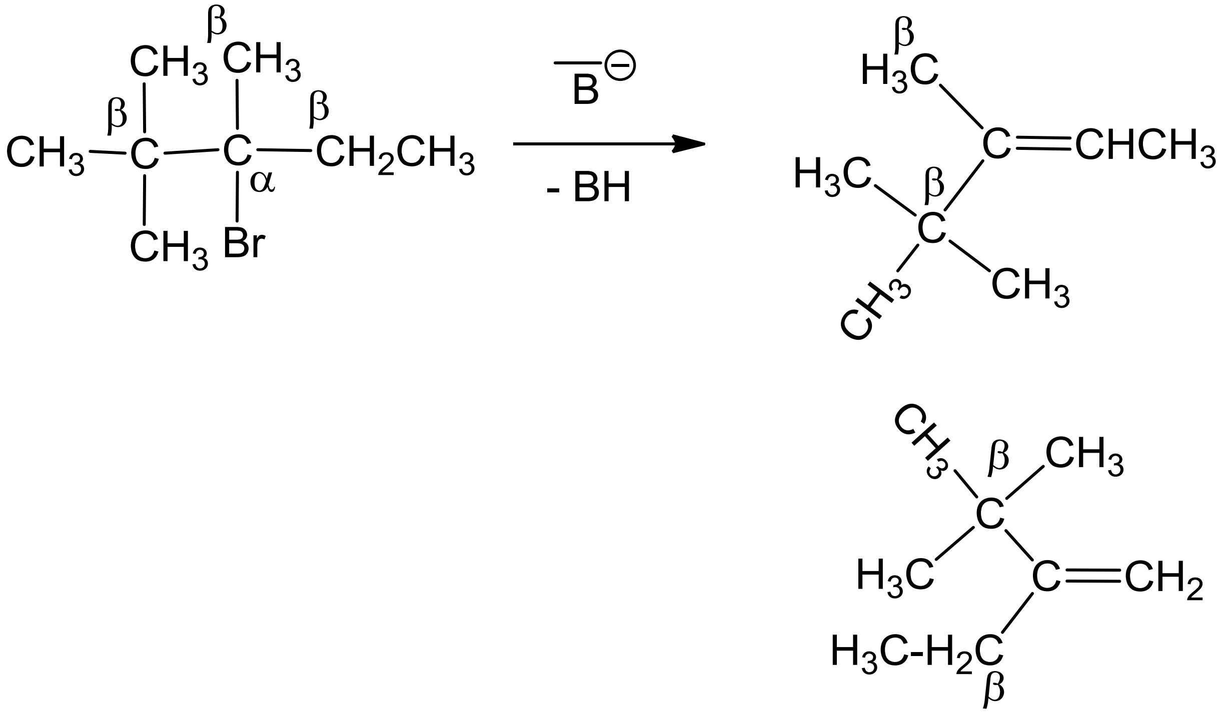
rate determining step

Elimination E1

At nonsymmetrical halogen derivatives, where are several types of β–hydrogen atoms, **Zajcev rule** is valid:

During elimination the most thermodynamically stable olefine is formed

(the hydrogen atom is splitted from that β-carbon, to obtain olefin with the most substituted carbons at double bond)



main product

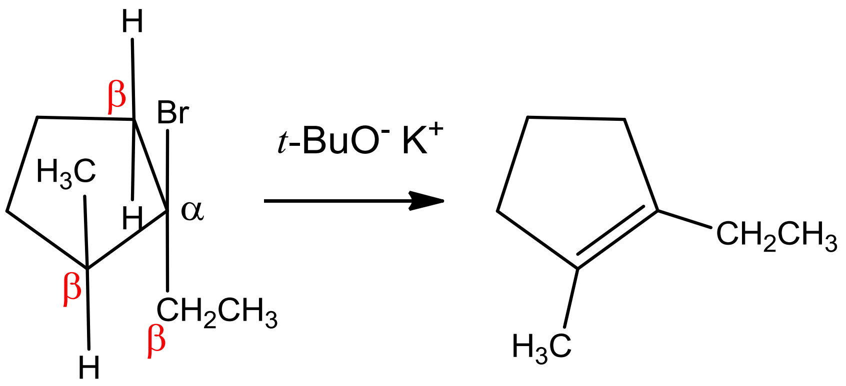
theoretically posible product is not formed

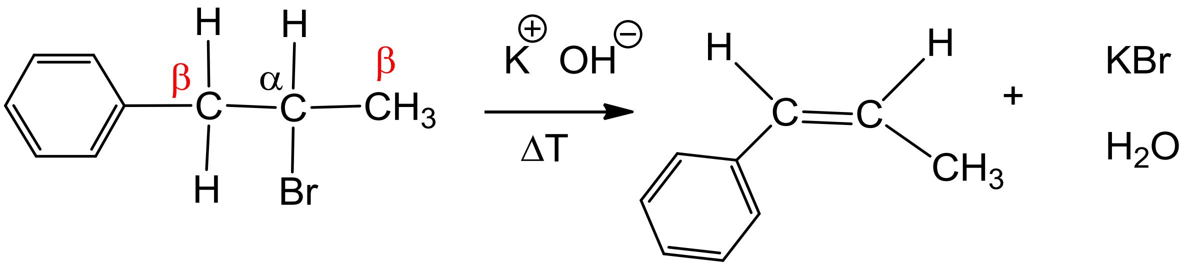
Elimination – Zajcev rule

At nonsymmetrical halogen derivatives, where are several types of β-hydrogen atoms, **Zajcev rule** is valid:

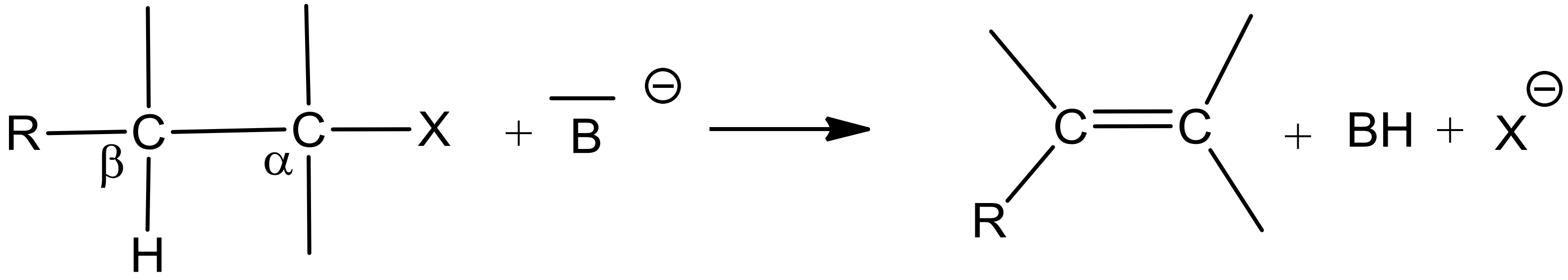
During elimination the most thermodynamically stable olefine is formed

(the hydrogen atom is splitted from that b-carbon, to obtain olefin with the most substituted carbons at double bond)





ELIMINATION E2



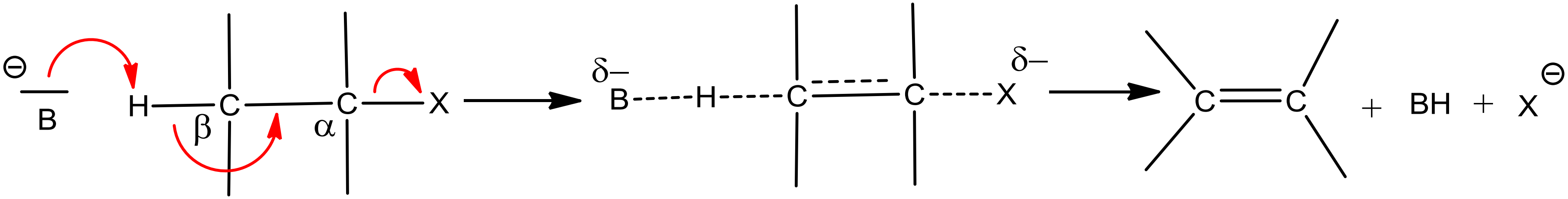
$$v = k \,.\, [\,RX] \,.\, [B^{\ominus}] = -\frac{d[RX]}{dt} = +\frac{d[alken]}{dt}$$

reaction bimolecular - elimination E2

reaction is characteristic for nonbranched halogen derivatives in the presence of bases

E2.exe

MECHANISM OF ELIMINATION E2

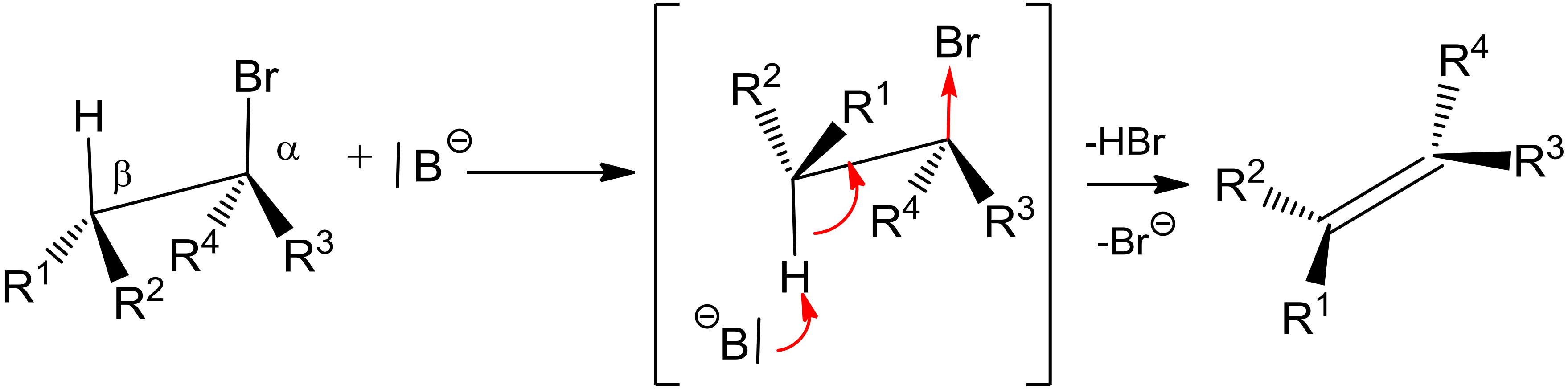


reaction coordinate:

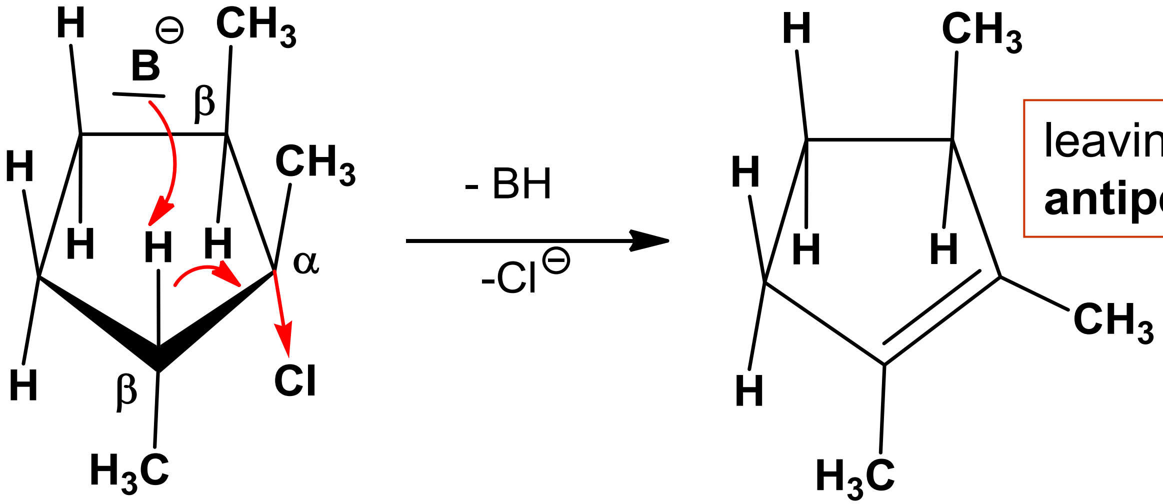
sterochemistry of E2: **reactions proceed stereospecifically**

orientation before elimination – atack of hydrogen atom in **antiperiplanar** conformation in respect to leaving halogen = ***trans*** **-elimination**

ELIMINATION E2 and stereochemie

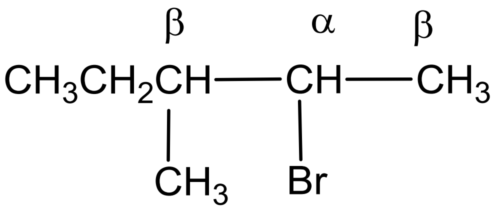


***trans*- elimination**

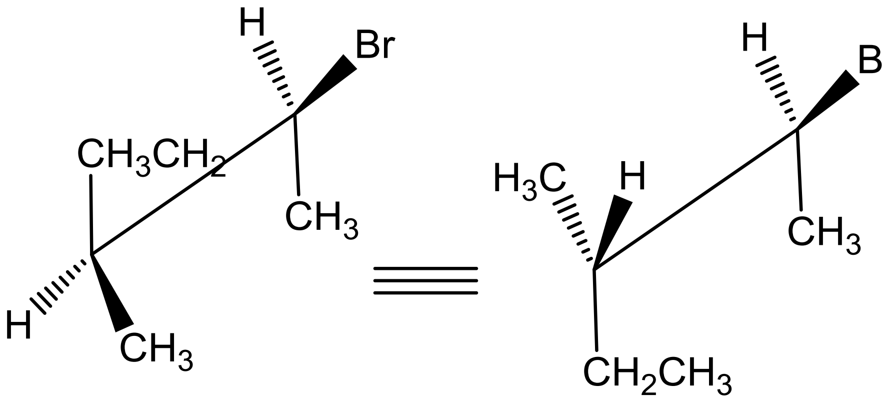


leaving groups are in
antiperiplanar conformation

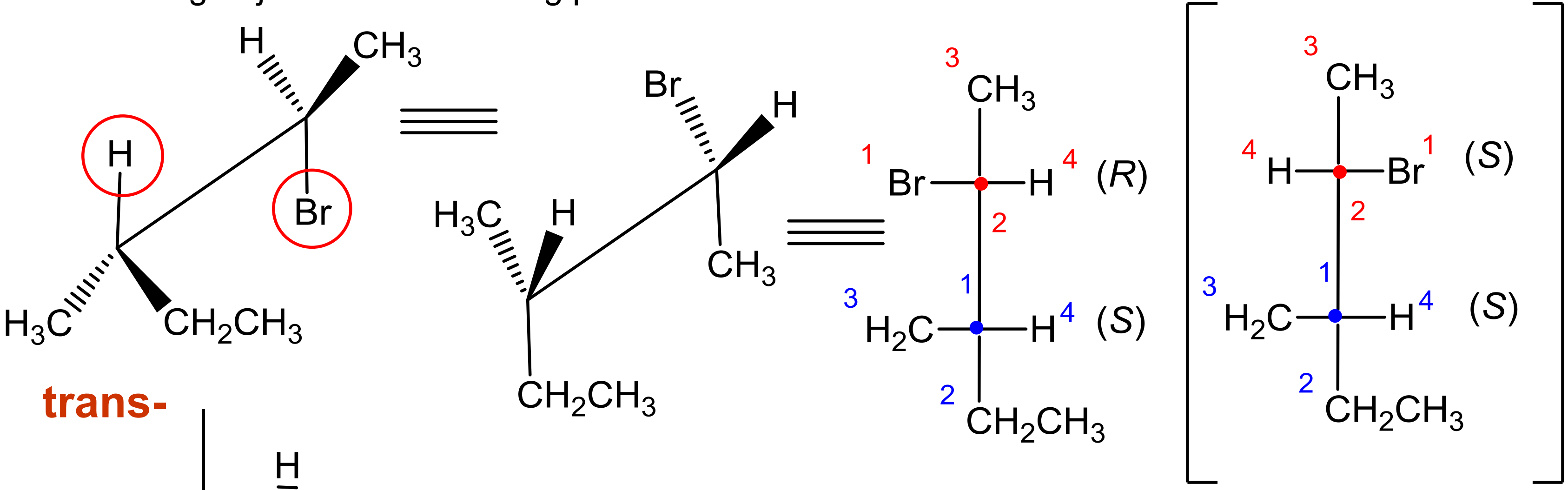
(2*R*,3*S*)-2-bromo-3-methylpentane

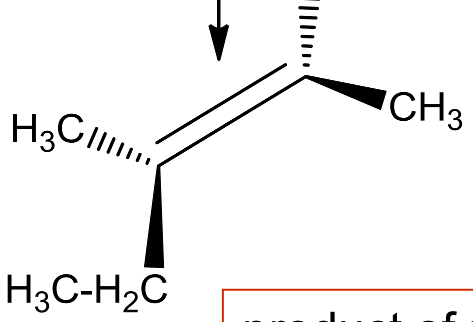


$$\overset{\beta}{\underset{|\;CH_3}{CH_3CH_2CH}}-\overset{\alpha}{\underset{|\;Br}{CH}}-\overset{\beta}{CH_3}$$



1. draw the proper formula
2. put the molecule into Fischer formula
3. specify the steric arrangement
4. find according Zajcev rule the leaving proton



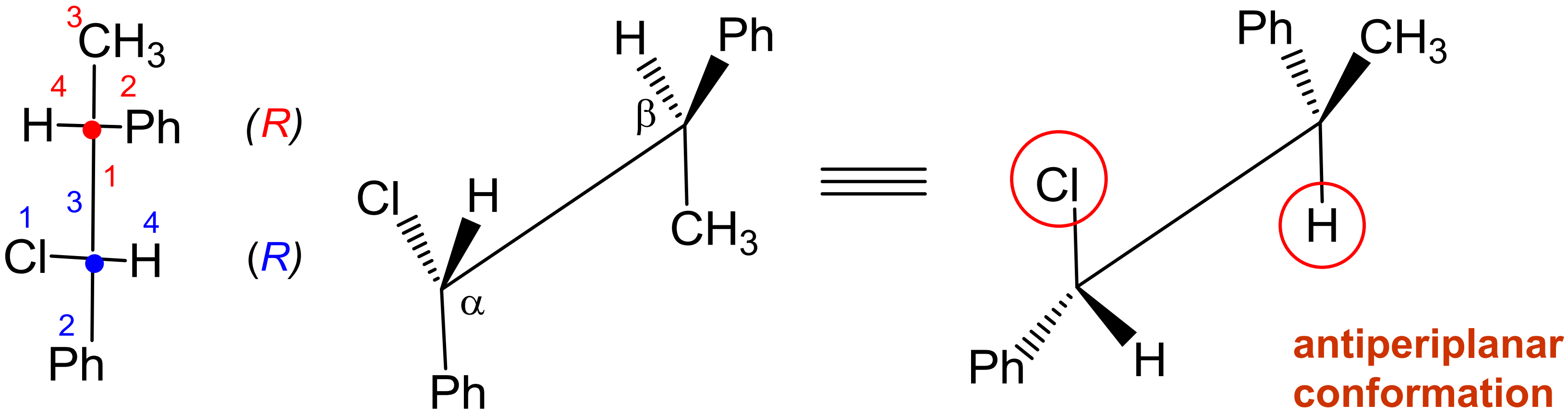


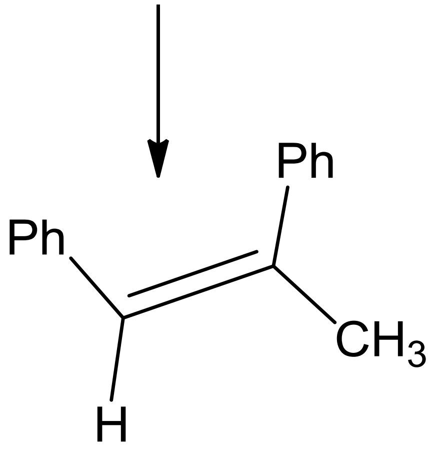
Eliminace proceeds stereospecifically **trans**.

5. adjust the leaving groups into antiperiplanar position
6. split off the leaving groups and find the proper name

product of reaction is **(*Z*)-3-methylpent-2-ene**

(1*R*,2*R*)-1-chloro-1,2-diphenylpropane $\xrightarrow{t\text{-BuO}^- \text{K}^+}$?

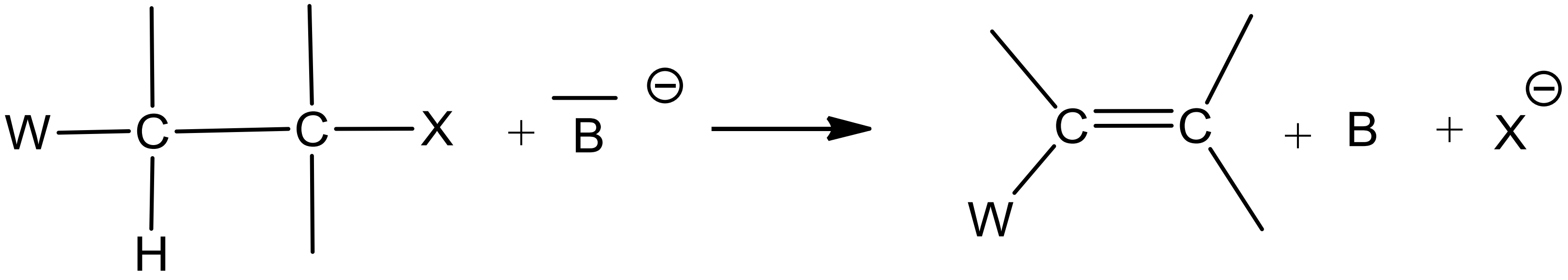




product:

(*Z*)-1,2-diphenylpropene

Elimination E1cB



$$v = k \cdot [RX] = -\frac{d[RX]}{dt} = +\frac{d[alken]}{dt}$$

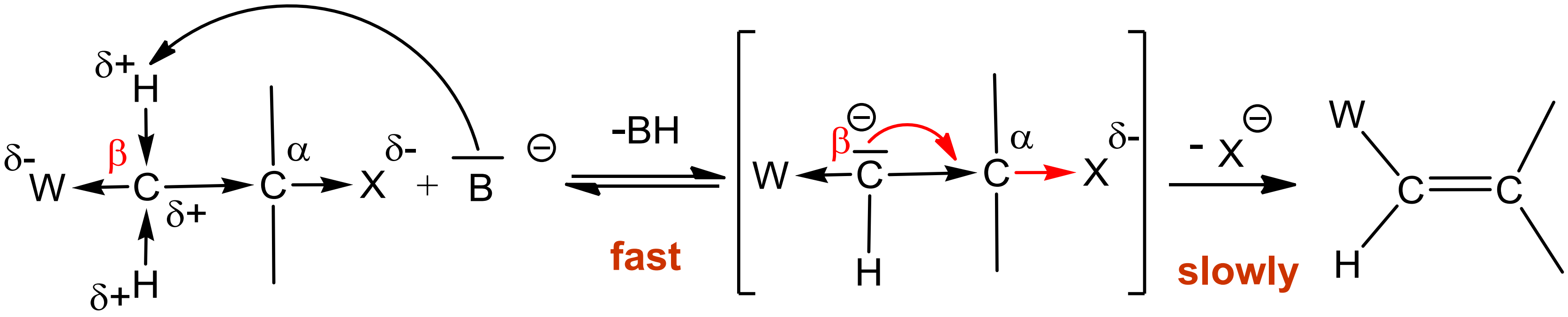
W – electronwithdrawing group

base catalysed monomolecular elimination

reaction is characteristic for halogen derivatives with an acidic hydrogen atom, which is primarily split off by a base and then in a slow step halogen anion is leaving

Reaction coordinate

Eliminace E1cB - mechanismus



W = electronwithdrawing group

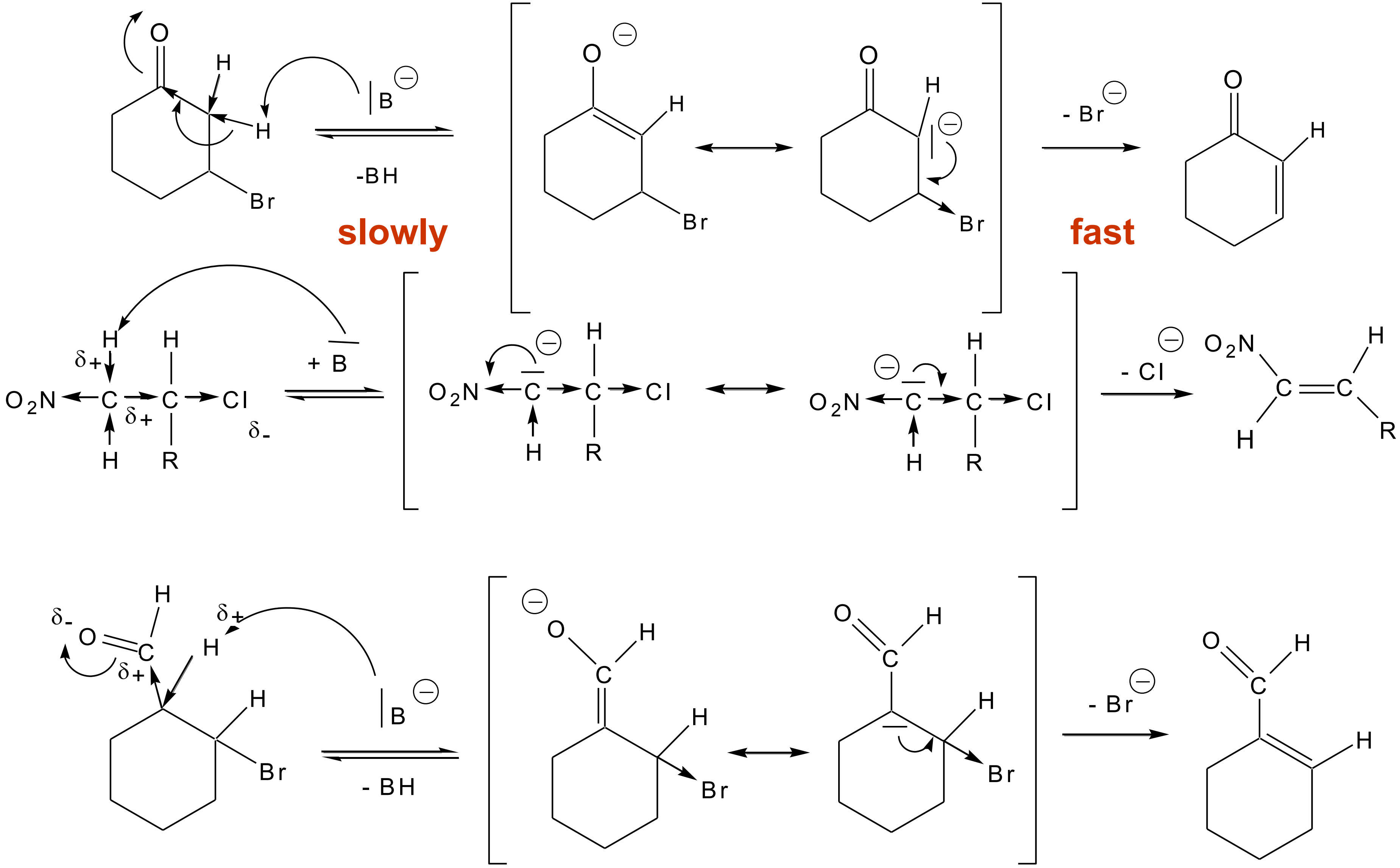
$$v = k \, . \, [\,RX] = - \frac{d[RX]}{dt} = + \frac{d[alken]}{dt}$$

base catalysed monomolecular elimination

reaction is characteristic for halogen derivatives with an acidic hydrogen atom, which is primarily split off by a base and then in a slow step halogen anion is leaving

Reaction coordinate

Some examples of E1cB eliminations



Influence of various factors upon reaction of substitution and elimination

	S_N1 / S_N2	**E1 / E2**	**S / E**
Temperature	-	-	preference E
Effect of base			
- concentration of base (increase)	preference S_N2	preference E2	preference E
-bulkines	S_N1	E2	E
-stenght of base (increase)	S_N1	E2	E
Effect of nucleophile	S_N2	E2	S
Efekt of substrate structure			
- increase α-branching	S_N1	E1	E
- increase β-branching	S_N1	E2	E

Elimination types

Elimination of hydrohalogens - dehydrohalogenation

water - dehydratation

halogens - dehalogenation

sulfonic acids

tertiary amines - Hofmann elimination of quarternary amonium hydroxides

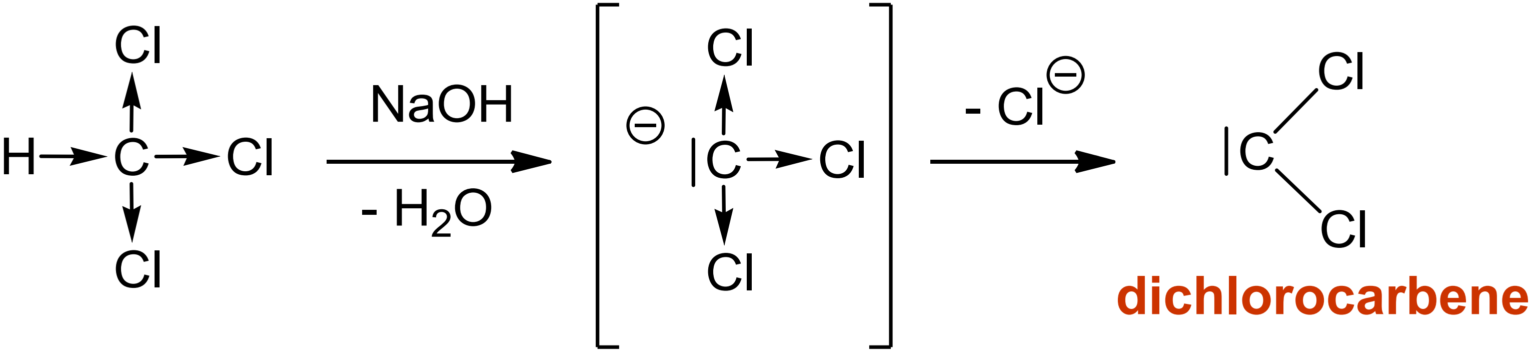
acetic acid - pyrolysis of acetates

COS + MeSH - Čugajev reaction

hydroxylamin - Cope aminoxides elimination

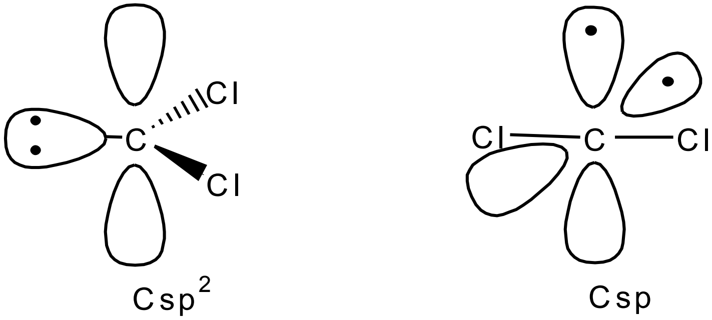
1,1- ELIMINATION (α–elimination)

α–eliminations are connected with preparation of reactive structures (intermediates) having electrophilic character– carbenes

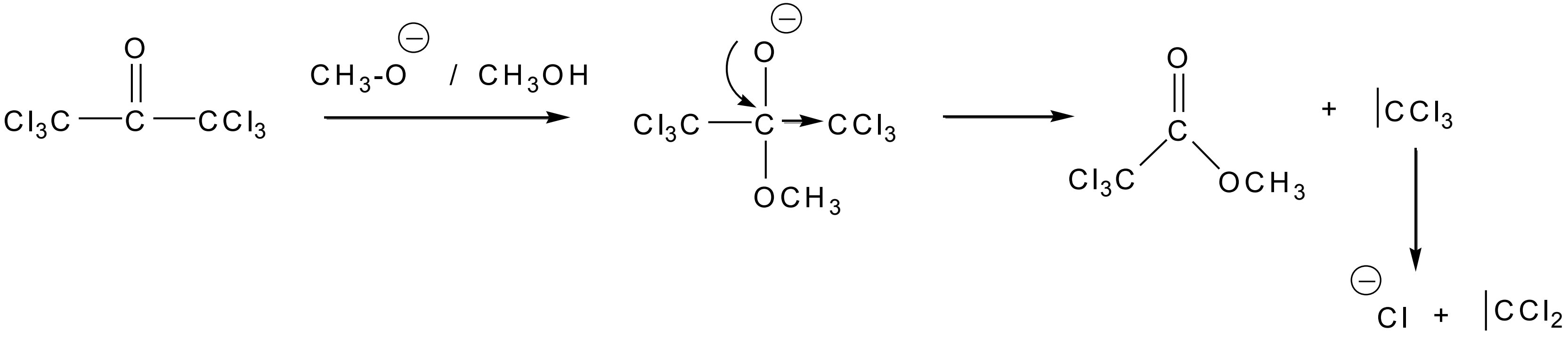


dichlorocarbene

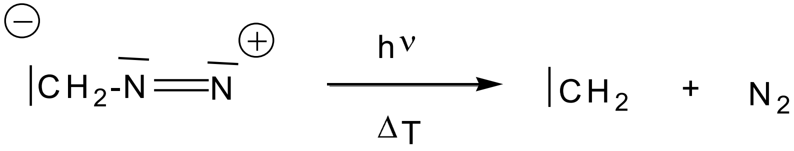
formation of carbenes is observed at systems where no β–hydrogen atom is present



Other methods of carbene preparation



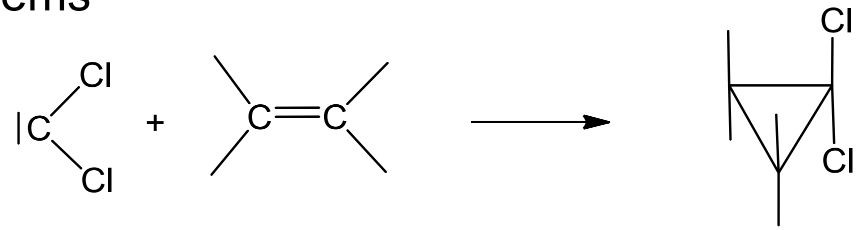
$$CH_2I_2 \xrightarrow{Zn} ZnI_2 + |CH_2$$

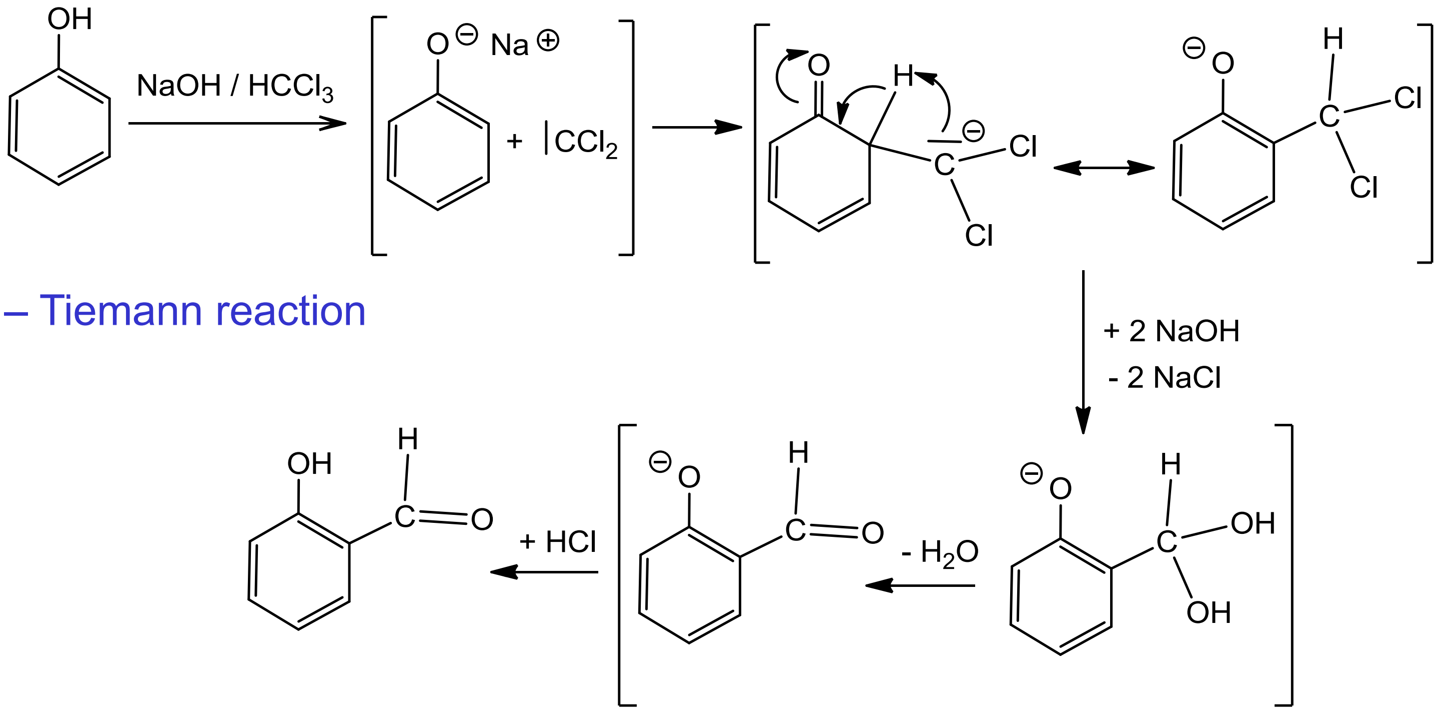


$$\overset{\ominus}{|}CH_2-\overline{N}=\overset{\oplus}{\overline{N}} \xrightarrow[\Delta T]{h\nu} |CH_2 + N_2$$

Carbenes and their properties

carbenes are characterized by **elektrophility** – (they enter reactions with electrondonating systems





Reimer – Tiemann reaction