

# Electrophilic & Free Radical Addition Reaction

B.Sc. Sem – VI

Paper : CC CH : 602

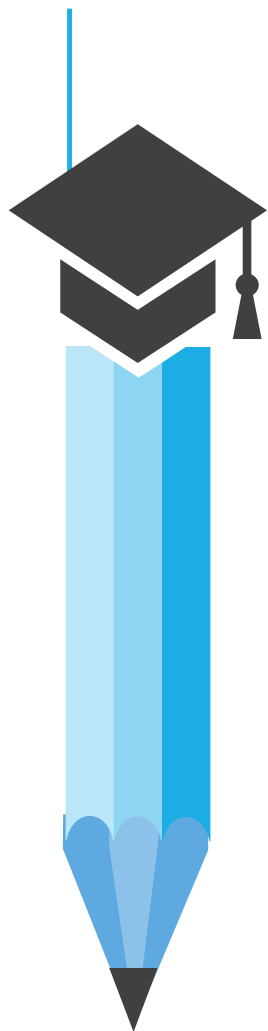
Unit – 1



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# SYLLABUS



- Addition to carbon – carbon double bond
- Markonikovs rule
- Electrophilic addition, orientation, reactivity
- Rearrangement, Dimerization, Alkylation
- Peroxide effect (Anti-markonikov)
- Free radical addition, Mechanism of peroxide initiated addition of HBr
- Syn and anti addition mechanism for addition of halogens
- Electrophilic addition to conjugated dienes (1:2 v/s 1:4 addition)
- Free radical addition to conjugated dienes & reactivity

- ❖ Organic chemistry by morrisson & boyed : V<sup>th</sup> edition
- ❖ Advanced organic chemistry by R.K.Bansal
- ❖ Organic chemistry by I.L.Finar volume I & II (V<sup>th</sup> edition)
- ❖ Organic reaction & mechanism II<sup>nd</sup> edition by P.S.Kalsi
- ❖ Organic chemistry by S.M.Mukharjee, S.P.Singh, R.P.Kapoor

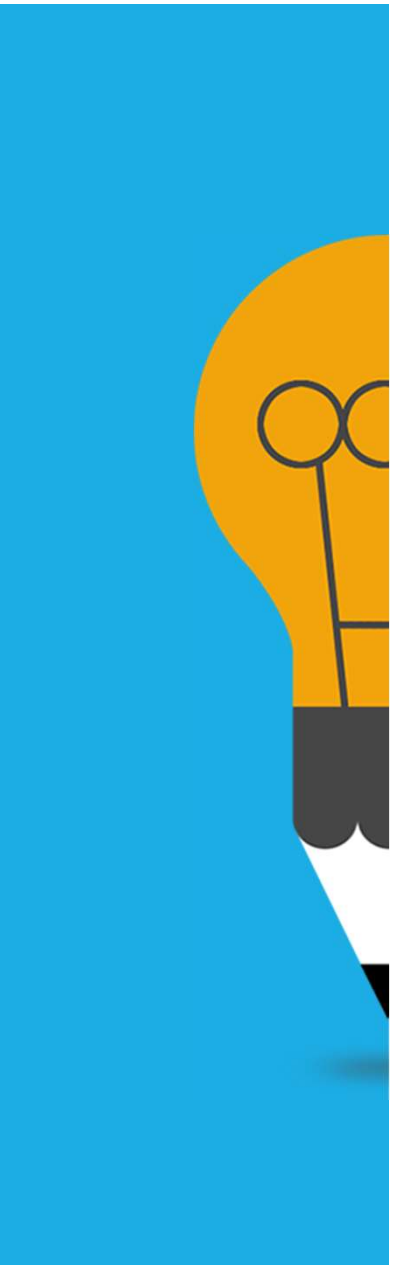
## REFERENCE BOOKS




## COs : Course Outcomes



To enable students about basic knowledge of Markonikovs & Anti-Markonikovs rule, Electrophilic addition, and free radical addition reaction.



- Homolytic Fission & Free Radical
- Heterolytic Fission & Electrophile
- Electrophile
- Addition reaction
- Free radicals
- Types of Addition reaction
  - Hydrogenation
  - Halogenation
  - Hydro halogenation
  - Hydration



**Electrophile** : Cation or Neutral molecule which are obtained by heterolytic fission and have tendency to accept electron pair is known as electrophile. eg.  $\text{NO}_2^+$ ,  $\text{Cl}^+$ ,  $\text{SO}_3\text{H}^+$  etc.

**Free Radical** : Atoms which are obtained by homolytic fission and having unpaired electrons are called free radical.

**Addition Reaction** : Unsaturated compound convert into saturated compound without loss of atoms.

# Type of Reactions

01

**Addition Reaction :** One molecule combine with other molecule and form new compound without loss of atoms.

02

**Elimination Reaction:** A pair of atoms or groups of atoms are removed from a molecules

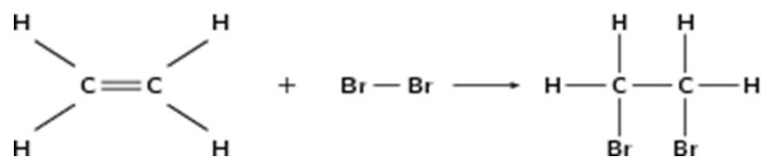
03

**Substitution Reaction:** One functional group is replaced by another functional group

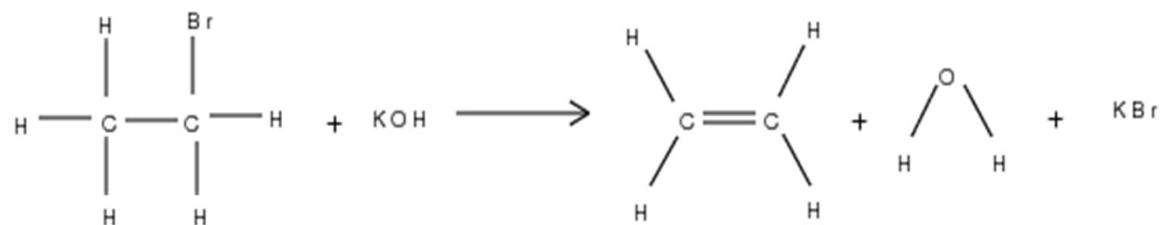
04

**Rearrangement Reaction:** Substituent moves from one atom to another atom in the same molecule.

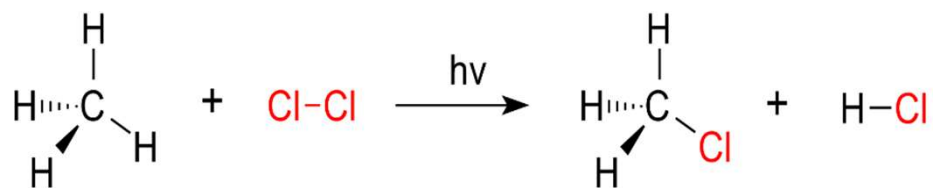
## Addition Reaction



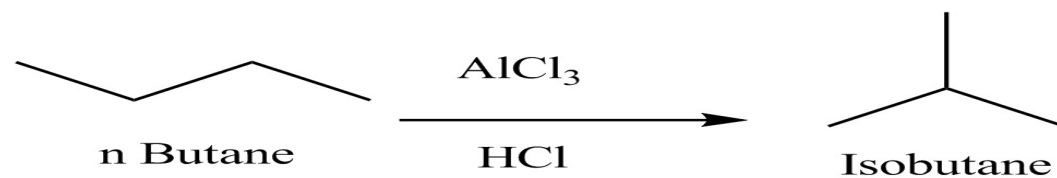
## Elimination Reaction



## Substitution Reaction



## Rearrangement Reaction

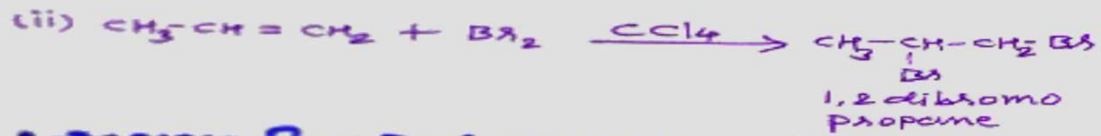
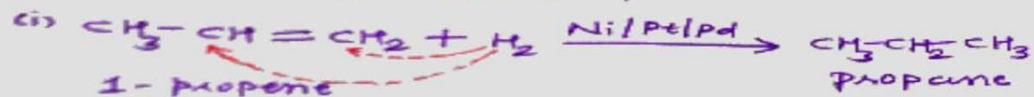




**• Addition Reaction :**

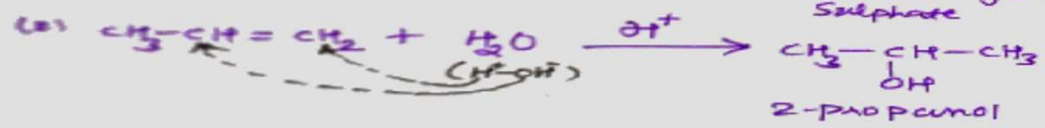
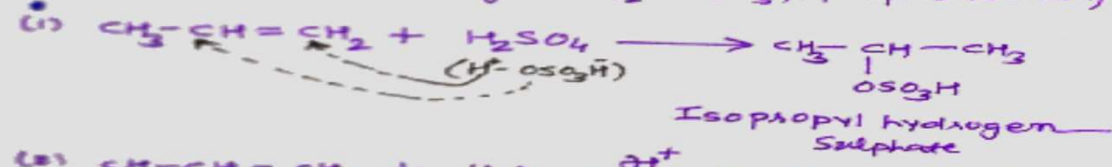
→ When unsaturated comp. reacts with any reagents at this time π bond breaks and new compound form without loss of any atoms. This kind of reaction is called addition reaction.

**• समप्रतिबन्धी अणुकील प्रक्रियायाः**  
(e.g. H<sub>2</sub>, Cl<sub>2</sub>...)

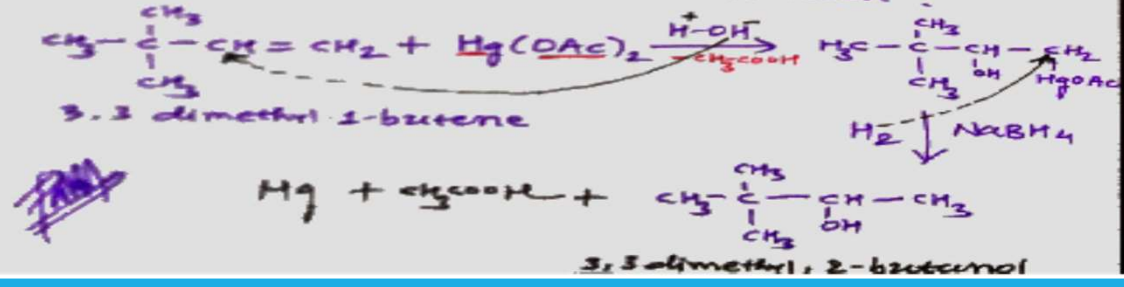


**• असमप्रतिबन्धी अणुकील प्रक्रियायाः**

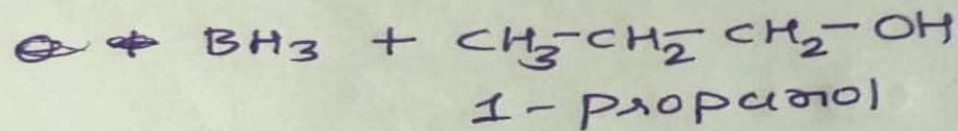
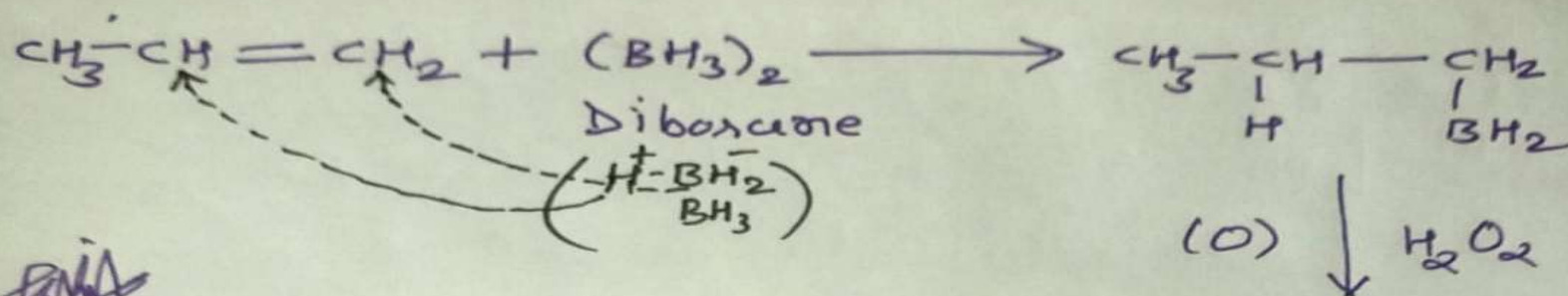
(e.g. H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O, Hg(OAc)<sub>2</sub>, BH<sub>3</sub>, polymerisation)



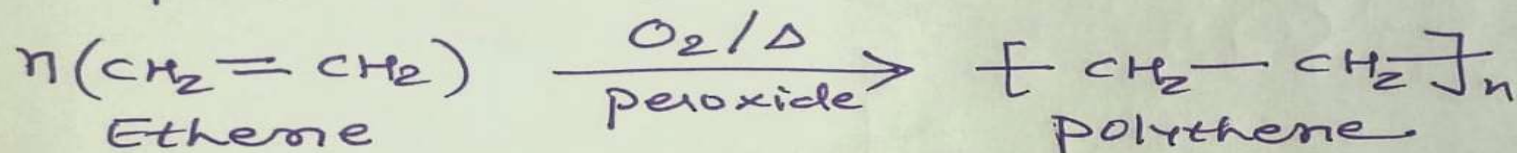
(3) Oxymercuration-Demercuration :



(4) Hydroboration - Oxidation (Anti markov...)



(5) Polymerisation:



## Markonikov's Rule

01

Rule

02

Examples

03

Mechanism

04

Other examples

05

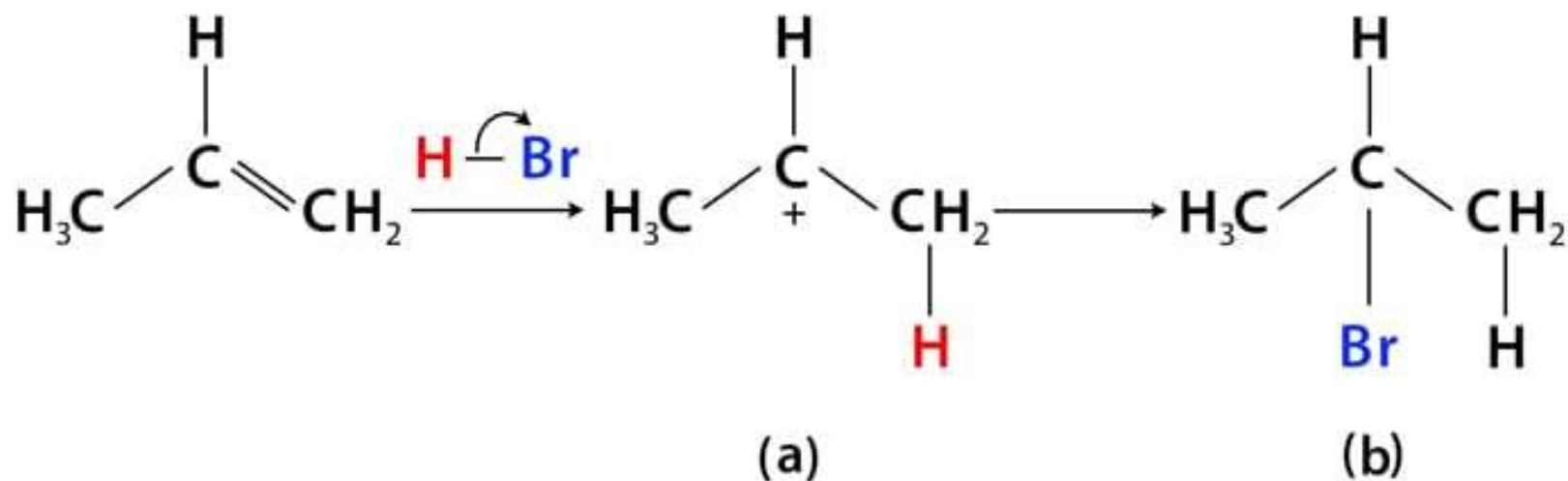
Potential energy diagram

## Markonikov's Rule :

Markonikov's rule also known as Markownikoffs rule. The Russian chemist Vladimir Vasilyevich Markonikov first formulated this rule in 1865.

**Rule :** When an unsymmetrical alkene reacts with an unsymmetrical reagent then more positive part of unsymmetrical reagent goes to the carbon that have more hydrogen atoms.

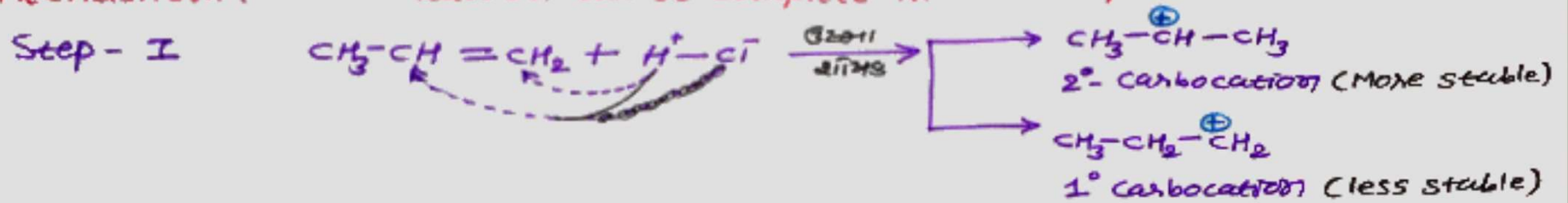
# Markovnikov's Rule Basic Mechanism



(a) •hydrogen (H) added to  $1^\circ$  carbon (C) for more stable carbocation

(b) •bromine (Br) added to  $2^\circ$  carbocation to give product

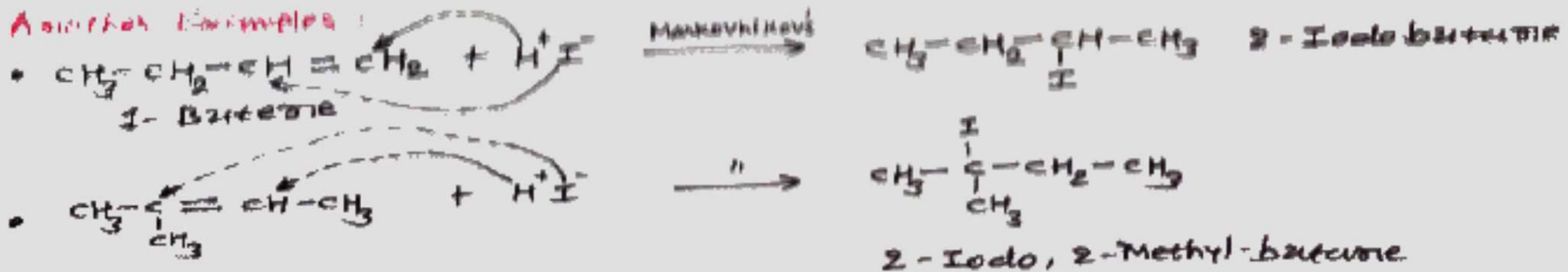
\* Mechanism: This reaction will be complete in two steps:

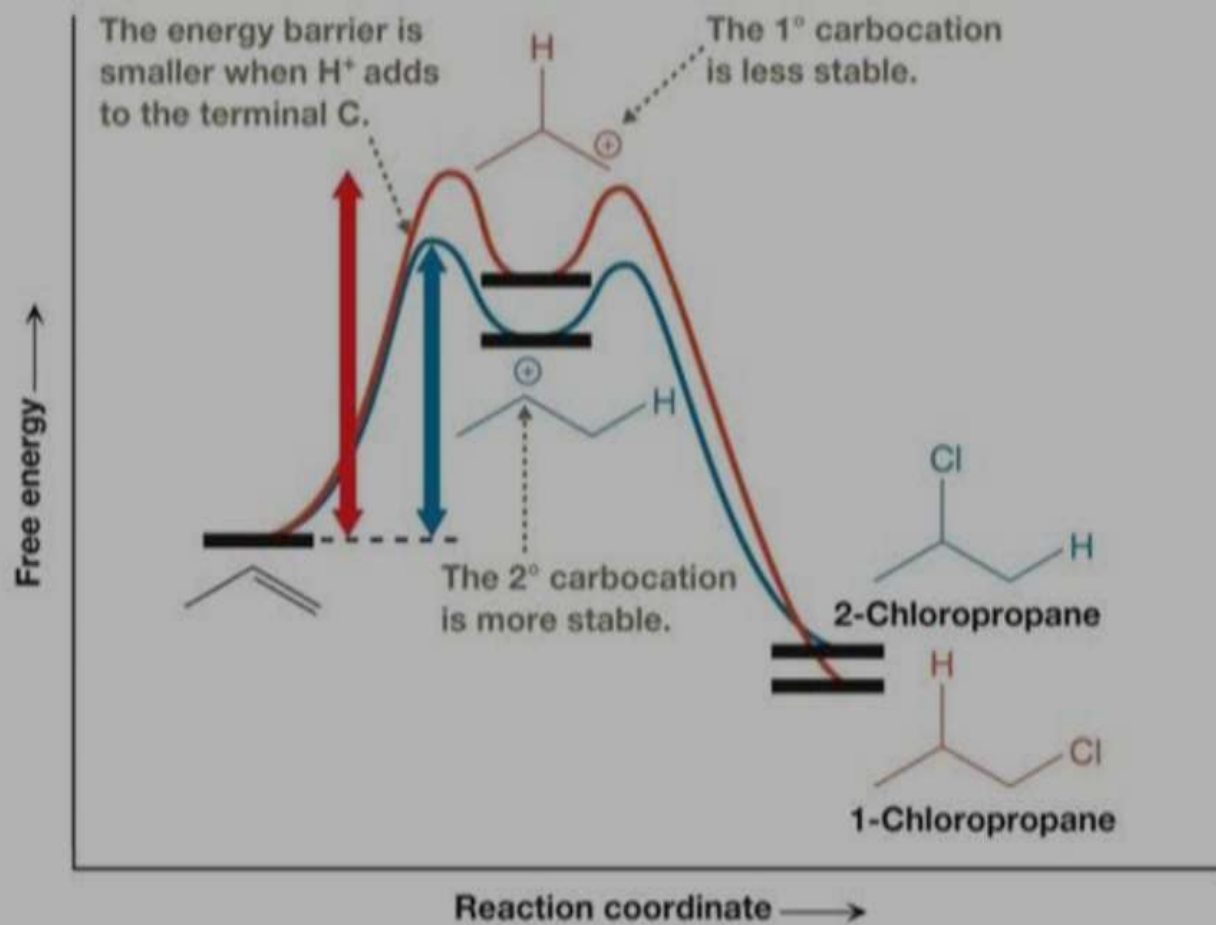


→ અહીં પ્રથમ તબક્કો ધીમો છે. આથી તે વેગનિર્ણાયક તબક્કો છે. આ તબક્કા દરમિયાન 2° કાર્બોકેશાયન બને છે જેના માટે  $\Delta G_2$  નું મૂલ્ય ઓછું છે આથી તેમાંથી બીજા તબક્કામાં બીજા તબક્કાનું ઝડપથી ઉત્પન્ન થાય છે. જ્યારે 1° કાર્બોકેશાયન માટે  $\Delta G_1$  નું મૂલ્ય વધુ છે આથી તે પ્રમાણમાં ઓછો સ્થાયી છે.



\* Another Examples:





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# Anti Markonikov's Rule: (Free Radical Addition)

01

Rule

02

Examples

03

Mechanism

04

Other examples

**Anti Markonikov's Rule:**  
**(Free Radical Addition)**



# Electrophilic Addition : Rearrangement

2<sup>o</sup> Carbonium ion  
(less stable)



3<sup>o</sup> Carbonium ion  
(More stable)

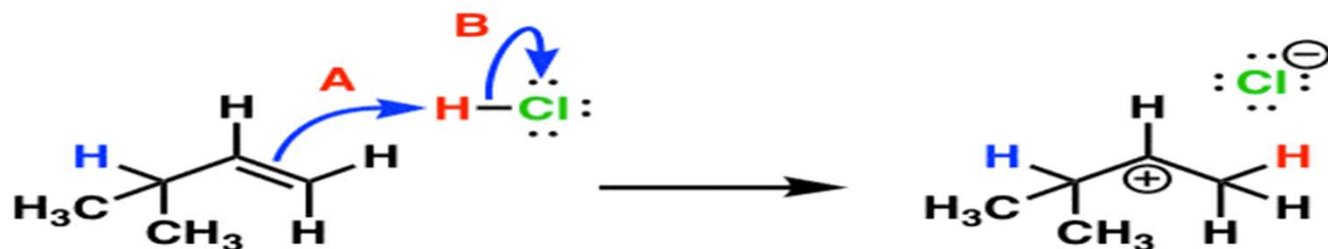


Product



Product

**Step 1 - attack of alkene on H-Cl (arrows A and B)**



|          | Form               | Break                                    |
|----------|--------------------|--|
| <b>A</b> | C <sub>1</sub> -H  | C <sub>1</sub> -C <sub>2</sub> ( $\pi$ ) |
|          | C <sub>2</sub> -H  | C <sub>3</sub> -H                        |
|          | C <sub>3</sub> -Cl | <b>B</b> H-Cl                            |

*Observation: secondary carbocation*

**Step 2 - rearrangement (arrow C)**

Recall the order of carbocation stability: tertiary > secondary > primary  
 Migration of the C-H bond from C<sub>3</sub> to C<sub>2</sub> results in a more stable carbocation!  
 This arrow says, "break the C<sub>3</sub>-H bond and form a new C<sub>2</sub>-H bond"



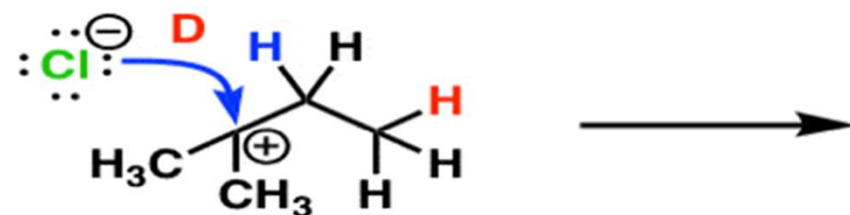
|          | Form               | Break                                    |
|----------|--------------------|--|
|          | C <sub>1</sub> -H  | C <sub>1</sub> -C <sub>2</sub> ( $\pi$ ) |
| <b>C</b> | C <sub>2</sub> -H  | C <sub>3</sub> -H                        |
|          | C <sub>3</sub> -Cl | H-Cl                                     |

*Secondary carbocation*

*Tertiary carbocation*

**a more stable carbocation**

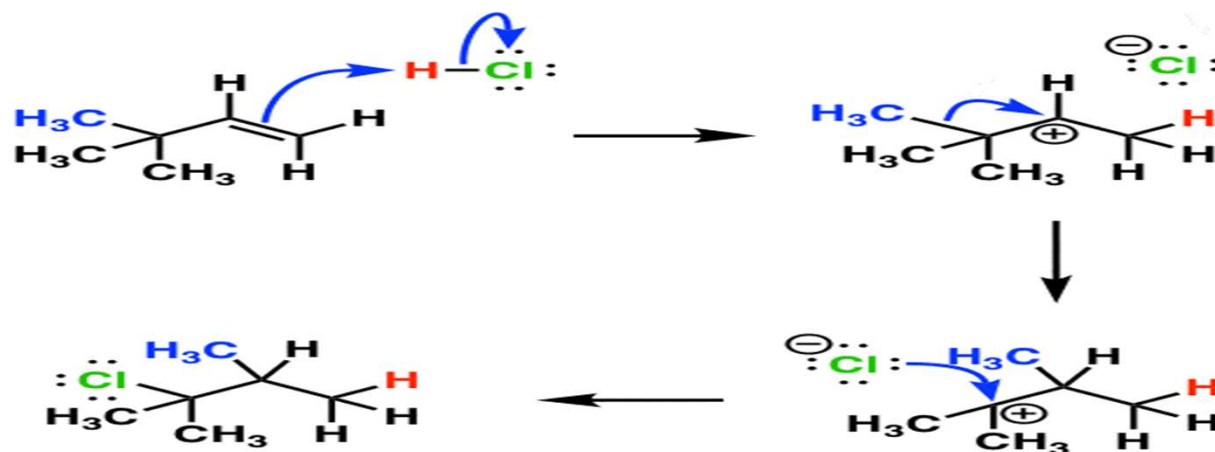
### Step 3 - Attack of nucleophile (arrow D)



*Tertiary carbocation*

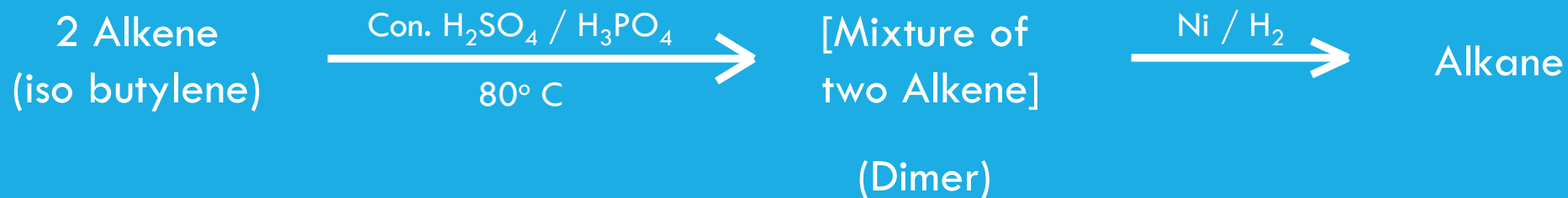
| Form                        | Break                          |
|-----------------------------|--------------------------------|
| C <sub>1</sub> -H           | C <sub>1</sub> -C <sub>2</sub> |
| C <sub>2</sub> -H           | ( $\pi$ )<br>C <sub>3</sub> -H |
| <b>D</b> C <sub>3</sub> -Cl | H-Cl                           |

Alkyl shift example:



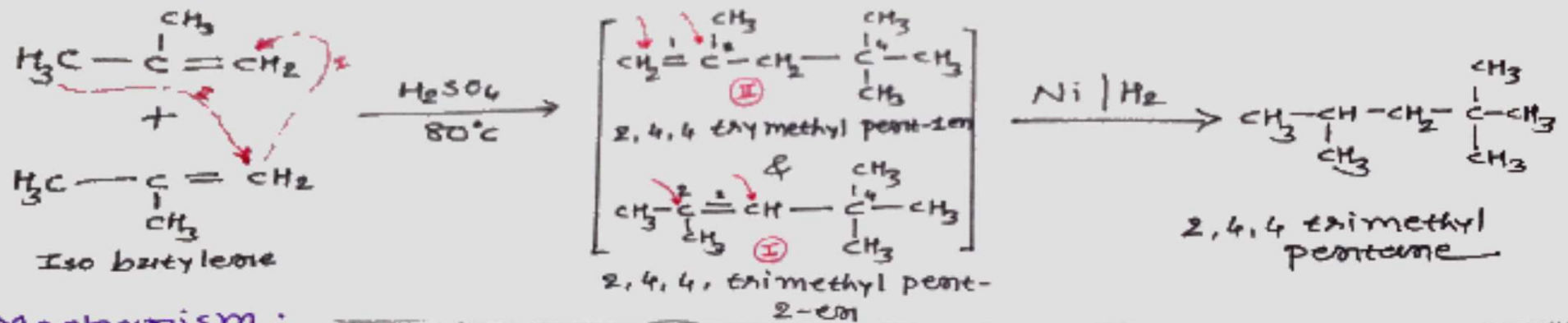
# Electrophilic Addition : Dimerization

(Dimerization of Isobutylene)

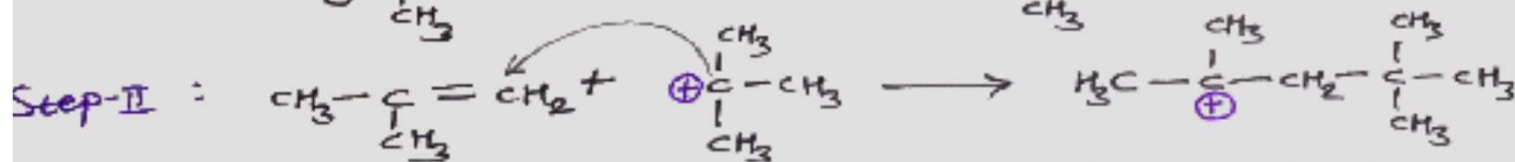
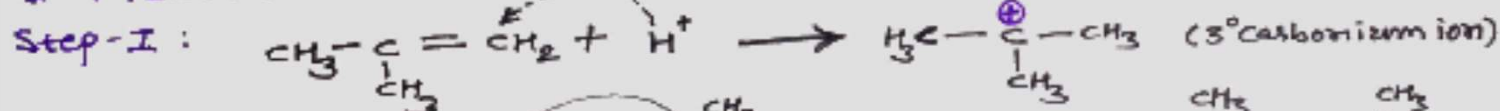




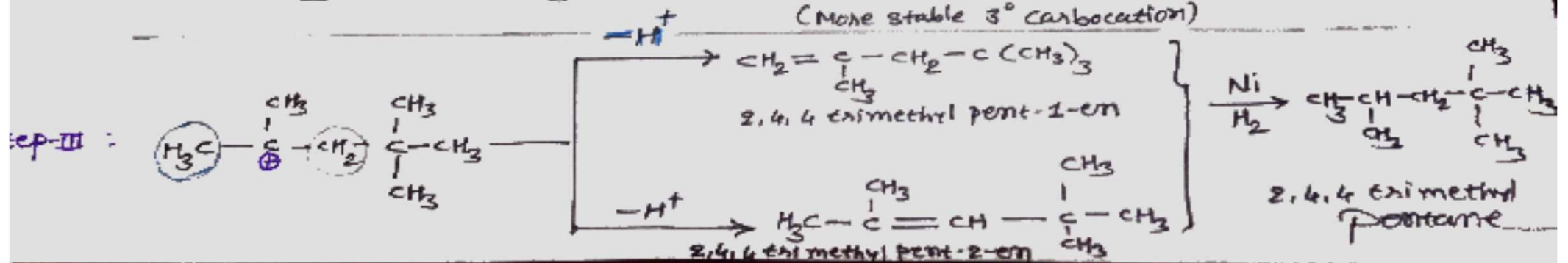
\* Electrophilic Addition: Dimerisation: (Reaction)



\* Mechanism:

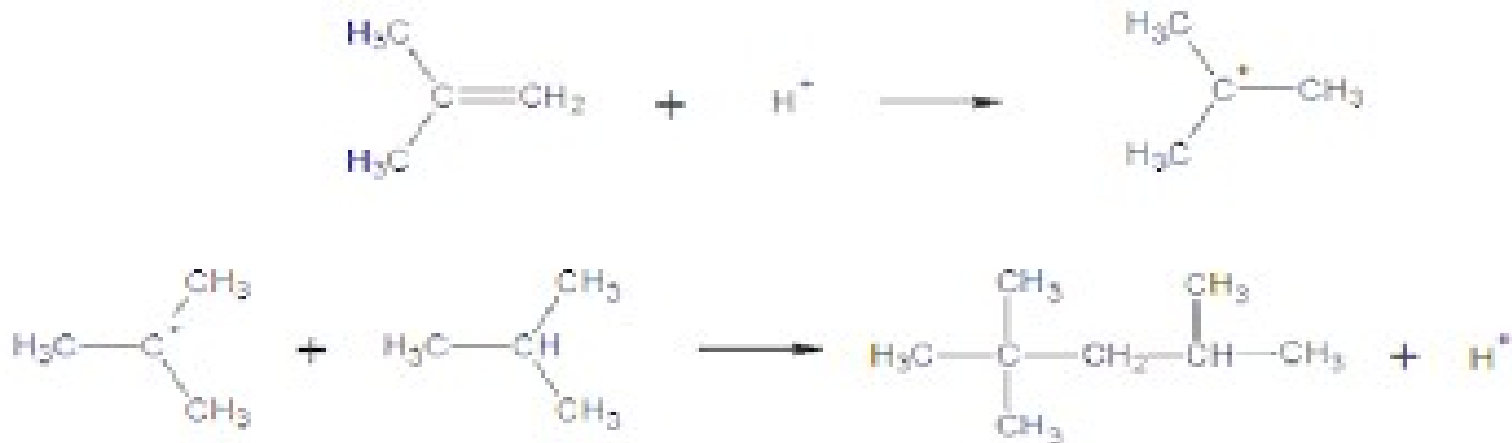
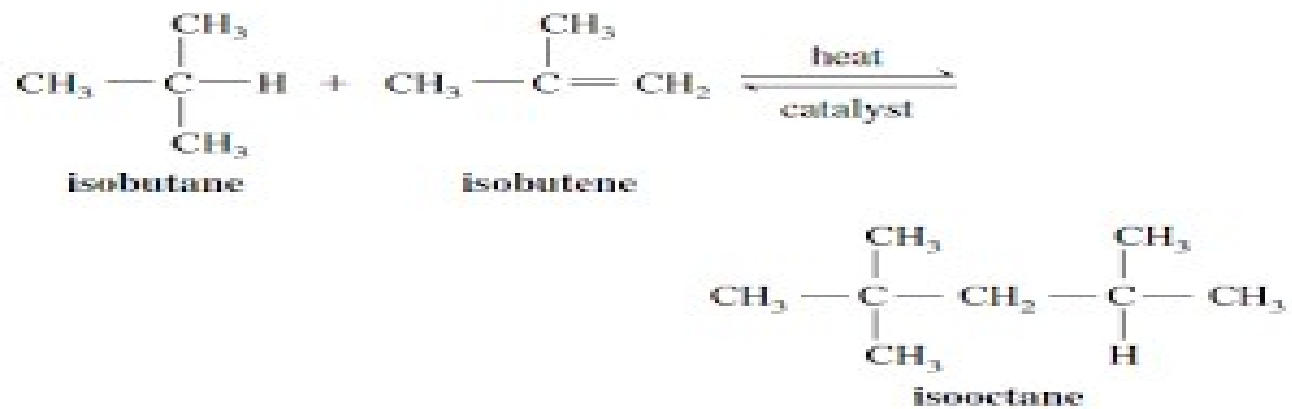


(More stable 3° carbocation)

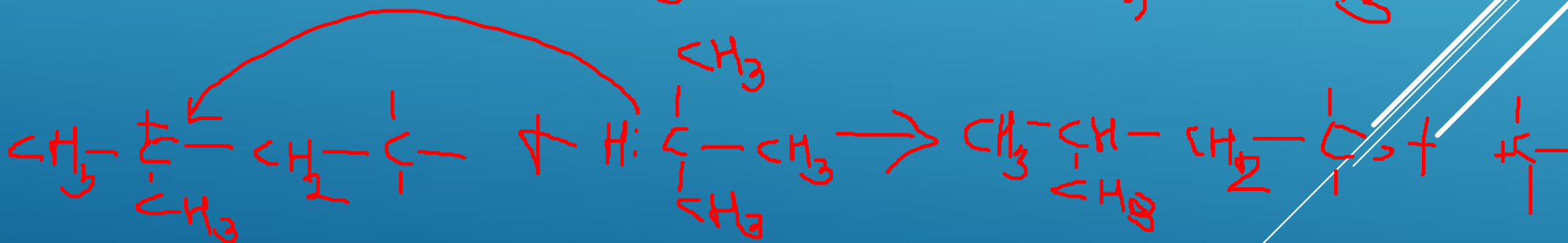
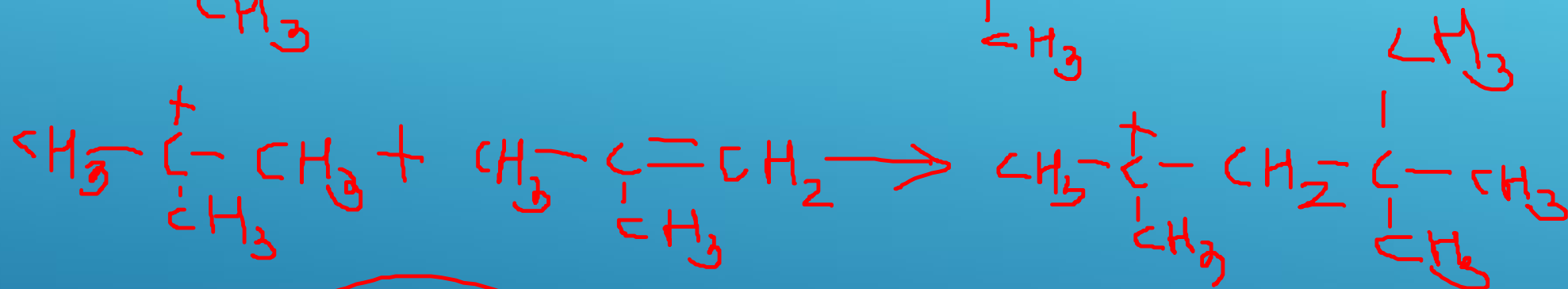
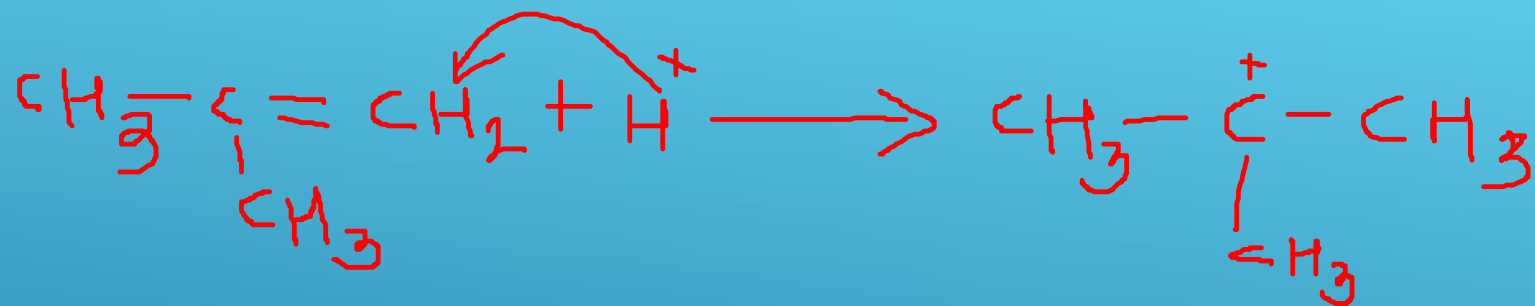


# Electrophilic Addition : Alkylation









# Polymerization of Diene by Free Radical Reaction

1:3 Butadiene



Poly 1:3 Butadiene

Isoprene



Cis – poly isoprene  
(Natural Rubber)

Natural Rubber



Vulcanized Rubber

chloroprene



Polychloroprene

મુક્તમૂલક રીતે ડાઈન નું જલુલીકરણ ~~જ~~ વજાર  
 - તથા તેના વિસ્થાપકોની જગાવટ :

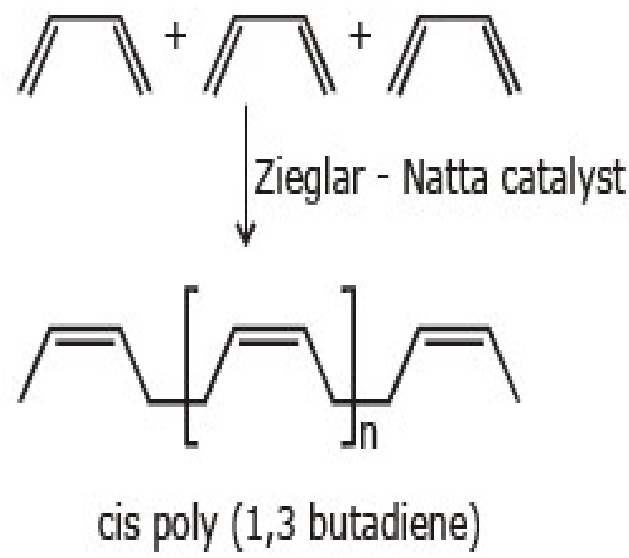
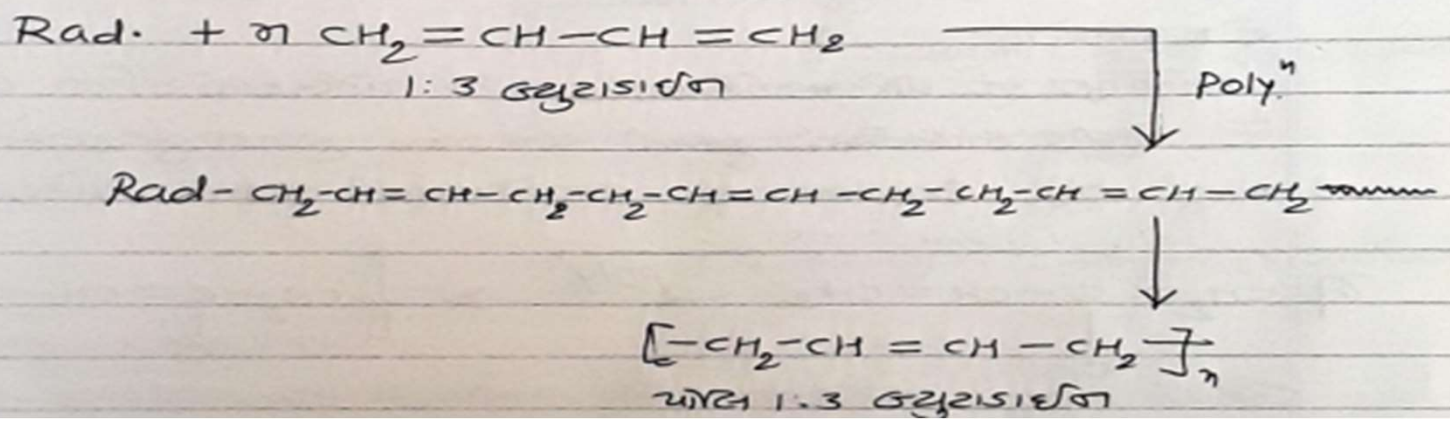
**Polymerisation of Diene by Free Radical Reaction :**

- 1:3 જુગ્ગસાઈન → ચોલે 1:3 જુગ્ગસાઈન
- ક્રાંતિયુગ → cis ચોલે સમસ્થાપન (જુગ્ગસાઈન)
- કુદરતીય → વાકે-વજાર
- ક્રાંતિયુગ → પાસિમ્પોઝીન

→ ડાઈન સંચાલકોનું મુક્તમૂલક ક્રિયાવિધિના જલુલીકરણ  
 કરવાથી જ વજાર ને તેના વ્યુત્પન્નો મુરત થાય છે.

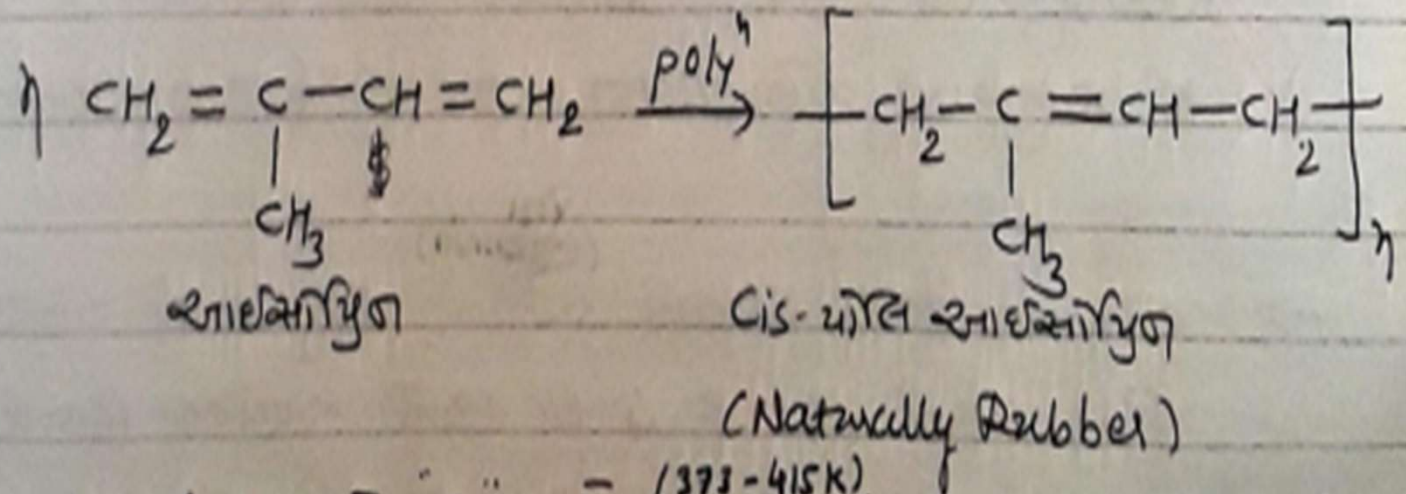
e.g.

1:3 જુગ્ગસાઈનનું મુક્તમૂલક ક્રિયાવિધિની મદદથી જલુલીકરણ  
 કરવાં ચોલે 1:3 જુગ્ગસાઈન મુરત થાય છે. આ પ્રક્રિયા 1:4 ચોલેની  
 દ્વારા થાય છે.



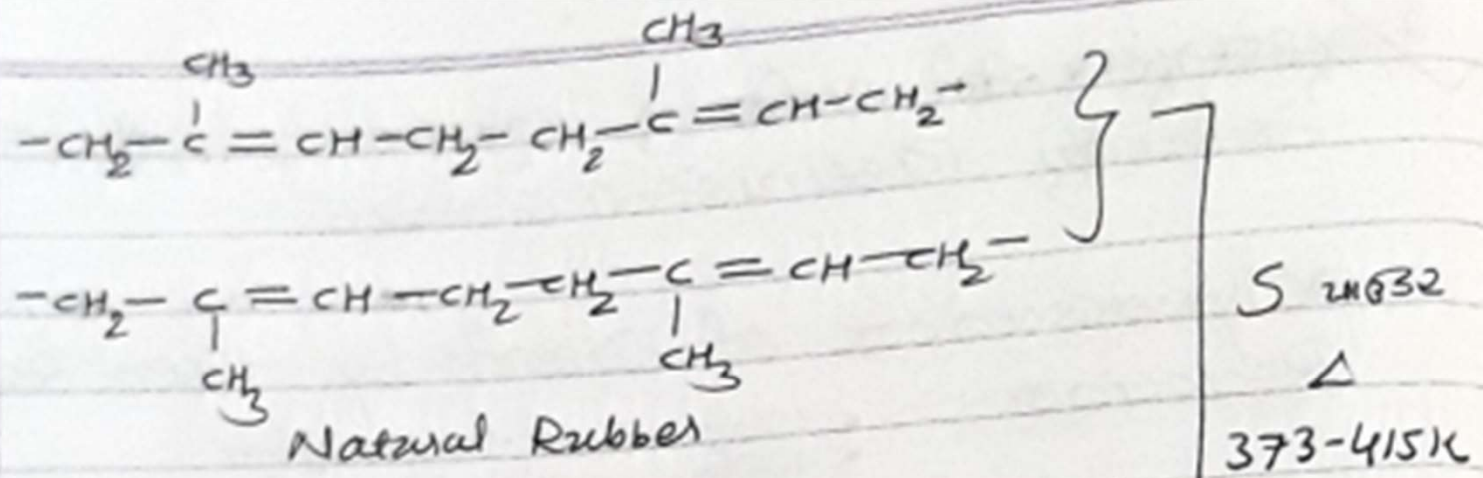


\* Naturally Rubber :

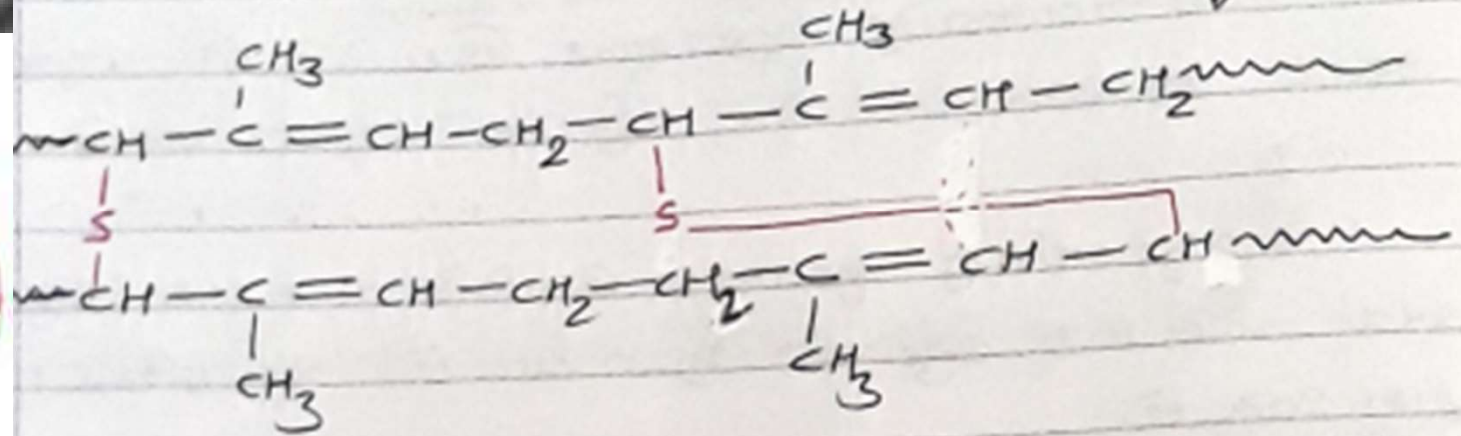


→ કુદરતી રબરને "S" આથે (373-415K) ગરમ કરતા કુદરતી રબર ની કો જીંટલા વચ્ચે "S" bridge બનાવે છે પરિણામે રબર સરળ & મજબૂત બને છે. આ પ્રક્રિયાને Vulcanisation કહે છે & આ રબરને Vulcanised Rubber કહે છે.





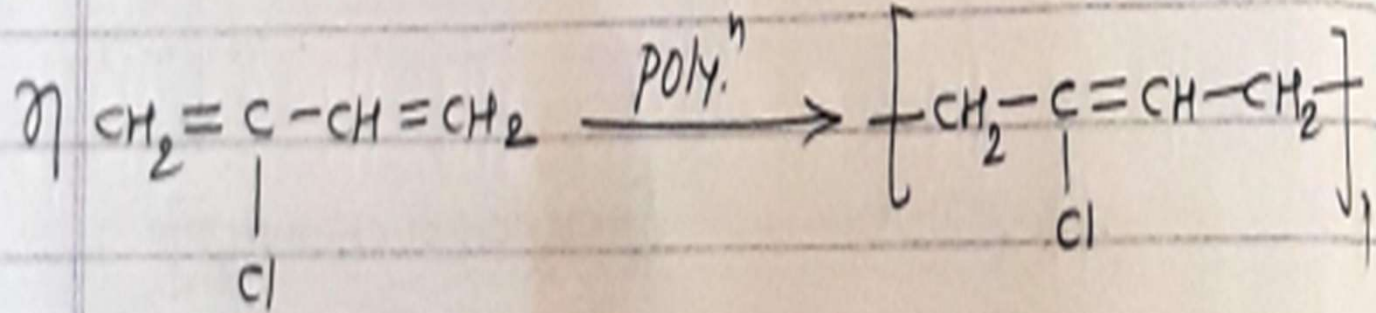
S 20832  
 $\Delta$   
 373-415K



Vulcanized Rubber

તે જ પુખાલો.

કલારોપિયન જુ પોલિમરાઈઝેશન કરવાથી પોલિકલારોપિયન બને છે જે કોટેલીક બાબતોમાં કુદરતી રક્ષકરક્તો મુલકા મુદ્દાદામાં વાપરે પરંતુ oil, Gasoline માં અકસાદેડતાની બાબતે અકિયાતા છે



Chloroprene

polychloroprene  
(Neoprene)



## Electrophilic Addition in Conjugated Diene or 1:4 Addition



# 1:4 Addition in Conjugated Diene :

કોન્જુગેટેડ સાઈન (અકોનવિટ દ્વિબંધ ધરાવતા) માં  
ઇન્-અનુરાગી યોગશીલન OR 1:4 યોગશીલન :

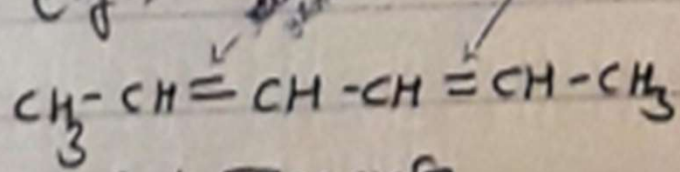
અકોનવિટ દ્વિબંધ ધરાવતા સાઈનની <sup>પોટા</sup> (બ્રહ્મચારી)  $Br_2$  સાથે યોગશીલ  
પ્રક્રિયા કરતાં 1 & 4 થા સ્થાને આવેલા દ્વિબંધ  
આગળ  $Br_2$  ક્રમશઃ ઉમેરાય છે & નીચાઈ તરફ  
ટ્રોફોલો આલ્ડેને મળે છે. આ પ્રક્રિયાને 1:4 યોગશીલ  
પ્રક્રિયા કહી શકાય છે.





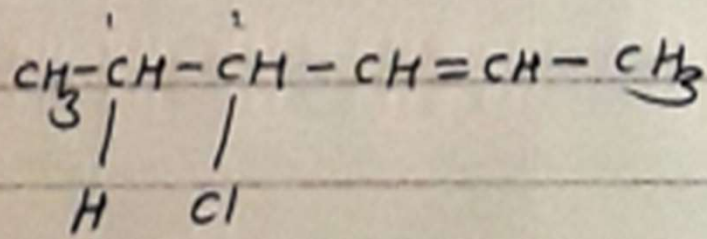
Step-III का उदाहरण

e.g.



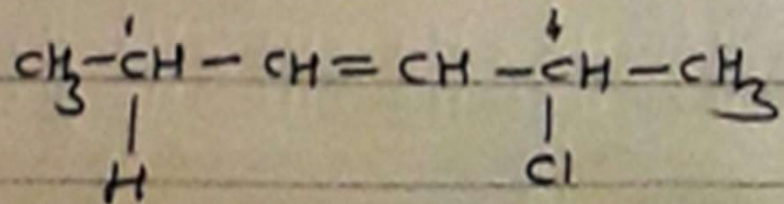
2,4-सुटकासिएन

HCl



4-इलाको, 2-सुटकासिएन (1:2 नियम)

+



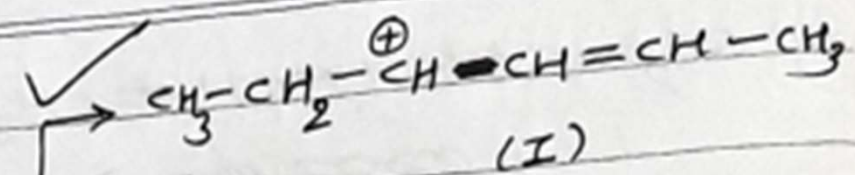
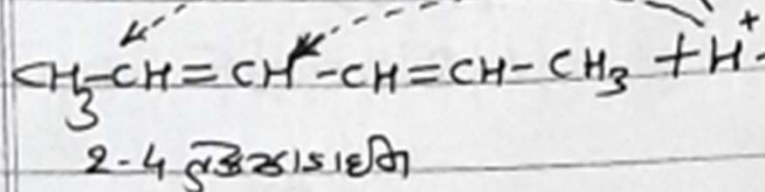
3-इलाको, 3-सुटकासिएन (1:4 नियम)

e.g. (3)

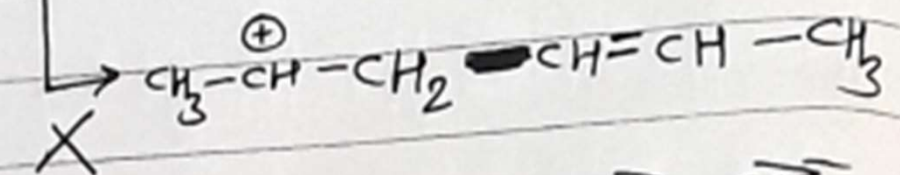
(15)

# Mechanism: 2,4-Heptadiene:

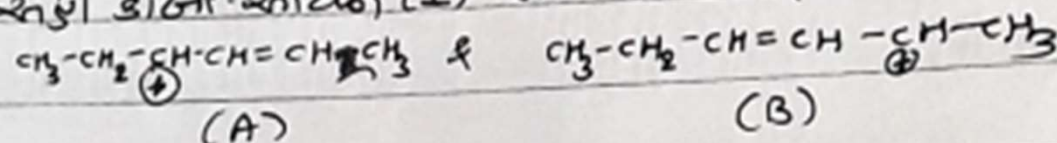
Step-I



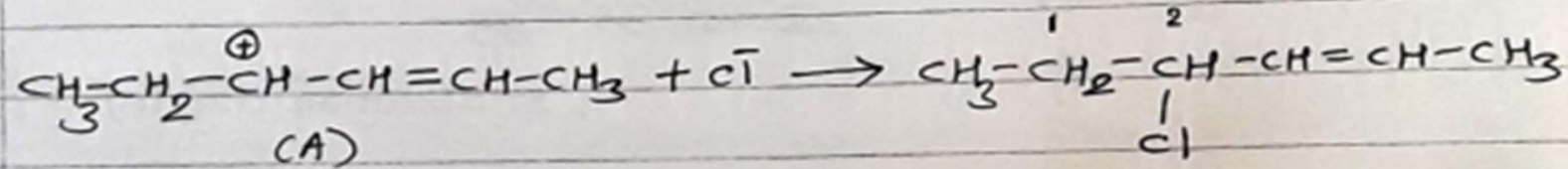
અલોઈલિક કાર્બો-આયન (સ્થાયી)



આમ પ્રથમ તબક્કામાં કોઈયુગેટે સ્થાનમાં ગભરો સકે છે તે સુગૃહીત પ્રક્રિયા થાય છે & સ્થાયી અલોઈલિક કાર્બો-આયન બને છે. અહીં કાર્બો-આયન (I) નાં બે સ્વરૂપો શક્ય છે.

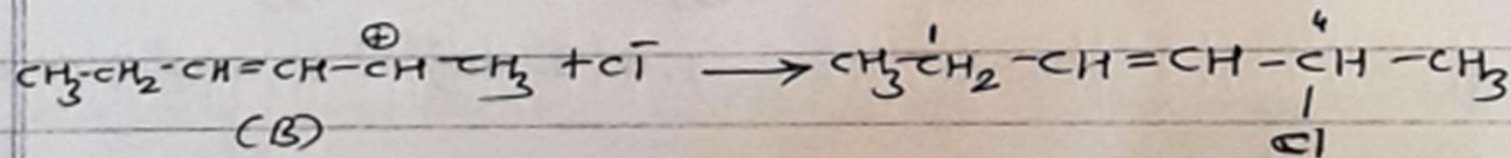


Step-II



(1:2 યોગશીલન)

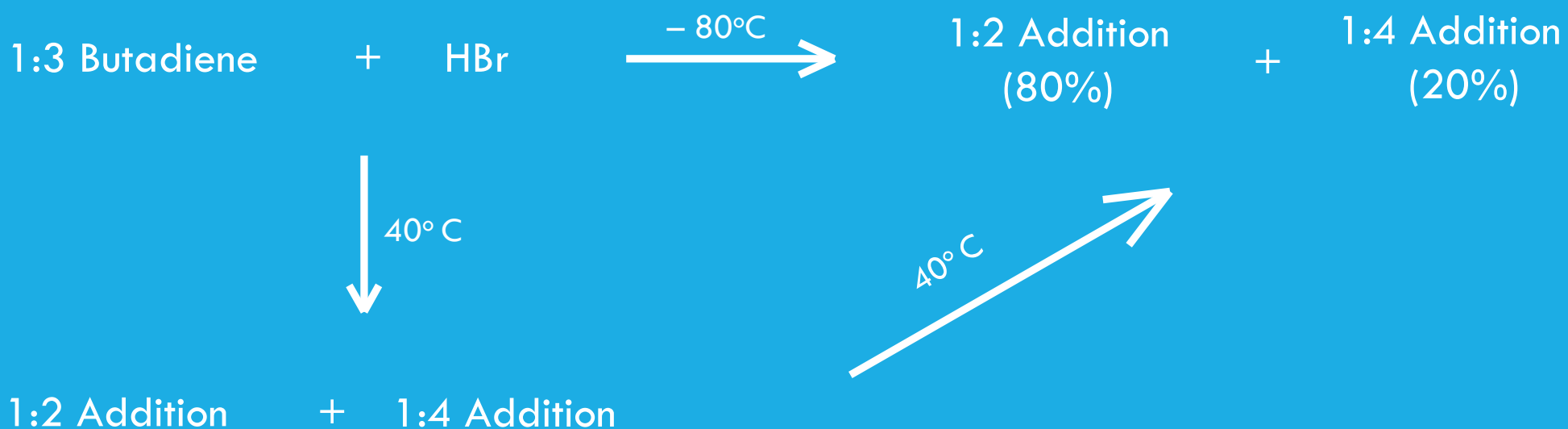
+



(1:4 યોગશીલન)

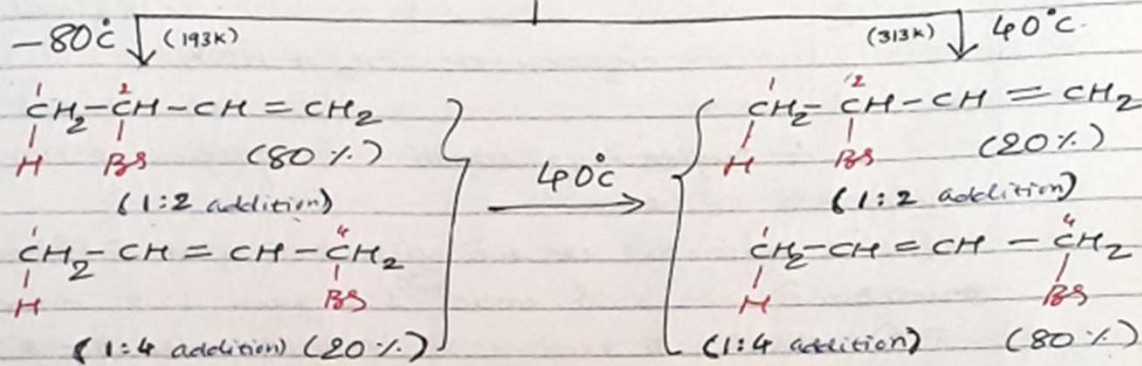
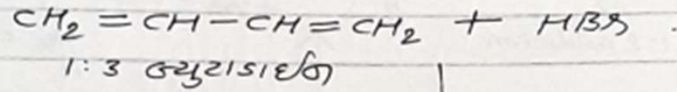
દ્વિતીય તબક્કામાં કાર્બો-સાયકલ (A) & (B) ની Cl<sup>-</sup> સાથે પ્રક્રિયા થવાં 1:2 કે 1:4 યોગશીલન પ્રક્રિયા થાય છે & આથી 1:2 યોગશીલન કે 1:4 યોગશીલન નીચક મળે છે.

# 1:2 Vs 1:4 Addition or Rate Vs Equilibrium



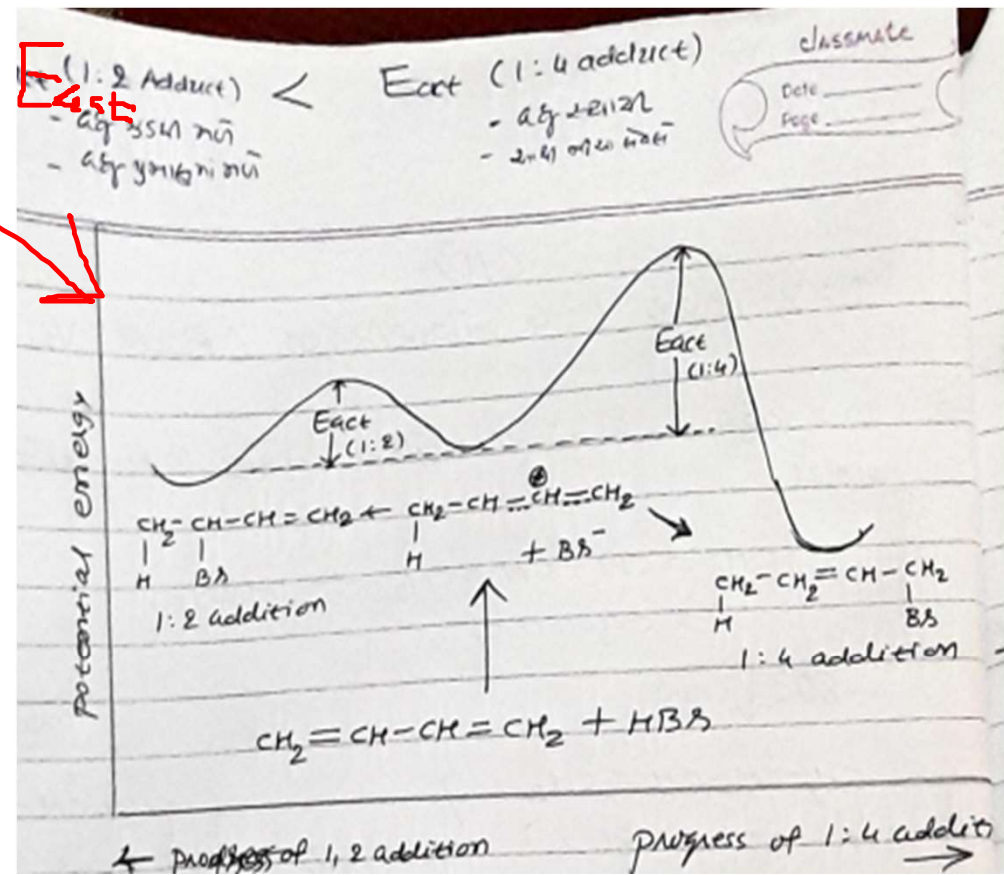
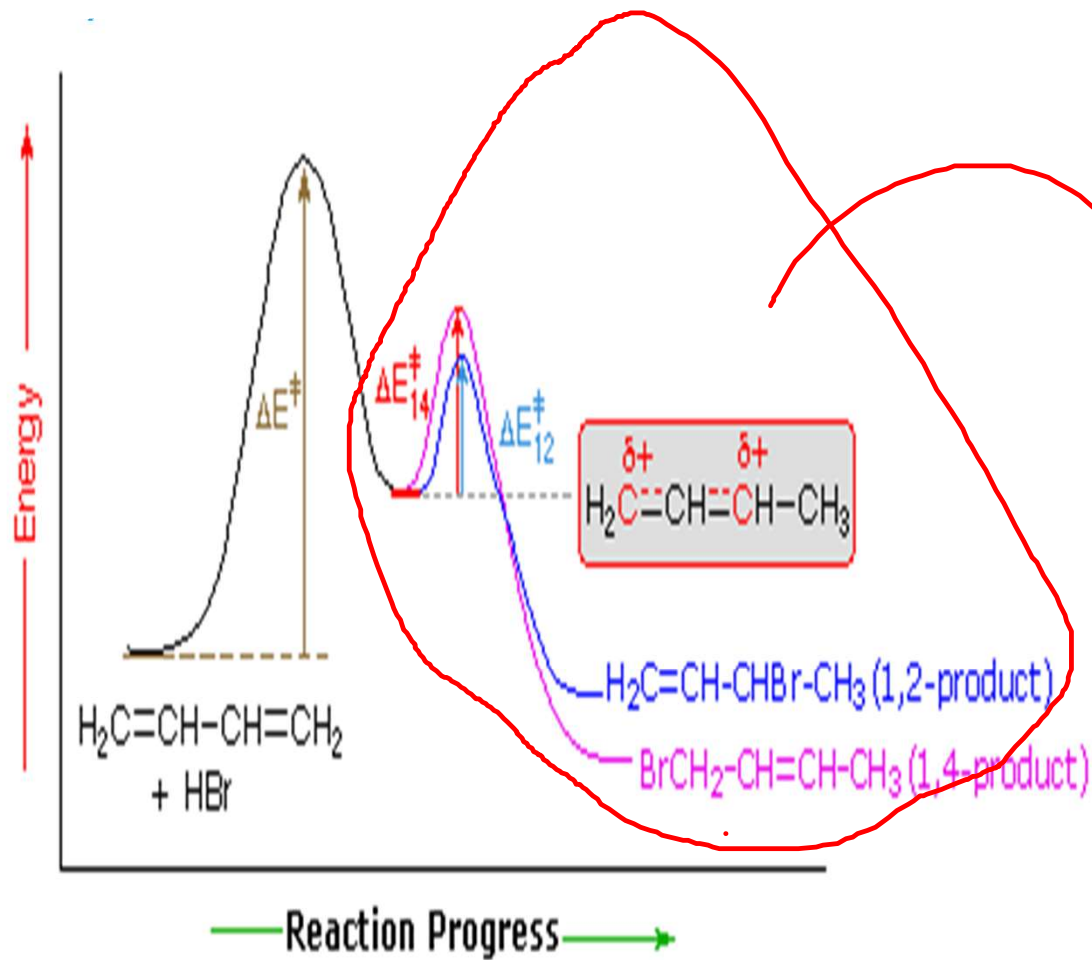
1:2 વિયુદ્ધ 1:4 સંતોલન (Rate Vs. Equilibrium)

1:2 વિયુદ્ધ 1:4 સંતોલન પ્રક્રિયા નીચેજ ઉ.દા. લઈને સમજાવવામાં આવેલ છે.



→ ઉપર દર્શાવેલા મુજબ 1:3 ઉચ્ચરિસિદ્ધિ ની HBr સાથે  $-80^\circ\text{C}$  તાપમાને પ્રક્રિયા કરવાથી 80% 1:2 & 20% 1:4 નીપજ મળે છે જ્યારે  $40^\circ\text{C}$  તાપમાને પ્રક્રિયા કરવાથી 20% 1:2 & 80% 1:4 નીપજ મળે છે. આ નીપજ તાપમાન પર આધારિત છે. આવી તરતની વચ્ચે સંતુલન સ્થાપાયેલું હોય છે. આવી વસ્તુઓમાં સંતુલન મિશ્રણમાં 1:4 નીપજ નું પ્રમાણ વધારે હોય છે.

→ આથી  $-80^\circ\text{C}$  તાપમાને 1:4 કરતાં 1:2 નીપજ વધુ પ્રમાણમાં મળે છે. આમતિ 1:4 કરતાં 1:2 નીપજ કુદરતી જગ છે. તાપમાન વધારવાથી આ મિશ્રણ આ સંતુલન મિશ્રણમાં ફેરવાય છે. આમ

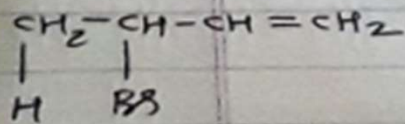
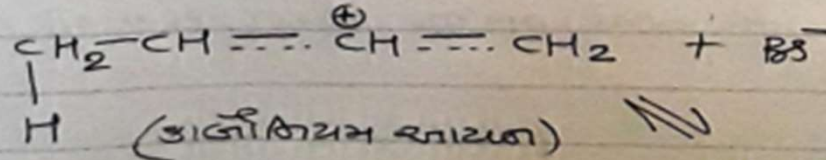
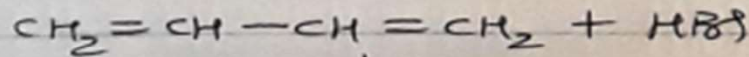


આલેન પરથી કહી શકાય કે,

અહીં 1:3 બ્રુકાઇનની HBr સાથે પ્રક્રિયા થતાં પ્રથમ કાર્બોકેટિયમ આયન ઉત્પન્ન થાય છે. આ કાર્બો-આયન<sup>મિડી</sup> 1:4 કરતાં 1:2 નીપજ ઝડપ મળે છે. આથી 1:4 કરતાં 1:2 નીપજની સક્રિયકરણ શક્તિ (E) ઓછી હોય છે. આમ છતાં પણ 1:2 નીપજ કરતાં 1:4 નીપજ વધુ સ્થાયી છે. આથી તેને સૌથી નીચા લેવેલ દર્શાવેલ છે.

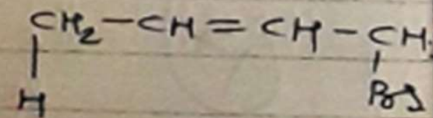
ઉપર દર્શાવેલા મુજબ 1:2 & 1:4 નીપજો (એલેનિલ બ્રુકાઇન) સરળતાથી આયનકરણ થઈ શકે છે. આથી આયન ઉત્પન્ન કરે છે. આથી 1:2 વધુ 1:4 નીપજ આ કાર્બો-આયન દ્વારા સંકુલન સ્થિતિ ધારણ કરે છે.

✓ અહીં 1:2 નીપજ ઝડપથી જન્ય છે & ઝડપથી આયનકરણ થાય છે. જ્યારે 1:4 નીપજ ધીમથી જન્ય છે & ધીમથી આયનકરણ થાય છે. આમ કોઈ T વધુ સ્થાયી (1:4) નીપજ મળે છે. અર્થાત્ 1:2 નીપજ આ 1:4 નીપજ કરતાં ઝડપથી જન્ય છે.



1:2 નીપજ

18



1:4 નીપજ



# Free Radical Addition in Conjugated Diene



# Syn and Anti Addition Reactions :

[https://www.youtube.com/hashtag/anti\\_products](https://www.youtube.com/hashtag/anti_products)

<https://www.youtube.com/watch?v=EbLLEbt9>

<https://youtu.be/EbLLEbt96Cs6Cs>

# Stereo Selective and Stereo Specific Reactions :

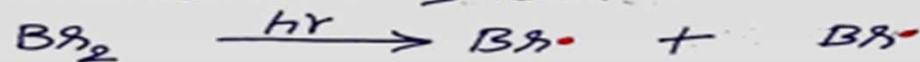
<https://youtu.be/wVAQ-HGf4vI>

<https://youtu.be/rAKjN99FlhU>

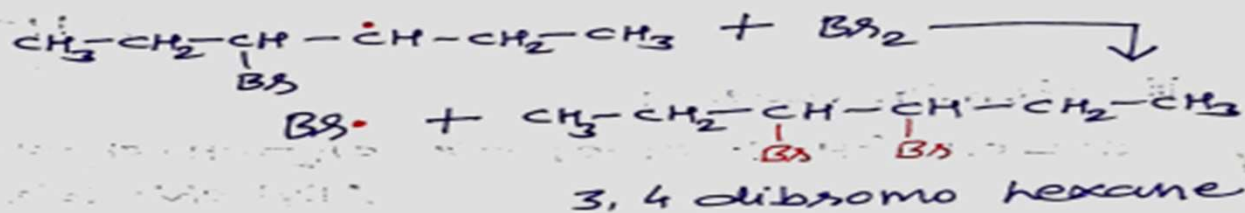
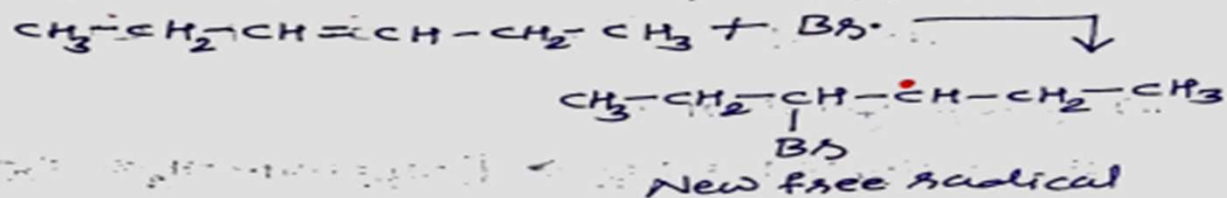
<https://youtu.be/VClr6T2NhLo>

## Free Radical Addition Reaction of 3-hexene with $\text{Br}_2$ :

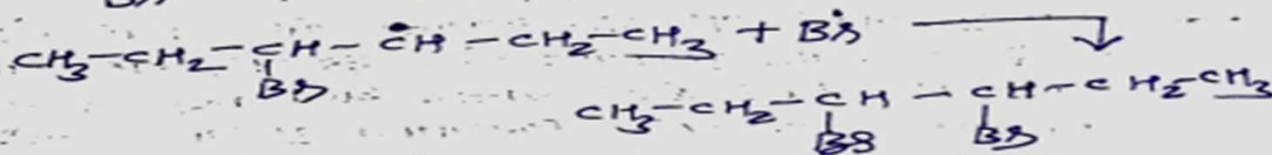
(i) Initiation : प्रारंभ :

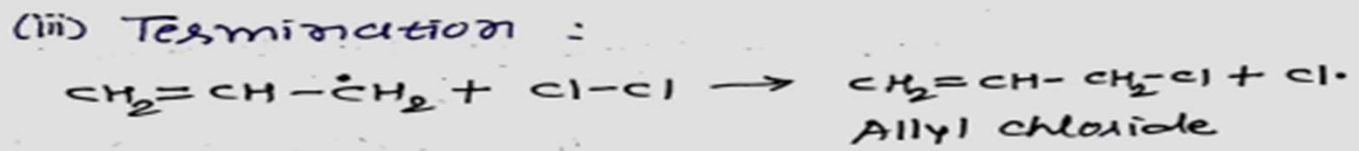
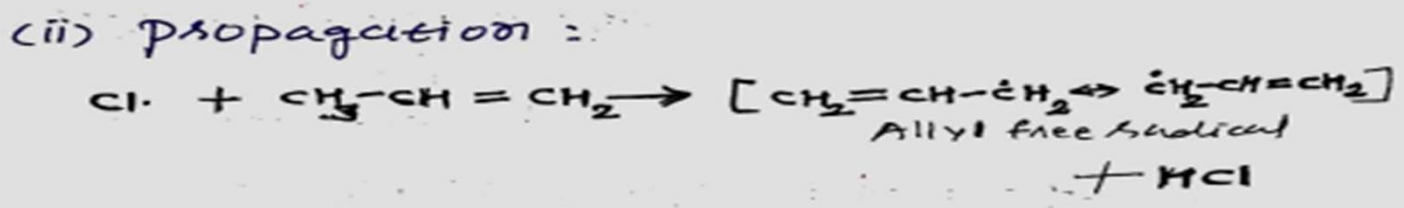
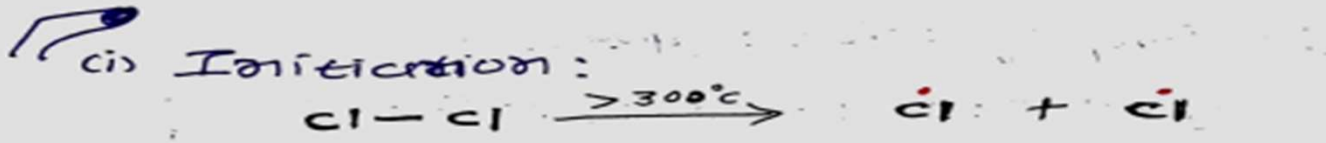
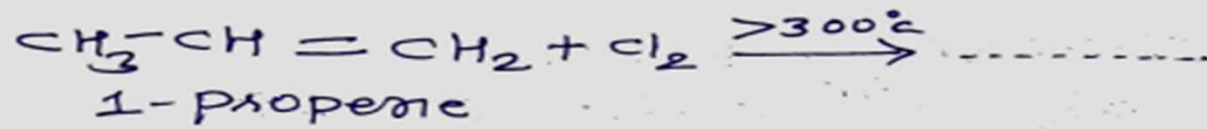


(ii) Propagation : प्रसारण :



(iii) Termination : अंत :

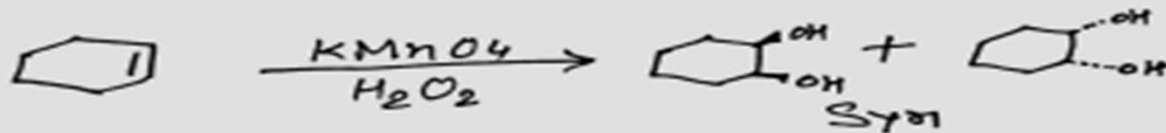
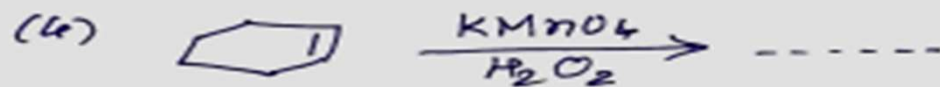
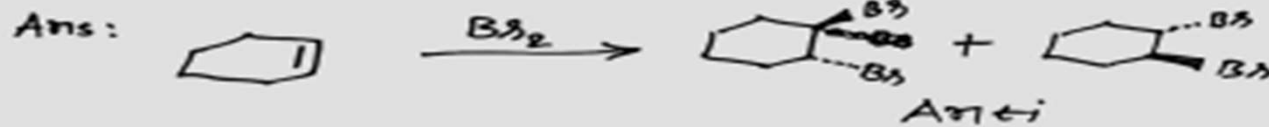
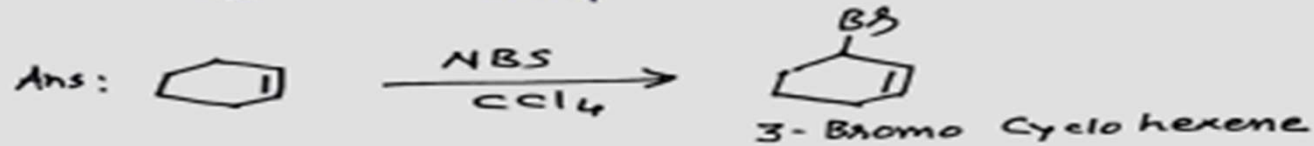
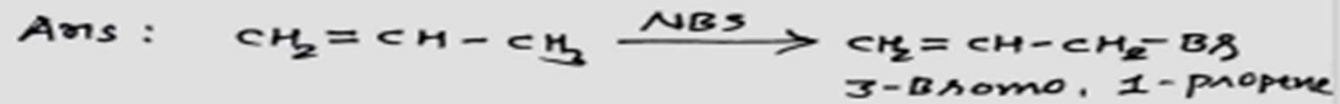




→ ક્રિયા વાચકને પ્રિન્ટની Cl<sub>2</sub> સાથેની પ્રક્રિયા થી એલાઇલ ક્લોરાઇડ બને છે. આ પ્રક્રિયા addition નથી પરંતુ substitution પ્રકારની છે.

→ આ પ્રક્રિયામાં π બંધ ધરાવતા પ્રિન્ટમાં Cl ઉમેરાય છે & વ્યવસ્થા પુલિવર્લ રીતે ફર પડે થઈ જાય છે. આથી π બંધને કોઈ અસર થતી નથી & આથી π વિભાજન જાડી પરંતુ વિસ્થાપન પ્રક્રિયા થવાથી એલાઇલ ક્લોરાઇડ બીજા તરીકે બને છે.

• प्रक्रिया पूर्ण करो. Complete the reactions:



# Short Summary of the Course :

## UNIT : 1

### Electrophilic & Free Radical Addition Reactions :

- @ Electrophile & examples @ Free Radical & examples @ Homolytic fission @ Heterolytic fission
- @ Addition reaction @ Markonikov's rule @ Anti Markonikov's rule
- @ Syn and Anti @ Stereo selective & Stereo specific reaction
- @ Chiral "C" d, l, D, L, Racemic mix. @ Optical isomer @ Geometrical isomer @ Enantiomer @ Meso compound
- @ Diene and Conjugated Diene @ Polymerisation reaction

## UNIT : 2

### Active Methylene Group Compounds:

- @ Active methylene group @ Compounds having active methylene group @ Keto enol tautomerism @ Condensation reactions with examples

## UNIT : 3

### Nucleophilic Aromatic Substitution Reactions :

- @ Nucleophile & examples @ Substitution reactions & examples @ Nucleophilic Aromatic Substitution & examples
- @ SN1 & SN2 reactions @ Induced effect @ Resonance effect @ Addition reaction @ Benzyne

# Formula For Grand Success in the Examinations

1. Positive Attitude towards Education
2. Confident on yourself & Know yourself
3. Perfect Planning
4. Time Management

↓  
**GRAND SUCCESS**





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THANK  
YOU!