(for Alkyl halide)

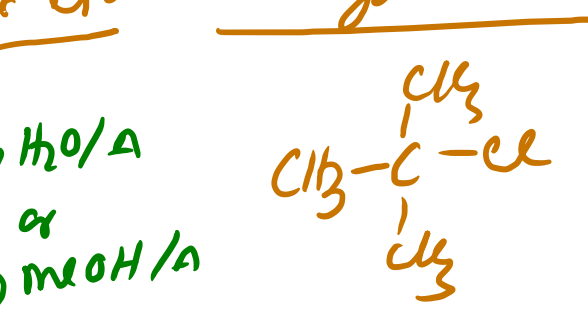
: Elimination Reaction : (E_2 complete)

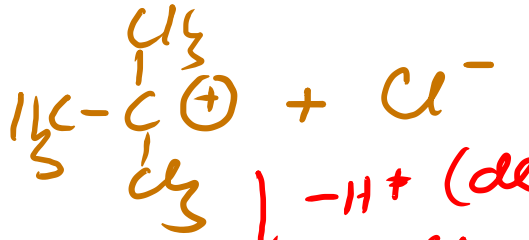
→ Saytzeff (major) ??

→ Hoffman (major)

: E1 : Dehydrohalogenation (specific/ more case)

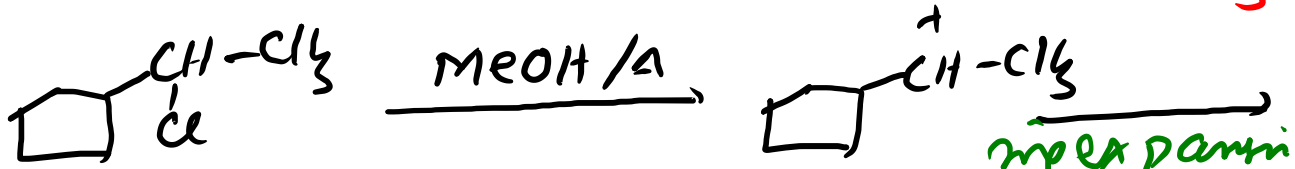
R-X
- i) H_2O/Δ or
- ii) $MeOH/\Delta$ or
- iii) $EtOH/\Delta$ or
- iv) ROH/Δ

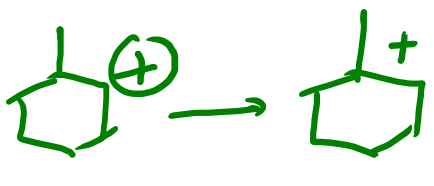




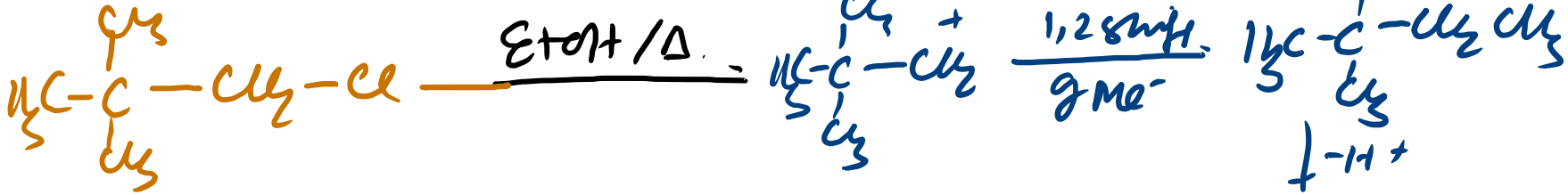
C⁺ Stability ∝ rate ↑

3° R-X > 2° R-X > 1° R-X

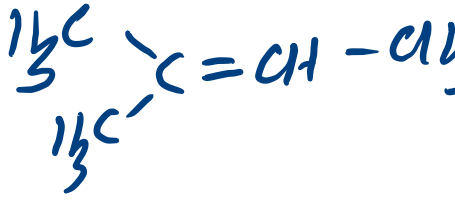




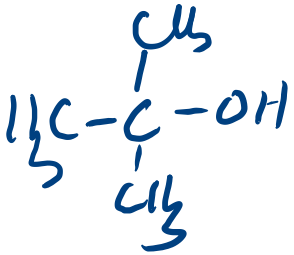
Alkene.



E1 always gives Saytzeff pdt as major pdt.



E_1 : E_1 for Alcohol : (Acid catalyst dehydration) (conc. H_2SO_4) H_3PO_4) KHSO4



conc. H_2SO_4 / 150°C – 180°C.

Saytzeff pdt is the major pdt

rearrangement pdt (alkene) is formed.

more stable alkene is the major pdt.

Purpose of PCl_5

$R \neq R'$

$R\text{-}OH + PCl_5 \xrightarrow{(SN1)} R\text{-}Cl + HCl + POCl_3$

$R\text{-}O\text{-}R' + PCl_5 \longrightarrow R\text{-}Cl + R'Cl + POCl_3$

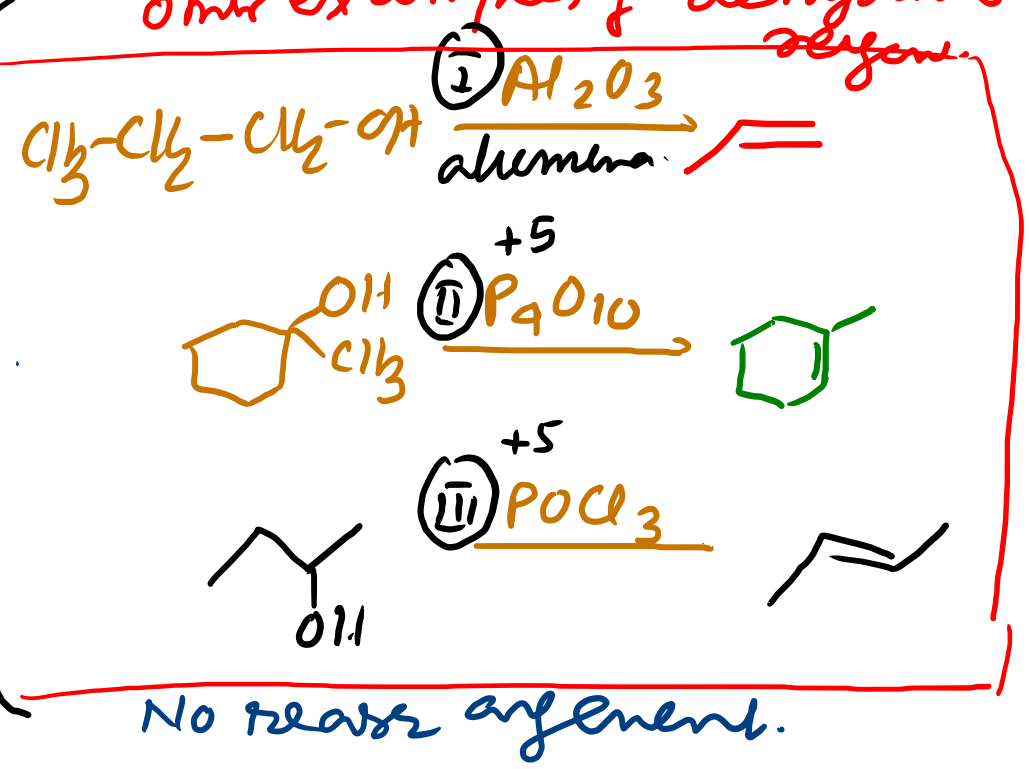
unsymmetrical ether.

mixture of alkyl halide

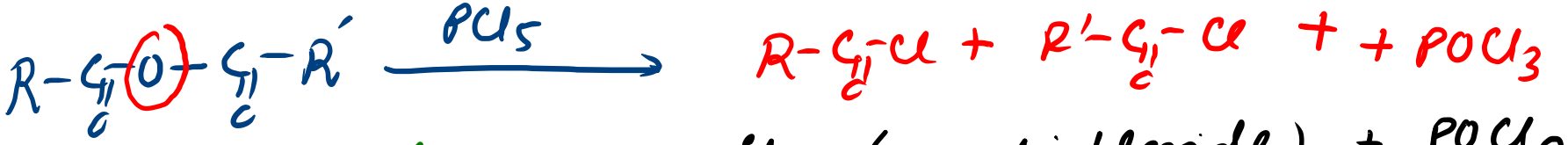
$R\text{-}\underset{\underset{O}{\|}}{C}\text{-}OH + PCl_5 \longrightarrow R\text{-}\underset{\underset{O}{\|}}{C}\text{-}Cl + HCl + POCl_3$

$R\text{-}\underset{\underset{O}{\|}}{C}\text{-}O\text{-}R' + PCl_5 \longrightarrow R\text{-}\underset{\underset{O}{\|}}{C}\text{-}Cl + R'Cl + POCl_3$

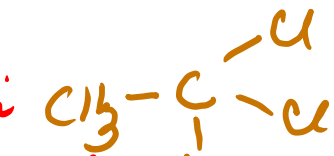
other examples of dehydrating agent.



No rearrangement.



How many reacti give gem dichloride on pdt.



: Ethylidene chloride. (gemdichloride.

a) 

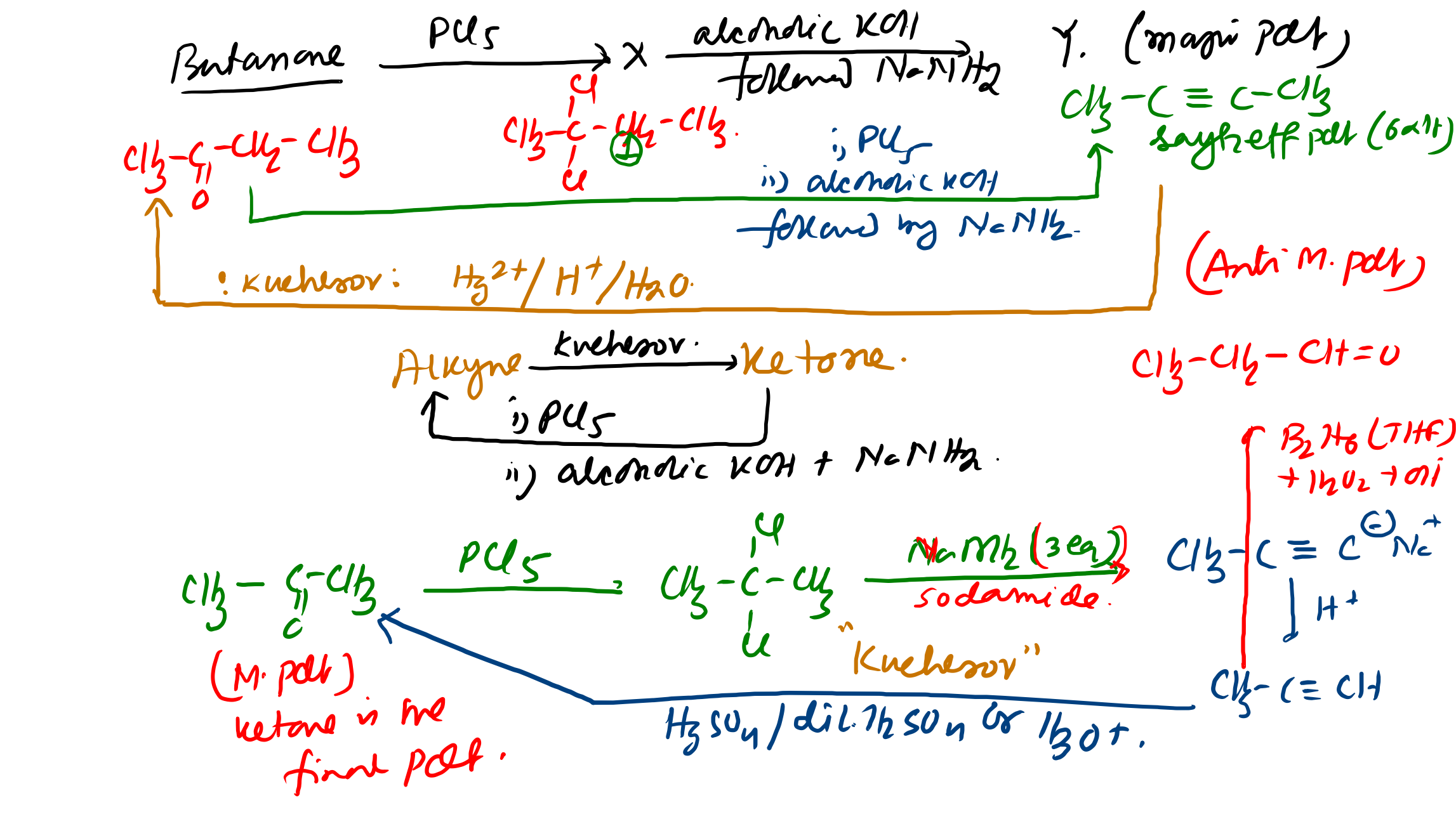
b) 

: Ethylene dichloride di (vicinal chloride)

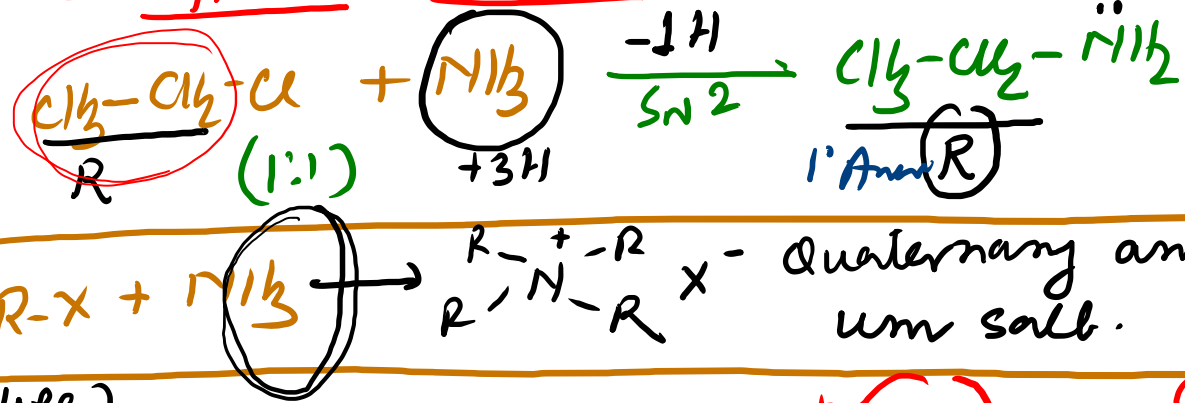
: Propylidene chloride.

c) 

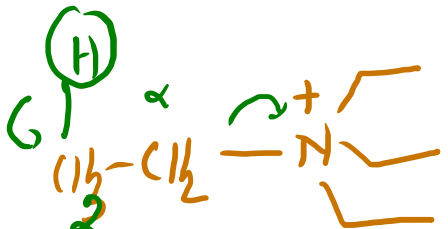
all


Butanone
PCl5
X
alcoholic KOH
followed NaNH2
Y. (major pdt)
CH3-C≡C-CH3
Saytzeff pdt (6 atm)
CH3-C(Cl)2-CH3
CH3-C(Cl)2-CH2-CH3
i) PCl5
ii) alcoholic KOH
followed by NaNH2
: Kucherov : Hg2+/H+/H2O
(Anti M. pdt)
Alkyne
Kucherov
Ketone
i) PCl5
ii) alcoholic KOH + NaNH2
CH3-CH2-CH=O
B2H6 (THF)
+H2O2 → OH
CH3-C≡C⊖Na⊕
H+
CH3-C≡CH
PCl5
CH3-C(Cl)2-CH3
NaNH2 (3eq)
sodamide
"Kucherov"
CH3-C(=O)-CH3
(M. pdt)
ketone is the
final pdt.
H2SO4/dil.H2SO4 or H3O+.

Hoffman exhaustive methylation:



$\bar{O}H$ | moist Ag_2O. ($Ag_2O + H_2O \rightarrow AgOH$ strong $\bar{O}H$)



$(CH_3CH_2)_4NOH$

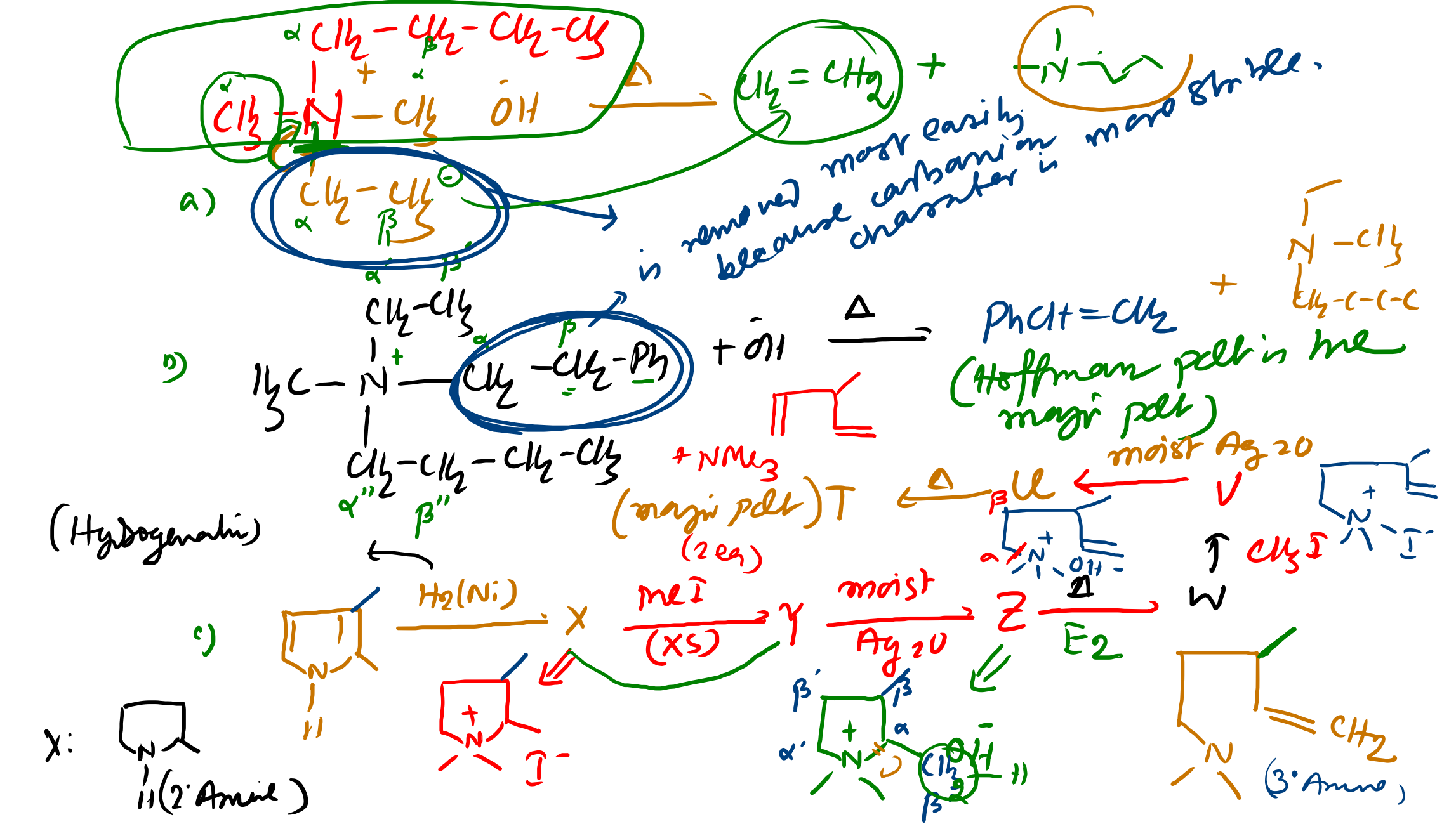
Quaternary ammonium hydroxide.

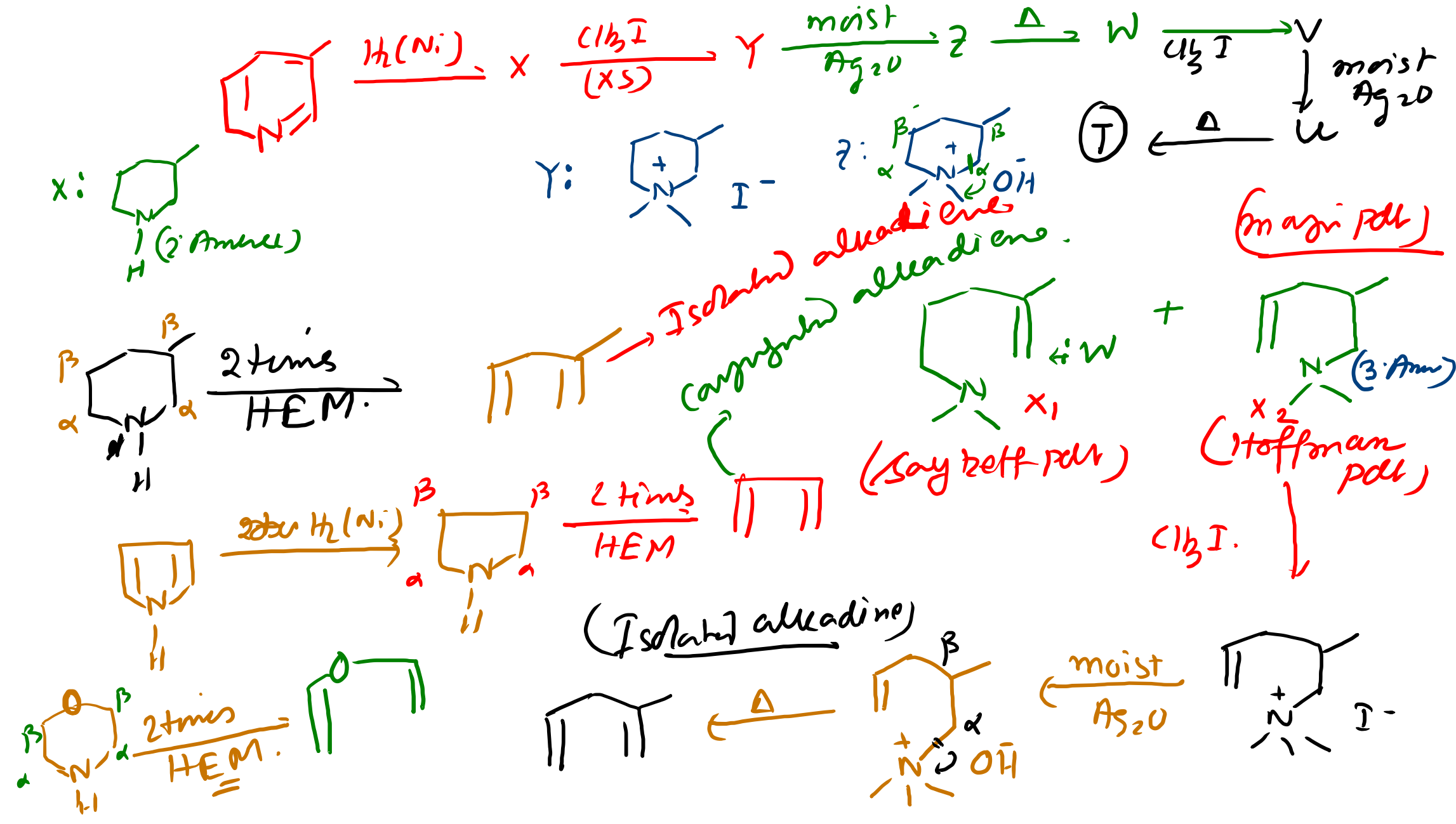
$\bar{O}H/\Delta$

Δ

$CH_2=CH_2 + NMe_3$

Hoffman pdt is the major pdt.


a)
b)
c)
(Hydrogenation)
+NMe3
(major pdt) T
(2 eq)
moist Ag2O
MeI
(XS)
H2(Ni)
E2
X:
(2° Amine)
(3° Amine)
is removed most easily because carbanion character is more stable.
(Hoffman pdt is the major pdt)


H2(Ni)
X
CH3I
(XS)
Y
moist
Ag2O
Z
Δ
W
CH3I
V
moist
Ag2O
U
Δ
T
X:
(2° Amine)
Y:
I⁻
Z:
OH
Isolated alkadiene
conjugated alkadiene.
(major pdt)
2 times
HEM.
+W
X1
(Saytzeff pdt)
+
(3° Amine)
X2
(Hoffman pdt)
CH3I.
2 times
HEM
(Isolated alkadine)
Δ
moist
Ag2O
OH
I⁻
2 times
HEM.

[conjugate base] : **E1CB: (very specific / rare case):** * different from E2

=> Alkyl halide (3°/2°/1°)

=> strong base (alcoholic KOH ; RO^-/Δ ; RO^- ; $RO^- + ROH$).

=> β carbon of alkyl halide should have such a group which has very high e⁻ withdrawing power.

a) * $O_2N-\overset{\beta}{H_2C}-\overset{\alpha}{CH}(CH_3)-Cl$ (L.G.) $\xrightarrow{OR^-/\Delta}$

EWG

$F_3C-\overset{\alpha}{C}H_2-\overset{\beta}{C}H_2-Cl \xrightarrow{\text{alc. KOH}} F_2C=CH_2$

[−F] (E1CB)

b) * $RO-\overset{O}{\overset{\|}{C}}-CH_2-CH(CH_3)-F$ (L.G.) $\xrightarrow{MeO^-/\Delta}$

EWG.

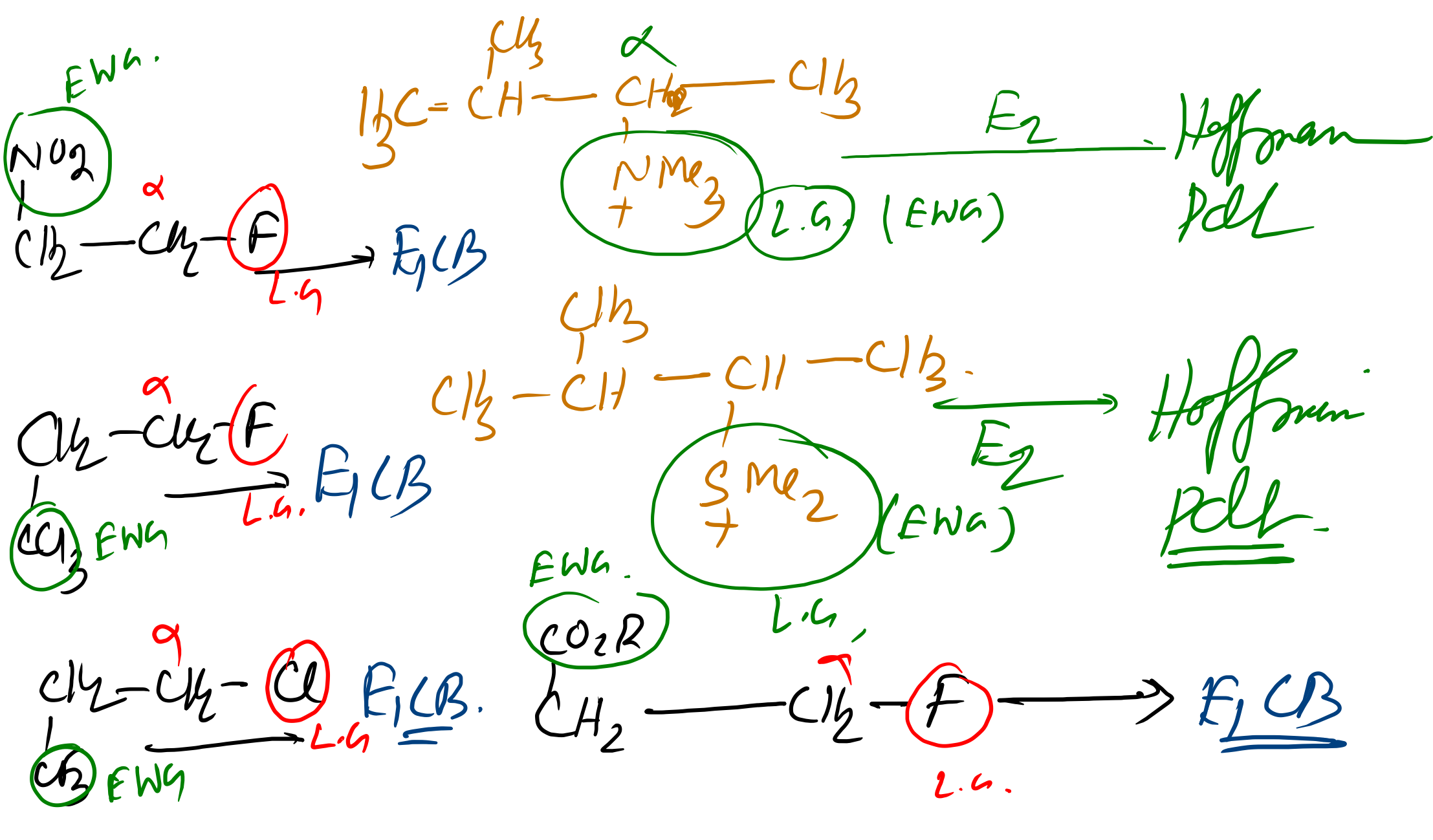
$PhCH(F)-\overset{\alpha}{C}H_2-\overset{\beta}{C}H=O \xrightarrow[E_1CB]{K_2CO_3/\Delta} PhCH=CH-CH=O$

F (L.G.) ; EWG.

c) * $CH_3-CH(CH_3)-\overset{O}{\overset{\|}{C}}-R$ / $CF_3-CH(CH_3)-\overset{O}{\overset{\|}{C}}-R$ $\xrightarrow{EtO^-/\Delta}$ $H_2C-CH(CH_3)-F$ (L.G.)

EWG.

$K_2CO_3 + H_2O \rightleftharpoons KOH + H_2CO_3$ Source of OH^-


EWG.
NO2
α
CH2—CH2—F
L.G
E1CB
CH3
α
H3C=CH—CH2—CH3
NMe3
+
L.G
(EWG)
E2
Hoffman
PdL
α
CH2—CH2—F
CCl3
EWG
L.G.
E1CB
CH3
CH3—CH—CH—CH3.
SMe2
+
(EWG)
E2
Hoffman
PdL
α
CH2—CH—Cl
CH3
EWG
L.G
E1CB.
EWG.
CO2R
CH2
CH2—F
L.G.
L.G.
E1CB

: Mechanism :

E1CB. $(O_2N)-\beta CH_2-CH_2-F \xrightleftharpoons{RO^{\ominus}\ slow\ K}$ $O_2N-\overset{\ominus}{C}H-CH_2-F$ (r.d.s.)

Hydrogen acidic ; removed.

$\ominus$ charge formed as intermediate.

$O_2N-CH=CH_2$

=> Unimolecular ; rate $= K[Int]$.

=> carbanion is formed as intermediate $= K.K'[R-X][Base]$.

2nd order reaction.

=>

HOMEWORK : α-Complete : $K' = \frac{Int}{[R-X][Base]}$

β-Complete.