: Elimination Reaction:

If any molecule is removed from a compound then it is example of elimination reaction

I. $-HX$: dehydrohalogenation.
II $-X_2$: dehalogenation
III $-H_2O$: dehydration.
IV $-H_2$: dehydrogenation.

} all are example of elimination reaction.

example of I.

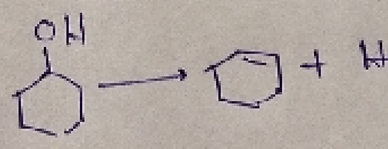
1. $CH_3-CH_2-Cl \longrightarrow CH_2=CH_2$ (only one alkene)

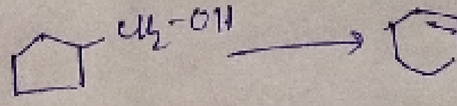
2. $H_3C-\underset{CH_3}{\overset{CH_3}{C}}-Cl \longrightarrow H_2C=\underset{CH_3}{\overset{CH_3}{C}}$ (only one alkene)

3. $H_3C-\underset{Cl}{CH}-\underset{CH_3}{CH}-CH_3 \longrightarrow CH_2=CH-\underset{CH_3}{CH}-CH_3$ (Hoffman alkene)

$+ H_3C-CH=\underset{CH_3}{C}-CH_3$.
(Saytzeff alkene)

(1) ; (2) ; (3) are example of dehydrohalogenation reaction ; (elimination reaction)

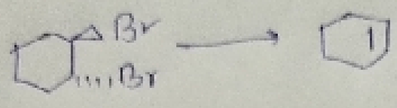
4. 

5 

6. $Me_3C-CH_2OH \longrightarrow Me_2C=CH\,Me$.

(4) ; (5) ; (6) are example of dehydration reaction (elimination reaction)

7. $CH_3-\underset{Cl}{CH}-\underset{Cl}{CH_2} \longrightarrow CH_3-CH=CH_2$

8. 

9. $\underset{Br}{CH_2}-CH=CH-\underset{Br}{CH_2} \longrightarrow CH_2=CH-CH=CH_2$

(7) ; (8) ; (9) are example of dehalogenation reaction which also are example of elimination reaction.

⇒ E_2 (2^{nd} order kinetics; bimolecular)

⇒ E_1 (1^{st} order kinetics; Unimolecular)

⇒ E_1CB. (C.B = conjugate base; Unimolecular but 2^{nd} order kinetics).

⇒ E_i (i = intramolecular; 1^{st} order & unimolecular mechanism).

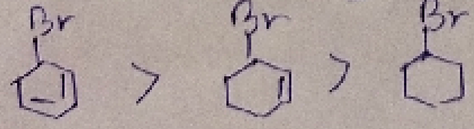
: E_2 :

⇒ strong base alcoholic KOH ; ROH + RO^- ; RO^- MeO^-/Δ ; EtO^-/Δ ; $^tBuOK/\Delta$; KNH_2 ↑ $NaNH_2$ gives E_2 mechanism.

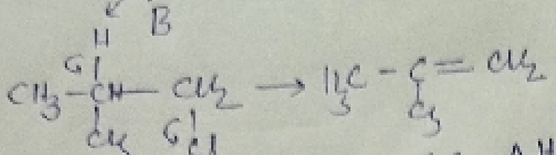
⇒ $3^\circ R\cdot X > 2^\circ R\cdot X > 1^\circ R\cdot X$

⇒ More stable alkene, faster is E_2 reaction

$CH_2=CH-CH_2-CH_2-Br$ > $CH_3-CH_2-CH_2-CH_2-Br$



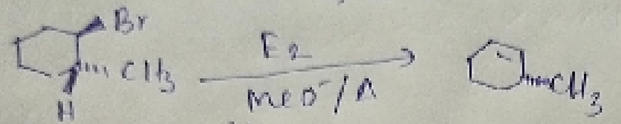
=> High temp. favours elimination reaction

=> 

ΔS = +ve; high temp $\Delta G = \Delta H - T\Delta S$ = more -ve. fast reaction.

=> Anti elimination; β-H is eliminated.

=> concerted.



(Can't be removed)

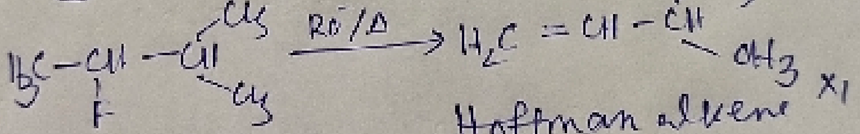
=> Saytzeff alkene major product
Hoffman alkene is minor product.

=> Sometimes Hoffman alkene (less stable alkene) can be formed as major product.

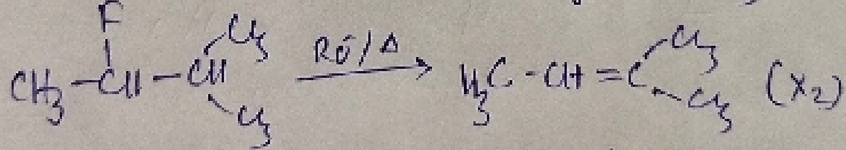
· Criteria: If L.G = -F / $-\overset{+}{N}R_3$ / $-N\overset{+}{M}e_3$ / $-S\overset{+}{M}e_2$

(A)

=

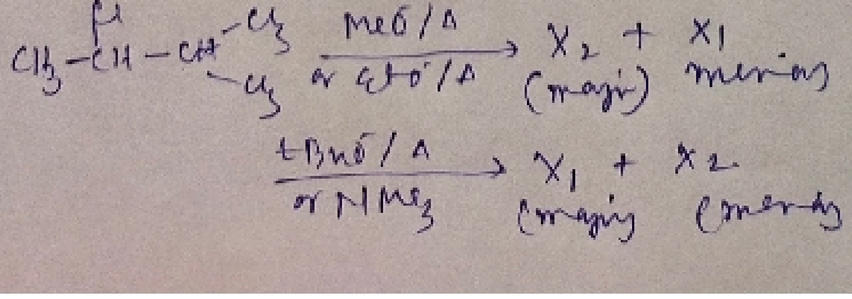


Hoffman alkene (major product) X_1

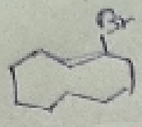
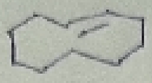
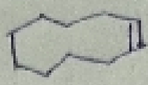


Saytzeff alkene (minor product)

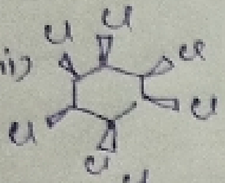
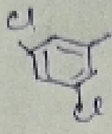
(B) Strong & bulky base tBuO⁻; NR_3 gives Hoffman product as major product.

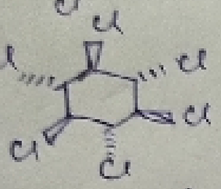


: Examples:

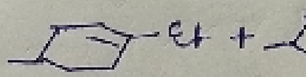
i)  alcoholic KOH →  + 

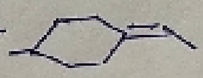
E-isomer Z-isomer (major product)

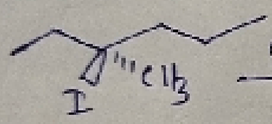
ii)  $\xrightarrow[\Delta]{RO^-/ROH}$  (Aromatic product)

iii)  $\xrightarrow[ROH]{RO^-}$ no alkene formation.

iv)  $\xrightarrow[KOH/\Delta]{\text{alcoholic}}$ No. of possible alkene



 [Total products = 4].

v)  $\xrightarrow[\Delta]{MeO^-/MeOH}$ Total alkenes = 6.

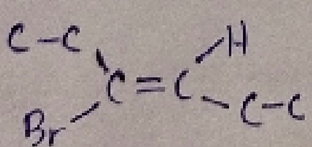
vi) $CH_2(I)-CH(OCH_2CH_3)_2 \xrightarrow{KOCMe_3} CH_2=CH-CH(OEt)_2$

vii) $CH_3-C(CH_3)(Cl)-CH(CH_3)_2 \xrightarrow{tBuO^-} H_2C=C(CH_3)-CH(CH_3)_2$ major product X_1

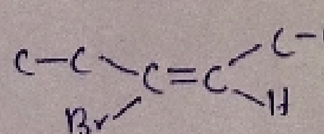
(Hoffmann alkene)

$\xrightarrow{tBuO^-} Me_2C=CMe_2$ minor product (X_2)

(Saytzeff product)

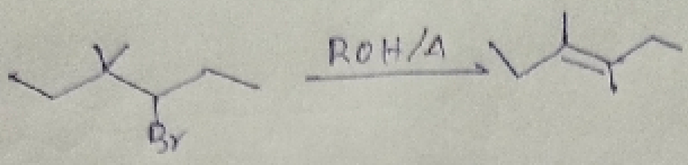
viii)  $\xrightarrow[-HBr]{NaNH_2}$ C-C-C≡C-C-C

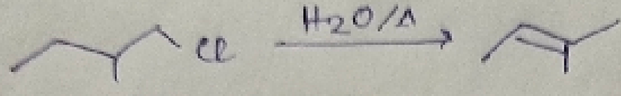
Anti elimination.

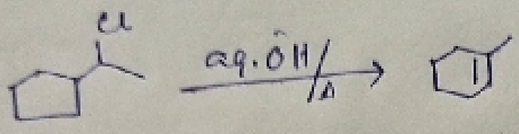
ix)  $\xrightarrow{NaNH_2}$ C-C=C=CH-C-C.

: Examples of E1:

i) $CH_3-\underset{Cl}{CH}-\underset{CH_3}{CH}-CH_3 \xrightarrow[\Delta]{EtOH} H_2C-CH=\underset{CH_3}{C}-CH_3$

ii) 

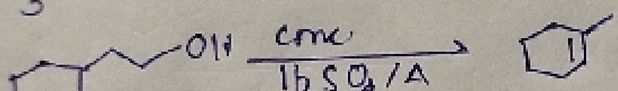
iii) 

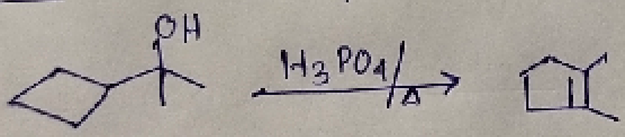
iv) 

(i)-(iv) are example of dehydrohalogenation reaction

v) 2 butanol $\xrightarrow{KHSO_4/\Delta}$ Trans but-2-ene + Cis but-2-ene + But-1-ene.

vi) $Me_3C-CH_2-OH \xrightarrow{H_3PO_4/\Delta} Me_2C=CH-CH_3$.

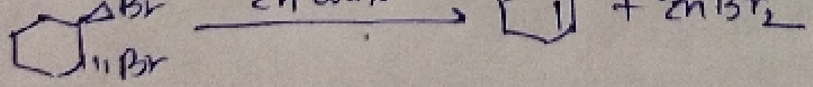
vii) 

viii) 

(v) - (viii) are example of dehydration reaction.

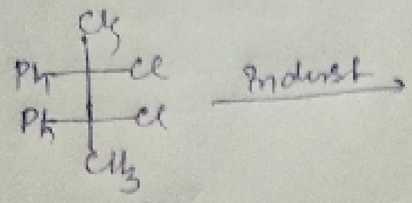
ix) Examples of E_2 reaction:

ix) $CH_3-\underset{Cl}{CH}-\underset{Cl}{CH_2} \xrightarrow{Zn\text{-}dust} CH_3-CH=CH_2 + ZnCl_2$

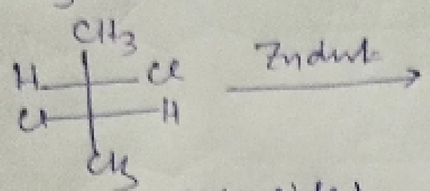
x) 

xi) $CH_3-\underset{Br}{CH}-\underset{Br}{CH}-CH_3 \xrightarrow[acetone]{NaI} CH_3CH=CH-CH_3$.

(ix), (x), (xi) are example of dehalogenation reaction.



(MAT)



(RAC).

(vicinal dihalide)

: E_1CB:

⇒ Alkyl halide.

⇒ strg base (alcoholic KOH; RO^-; $RO^-/ROH/\Delta$).

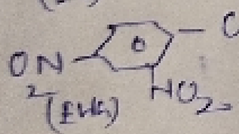
⇒ β-carbon must have groups having -I & -R effect (strg e withdrawing group)

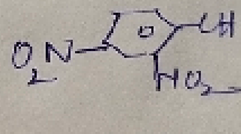
Example:

$R-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-X \xrightarrow{RO^-/\Delta} R\underset{\underset{O}{\|}}{C}-CH=CH_2$ (EWG) (L.G)

$R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-CH_2-CH_2-X \xrightarrow[\Delta]{RO^-/ROH} R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-CH=CH_2$ (EWG) (L.G)

$F_3C-CHF_2 \xrightarrow{meO^-/\Delta} F_2C=CF_2$ (L.G)



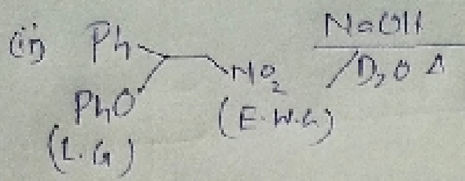
$\xrightarrow{EtO^-/\Delta}$ 

$Cl_2C=CHCl \xrightarrow[KOH/\Delta]{alcoholic} HC\equiv C-Cl$.

If E_1CB is carried out in presence of OD^-/D_2O or $meO^-/MeOD$ then D is incorporated in the β-carbon in product.

(i) $R-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-X \xrightarrow[D_2O]{OD^-/D} R-\underset{\underset{O}{\|}}{C}-CH=CHX$

$R-\underset{\underset{O}{\|}}{C}-\overset{+}{C}D=CHX$

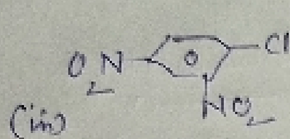
(ii) 

The possible products

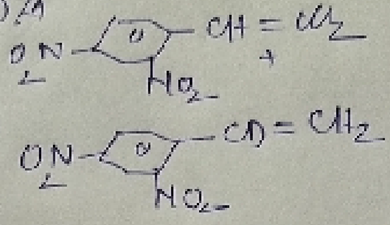
$PhCH=CH-NO_2$

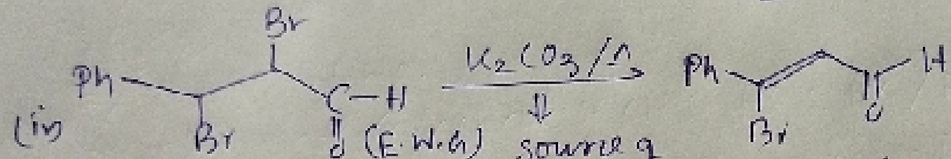
or

$PhCH=CD-NO_2$

(iii) 

The possible products



(iv) 

source of $\overset{\ominus}{O}H$ (its aq. solution is basic).

(i); (ii); (iii); (iv) are examples of E_1CB.

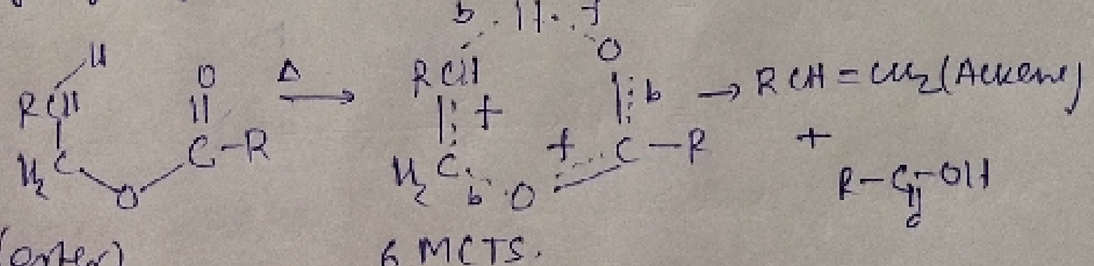
E_i (intramolecular elimination)

i) Pyrolysis of ester (heating of ester in absence of O_2)

ii) Pyrolysis of xanthate.

iii) Cope reaction.

Pyrolysis of ester:



(ester)

6 MCTS.

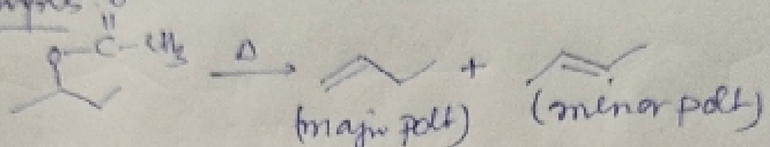
(syn elimination)

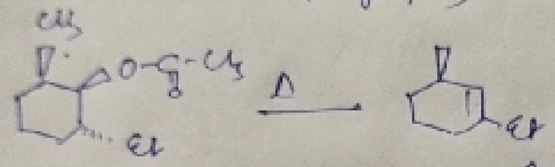
[H R-O-C(=O)-R are removed from same side] whereas E_2 is example of anti elimination.

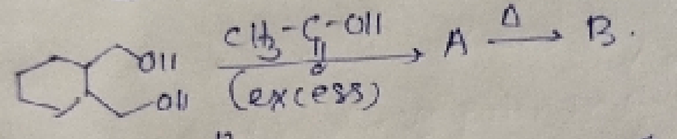
Features of Pi:

⇒ single step; 6membered cyclic TS.
⇒ Unimolecular; rate = k [ester].
⇒ syn elimination.
⇒ no reagent is required from outside.
⇒ Intramolecular elimination
⇒ Hoff man product is found as major product.

Example:

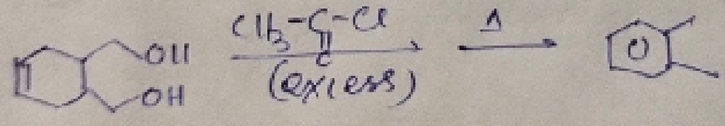
a) 

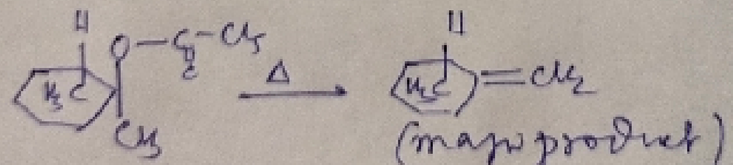
b) 

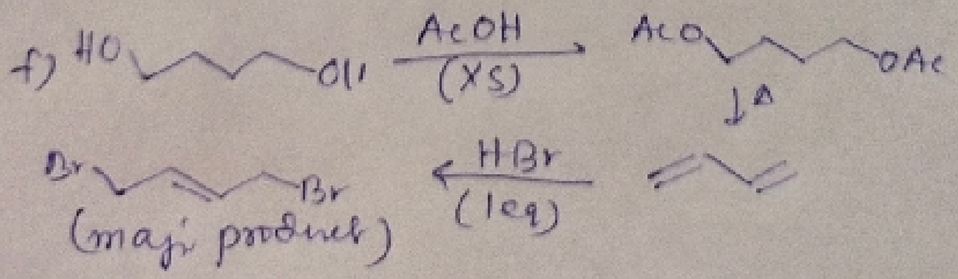
c) 

A =>

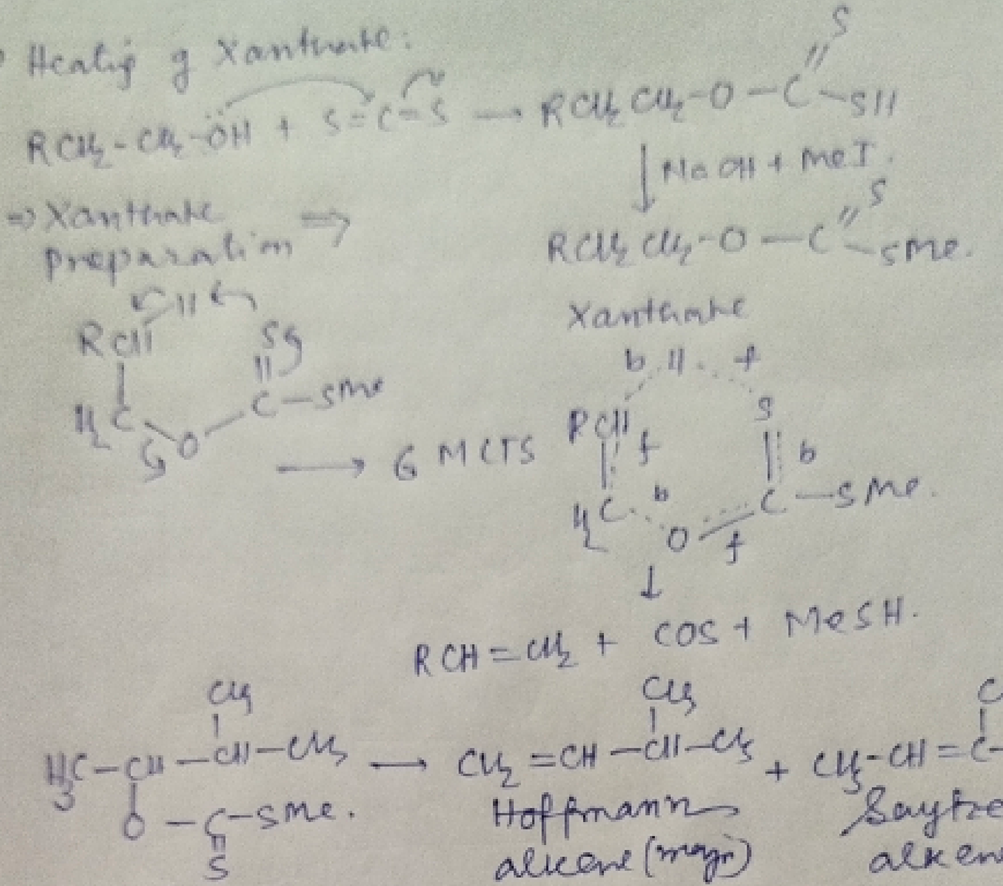
B →

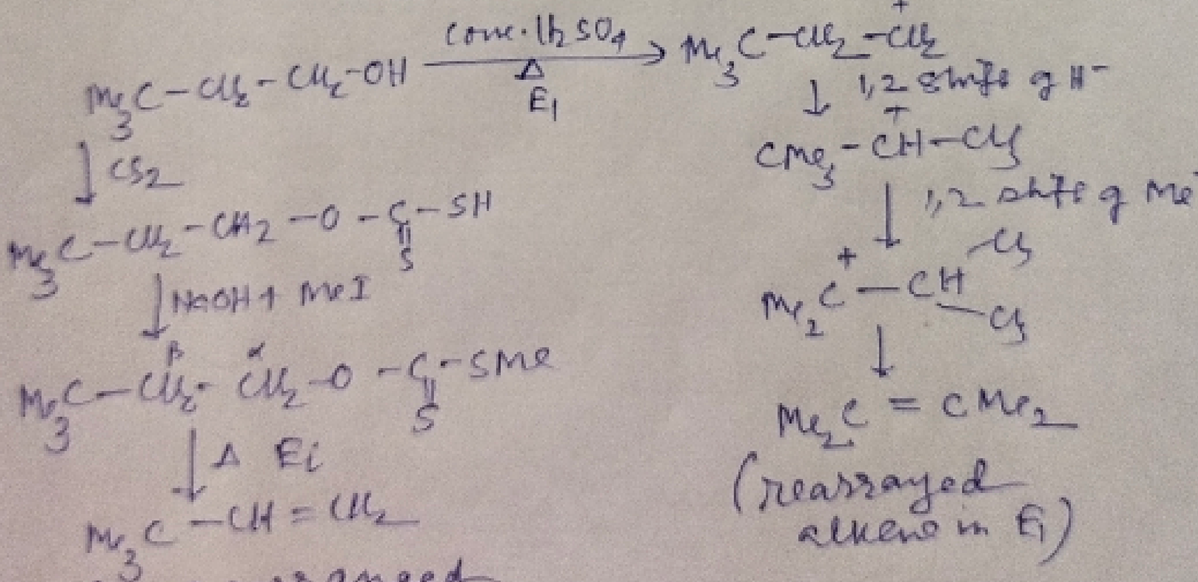
d) 

e) 

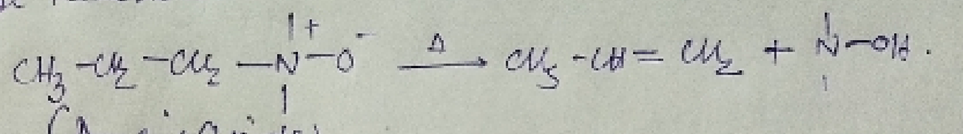
f) 

(ii) Healing g Xanthate:

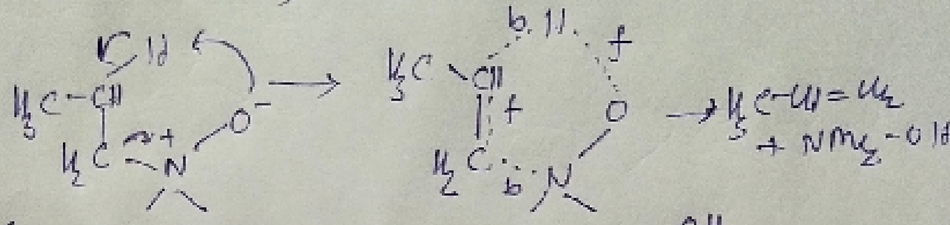




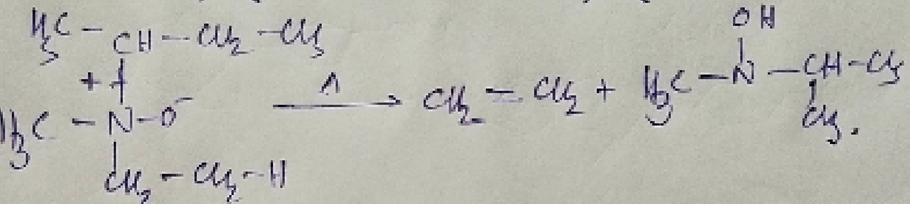
: Cope Reaction:



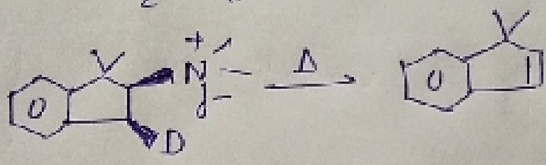
(Amine Oxide)



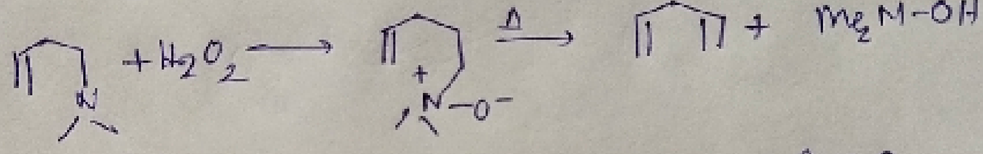
a)



b)

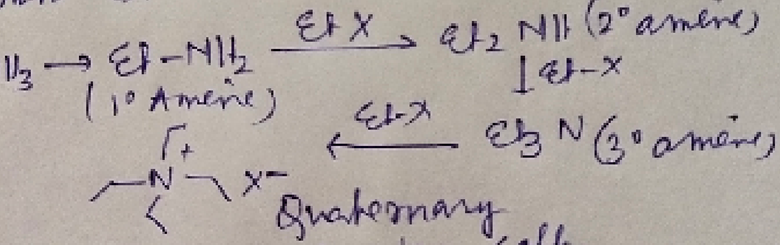


c)



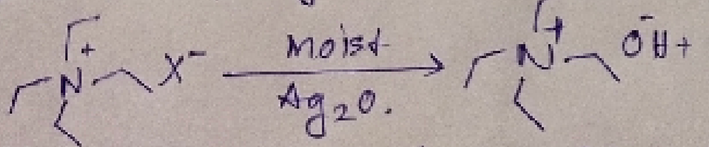
Example (specific) of E_2 mechanism where Hoffman product is the major product:

; Hoffmann exhaustive methylation:

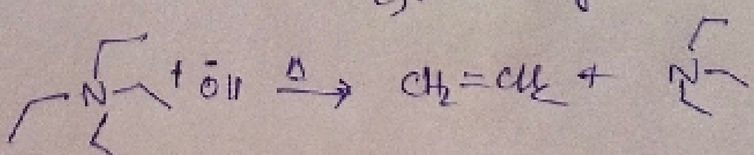


Quaternary ammonium salt.

It is example of 4 times S_N2 reaction.



Quaternary ammonium hydroxide.



Rate of dehydrohalogenation:

a) $CH_3-CH_2-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 > CH_3-CH_2-\underset{\underset{Br}{|}}{CH}-CH_2-CH_3 > CH_3CH_2CH_2-\underset{\underset{Br}{|}}{CH}-CH_3 > CH_3CH_2CH_2CH_2-\underset{\underset{Br}{|}}{CH_2}$

b) $CH_3-CH_2-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{CH}}-CH_2 > CH_3-CH_2-CH_2-CH_2-Br > H_3C-CH_2-Br$

What are the major products & minor products when following quaternary ammonium hydroxide undergoes heating.

a) $CH_3-CH_2-\overset{\overset{+}{N}Me_3}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3 \xrightarrow{\Delta} CH_3-CH=CH-\overset{\overset{CH_3}{|}}{CH}-CH_3 + NMe_3$ (minor product)

$+ \quad CH_3-CH_2-CH=\overset{\overset{CH_3}{|}}{C}-CH_3$ (major product)

b) $CH_3-CH_2-CH_2-\overset{\overset{+}{|}}{\underset{\underset{CH_2-CH_2-H}{|}}{N}}-\underset{CH_2-CH_3}{\overset{CH_2-CH_3}{|}}-CH_2-CH_3 \xrightarrow{\Delta} CH_3-CH=CH_2 + N\overset{npr}{Et_2}$

minor product

$CH_2=\overset{+}{C}H_2 + npr_2NEt.$

c) $CH_3-CH_2-\overset{\overset{CH_3}{|}}{\overset{+}{N}}-CH_2-CH_2-Cl \xrightarrow{\Delta} CH_2=CH_2 + ClCH_2CH_2NMe_2$

(minor product)

$CH_2=\overset{+}{C}H-Cl. + EtNMe_2$

(major product)

$CH_3-CH_2-\overset{\overset{CH_3}{|}}{\overset{\oplus}{N}}-CH_2-CH_2-Ph \xrightarrow{\Delta} CH_2=CH_2 + \underset{CH_2CH_3Ph}{\overset{CH_3}{|}}N-nBu$

$\underset{CH_2-CH_2-CH_2-CH_3}{|} \quad \ddot{O}H$

(minor pdt)

$+ CH_2=CH-Ph$

(major product)