

Electrophilic & Free Radical Addition Reaction

B.Sc. Sem – VI

Paper : CC CH : 602

Unit – 1

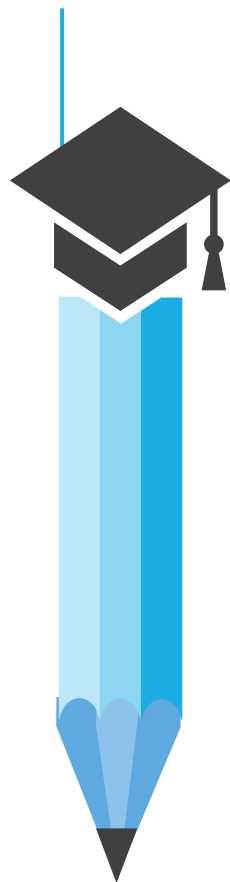


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SYLLABUS



- 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 : Vth edition
- ❖ Advanced organic chemistry by R.K.Bansal
- ❖ Organic chemistry by I.L.Finar volume I & II (Vth edition)
- ❖ Organic reaction & mechanism IInd 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. NO_2^+ , Cl^+ , SO_3H^+ 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

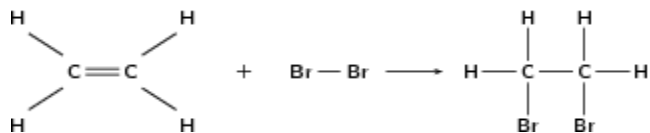
03

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

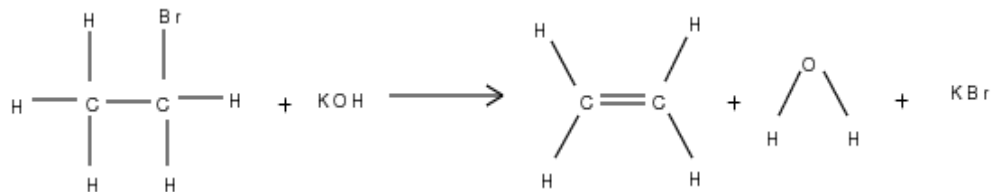
04

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

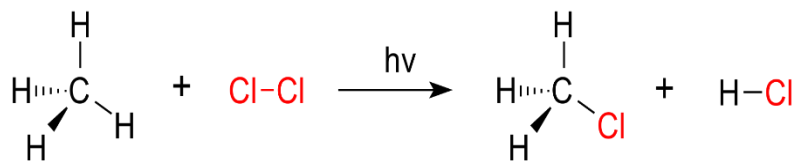
Addition Reaction



Elimination Reaction



Substitution Reaction



Rearrangement Reaction

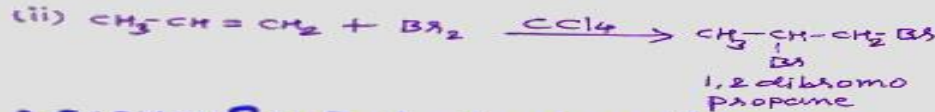


• Addition Reaction :

→ 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.

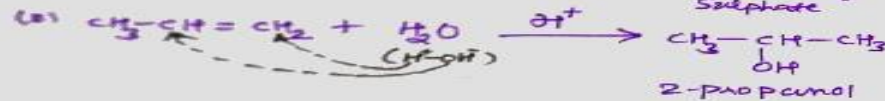
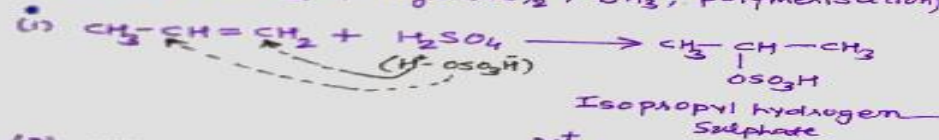
• समप्रतिबन्धी अणुकील युद्धियाः :

(e.g. H_2 , Cl_2 ...)

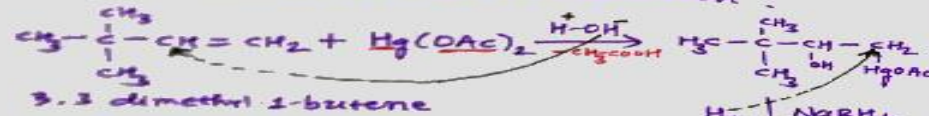


• असमप्रतिबन्धी अणुकील युद्धियाः :

(e.g. H_2SO_4 , H_2O , $Hg(OAc)_2$, BH_3 , polymerisation)



(3) Oxymercuration-Demercuration :

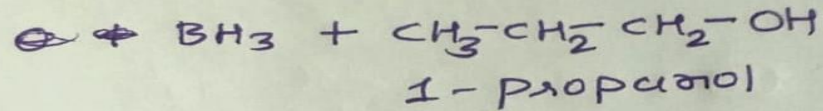
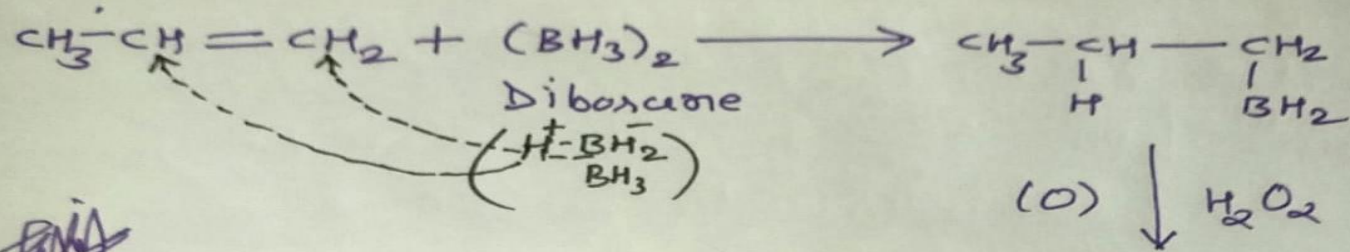


~~Final~~

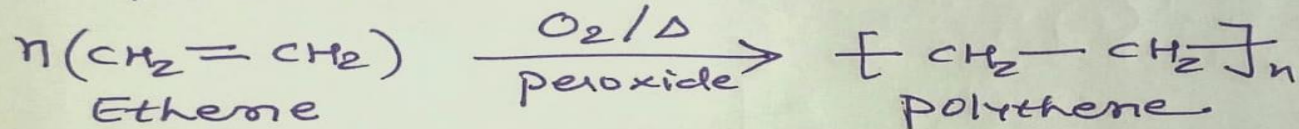


3,3-dimethyl-2-butanol

(4) Hydroboration-Oxidation (Anti Markovnikov)



(5) Polymerisation:



Markonikov's Rule

01

Rule

02

Examples

03

Mechanism

04

Other examples

05

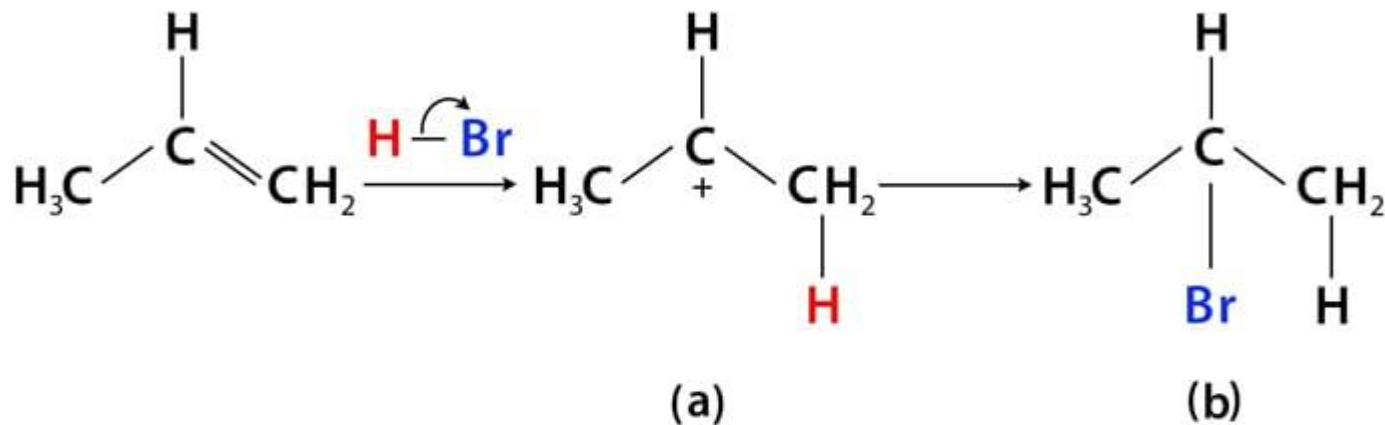
Potential energy diagram

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.

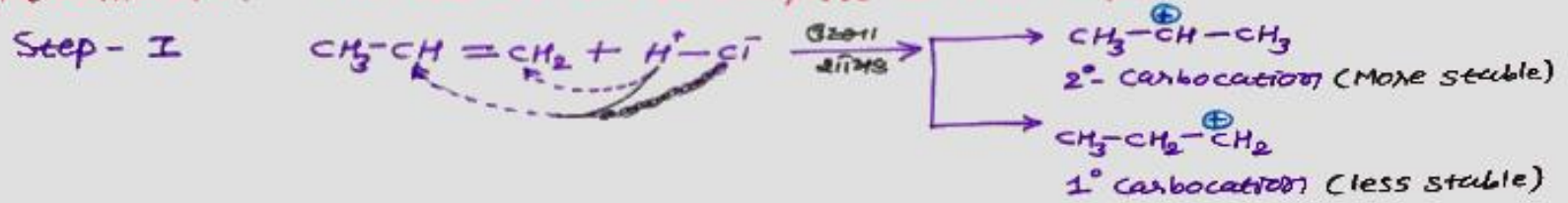
Markovnikov's Rule Basic Mechanism



(a) •hydrogen (H) added to 1° carbon (C) for more stable carbocation

(b) •bromine (Br) added to 2° carbocation to give product

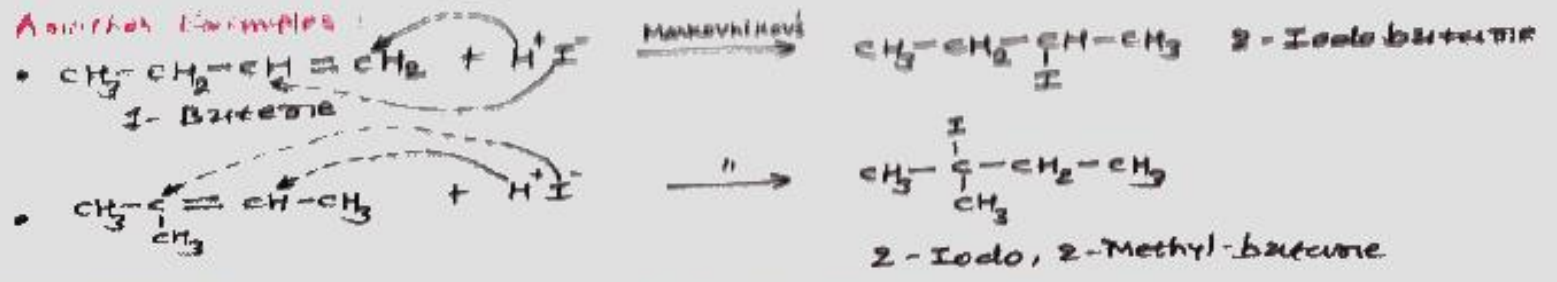
* Mechanism: This reaction will be complete in two steps:

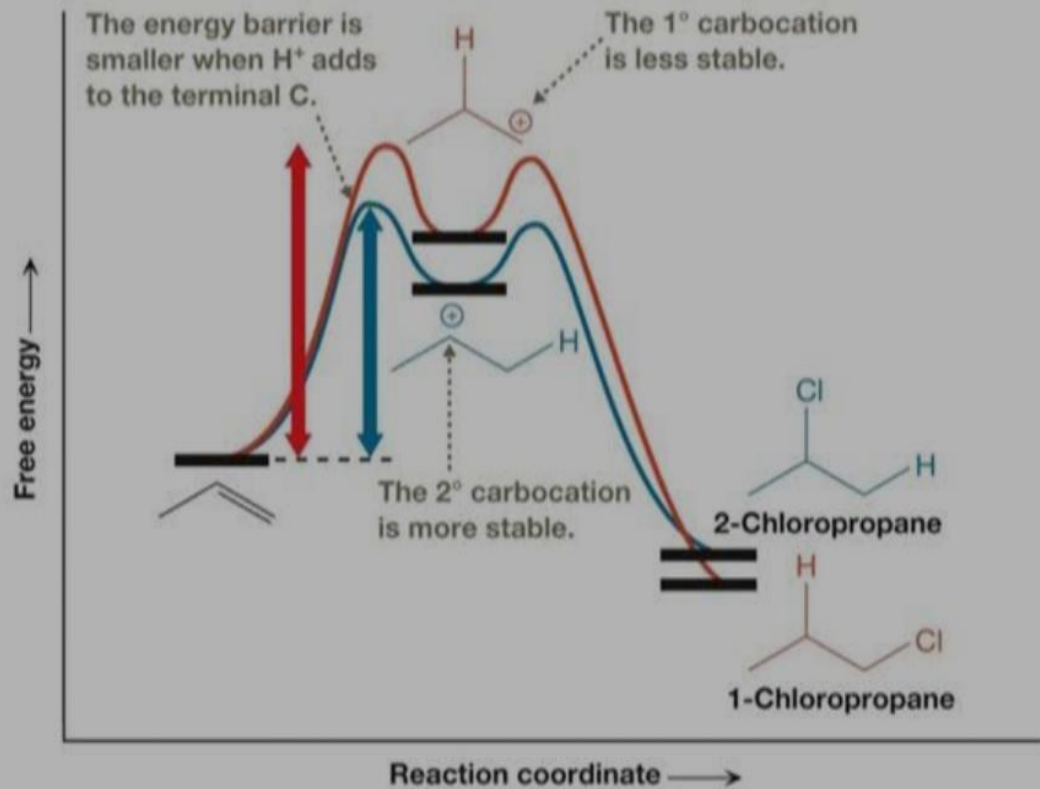


→ આથી પ્રથમ તબક્કો ધીમો છે. આને તે લેગિમિટારીસ તબક્કો છે. આ તબક્કા દરમિયાન 2° કાર્બોકેશન બને છે જેના માટે ΔG₂ નું મૂલ્ય ઓછું છે આથી તેમાંથી બીજા તબક્કામાં બીજા તબક્કાનું ઝડપથી ઉત્પન્ન થાય છે. જ્યારે 1° કાર્બોકેશન માટે ΔG₁ નું મૂલ્ય વધુ છે આથી તે પ્રમાણમાં ઓછો સ્થાન છે.



* Another Examples:





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Anti Markonikov's Rule: (Free Radical Additi on)

01

Rule

02

Examples

03

Mechanism

04

Other examples

Anti Markonikov's Rule:
(Free Radical Addition)

Electrophilic Addition : Rearrangement

2° Carbonium ion
(less stable)

Rearrangement



3° Carbonium ion
(More stable)

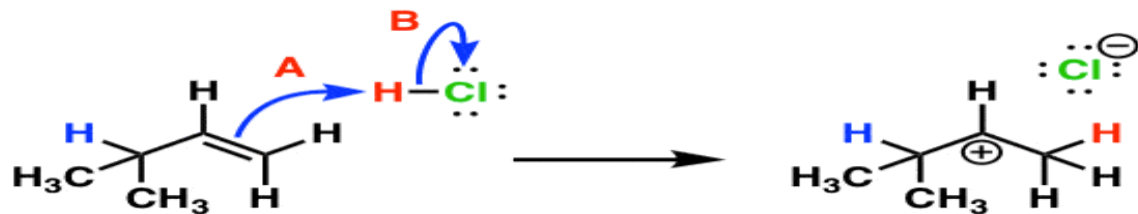


Product



Product

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

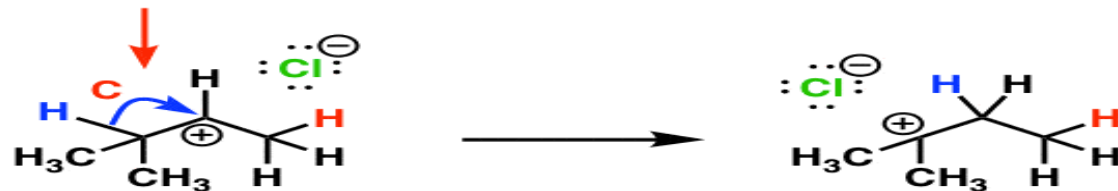


	Form	Break
A	C ₁ -H	A C ₁ -C ₂ (π)
	C ₂ -H	C ₃ -H
	C ₃ -Cl	B H-Cl

Observation: secondary carbocation

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

Recall the order of carbocation stability: tertiary > secondary > primary
Migration of the C-H bond from C₃ to C₂ results in a more stable carbocation!
This arrow says, "break the C₃-H bond and form a new C₂-H bond"



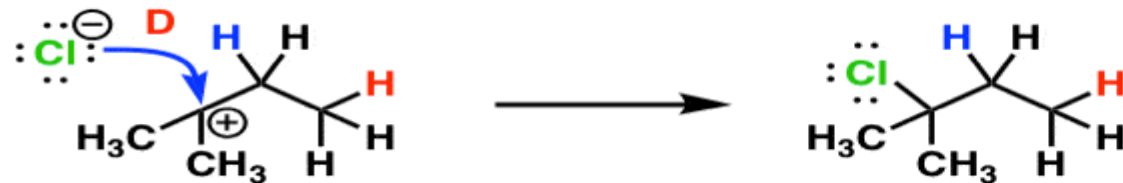
Secondary carbocation

Tertiary carbocation

a more stable carbocation

	Form	Break
	C ₁ -H	C ₁ -C ₂ (π)
C	C ₂ -H	C C ₃ -H
	C ₃ -Cl	H-Cl

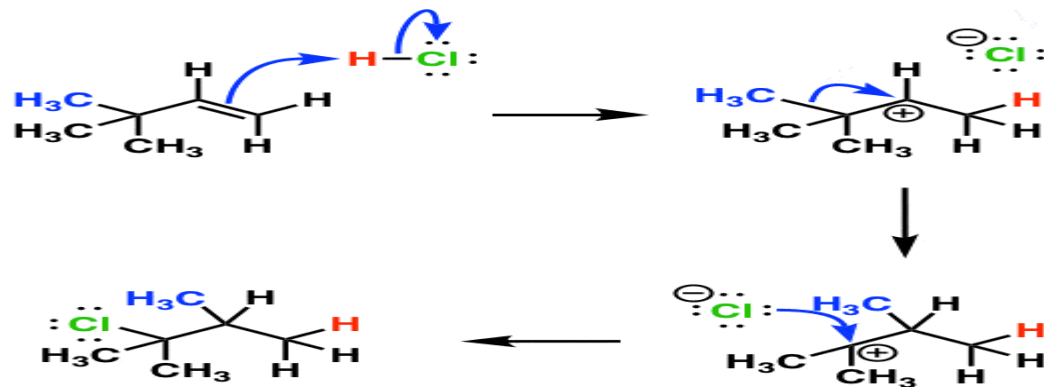
Step 3 - Attack of nucleophile (arrow D)



Form	Break
C ₁ -H	C ₁ -C ₂
C ₂ -H	(π) C ₃ -H
D C ₃ -Cl	H-Cl

Tertiary carbocation

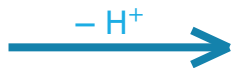
Alkyl shift example:



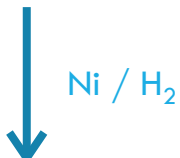
Electrophilic Addition : Dimerization

(Dimerization of Isobutylene)



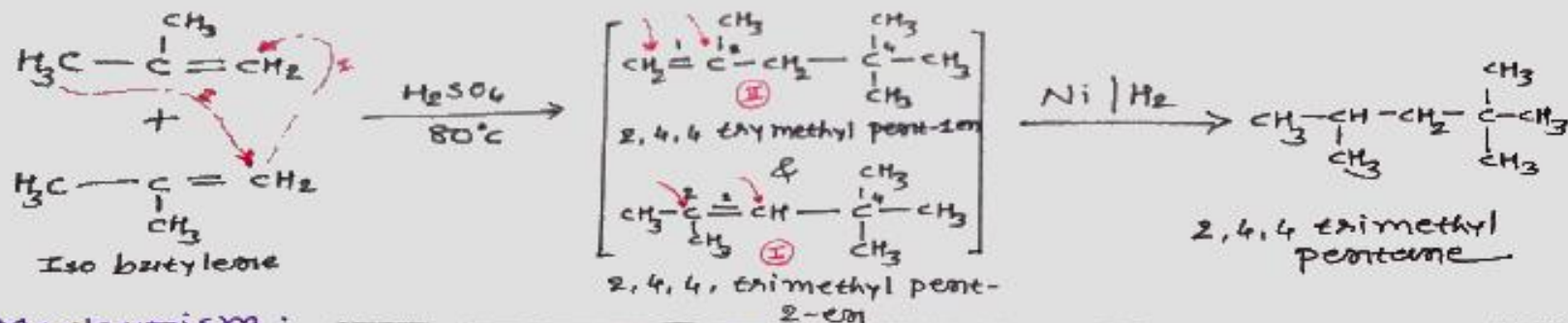


2,4,4 tri methyl 1-pentene
&
2,4,4 tri methyl 2-pentene

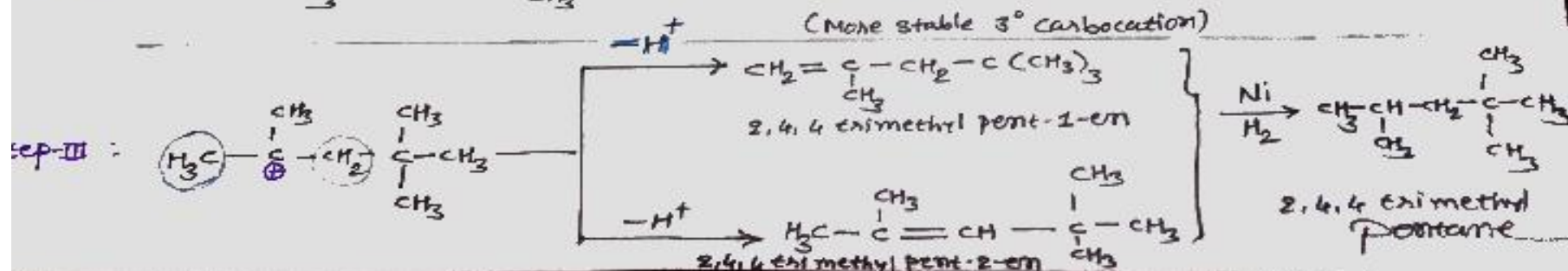
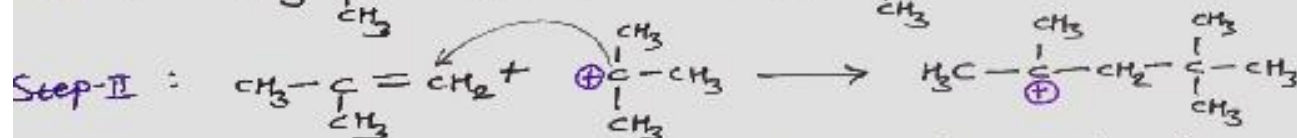
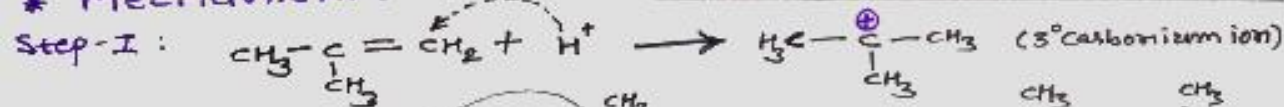


2,4,4 tri methyl pentane

* Electrophilic Addition: Dimerisation: (Reaction)

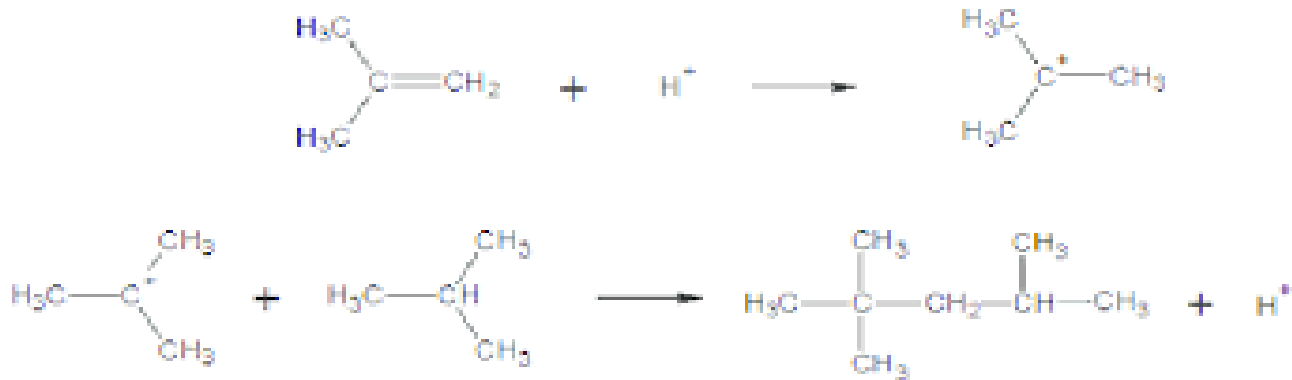
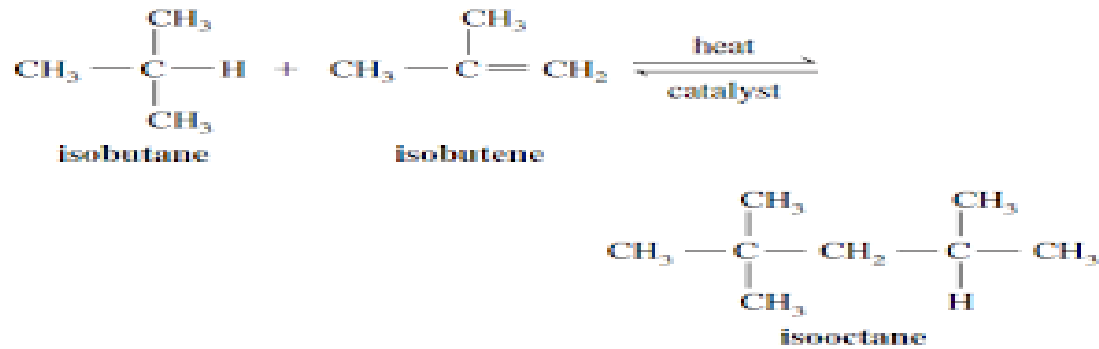


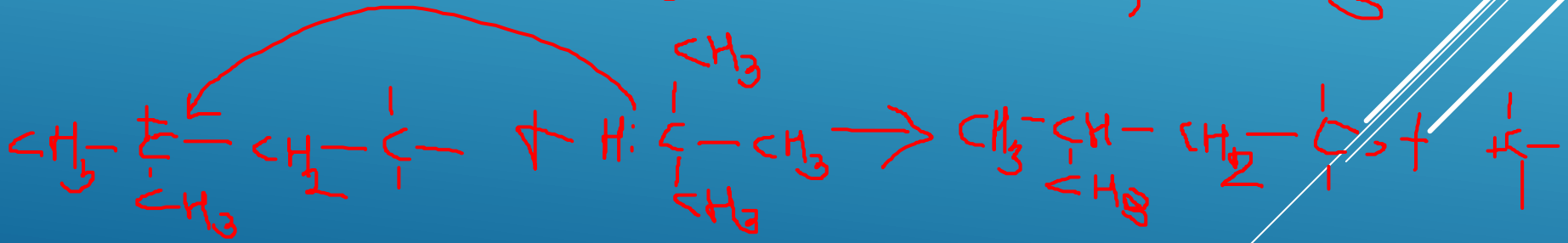
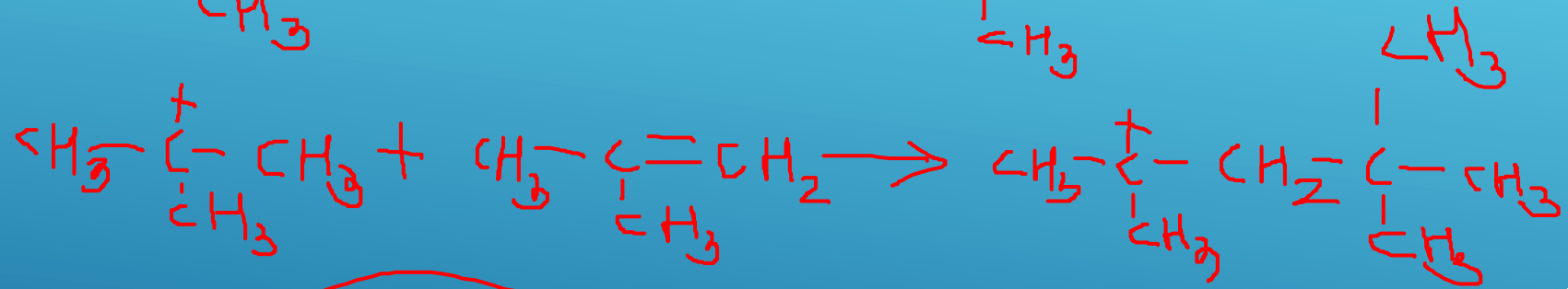
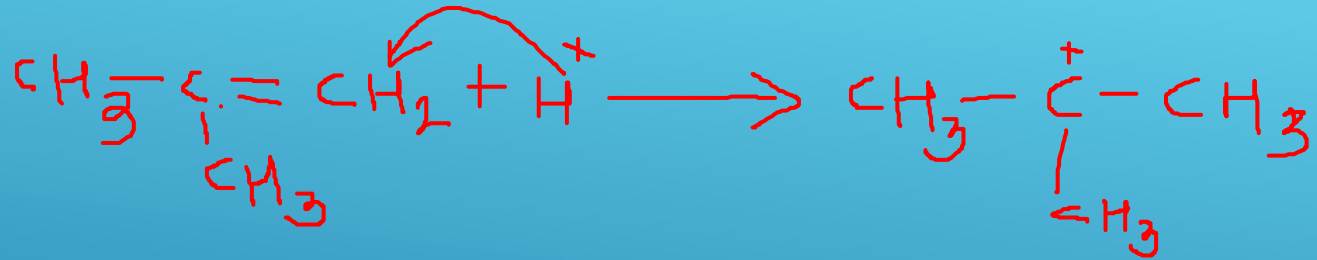
* Mechanism:



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

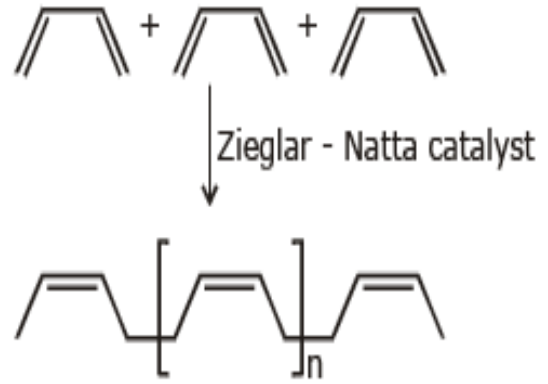
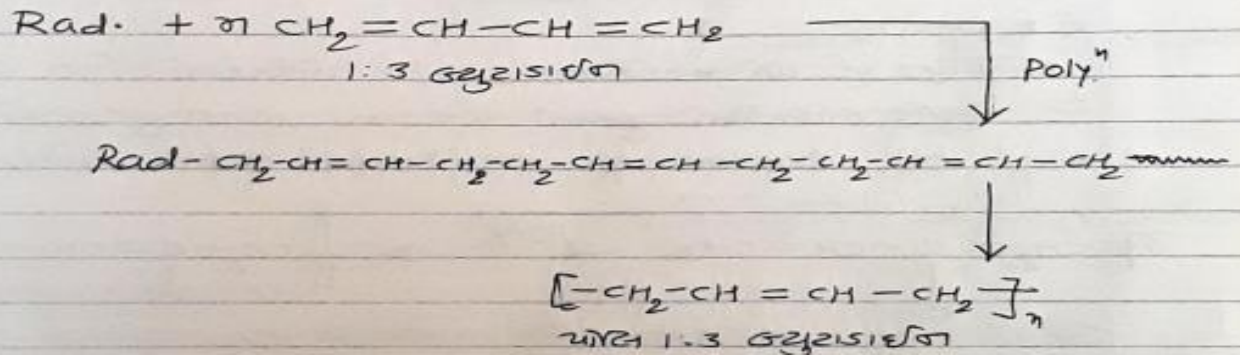
મુક્તમૂલક રીતે ડાઈન નું જાળવી રાખવા ~~કે~~ વજાર
 - તથા તેની વિસ્થાપકોની જગાવર :

Polymerisation of Diene by Free Radical Reaction :

- 1:3 ક્રમસાથેન → પોલિ 1:3 ક્રમસાથેન
- સંપૂર્ણ → CIS પોલિ ક્રમસાથેન (જેટાબંધ)
- ફેરબરગ → CIS-સુખ
- સ્ક્રોલિયન → પોલિ-સુખ

→ ડાઈન સંચાલનાર મુક્તમૂલક ક્રિયાવિધિની જાળવી રાખવા
 કરવાની જ વજાર કે તેની વ્યુત્પાદનો મુરત થાય છે.
 e.g.

1:3 ક્રમસાથેનનું મુક્તમૂલક ક્રિયાવિધિની મદદથી જાળવી રાખવા
 કરવા પોલિ 1:3 ક્રમસાથેન મુરત થાય છે. આ પ્રક્રિયા 1:4 સંચાલિત
 દ્વારા થાય છે.

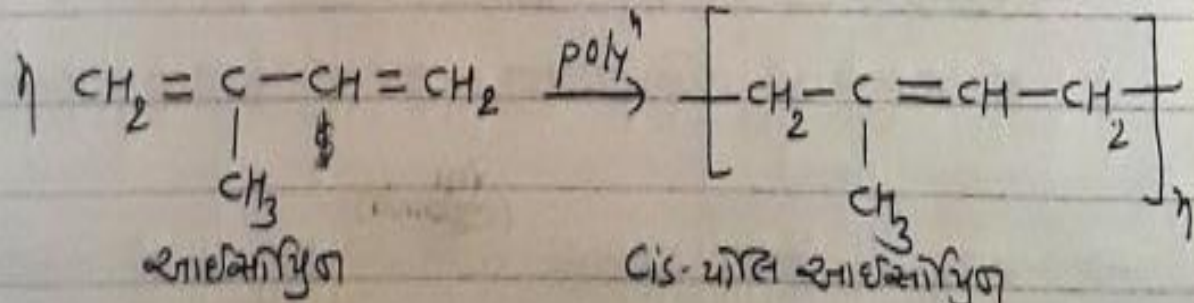


cis poly (1,3 butadiene)





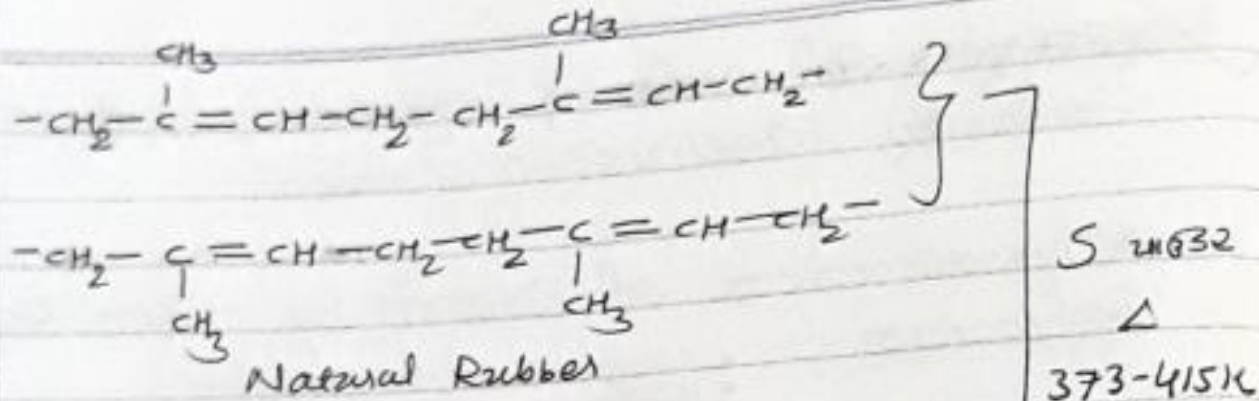
* Naturally Rubber :



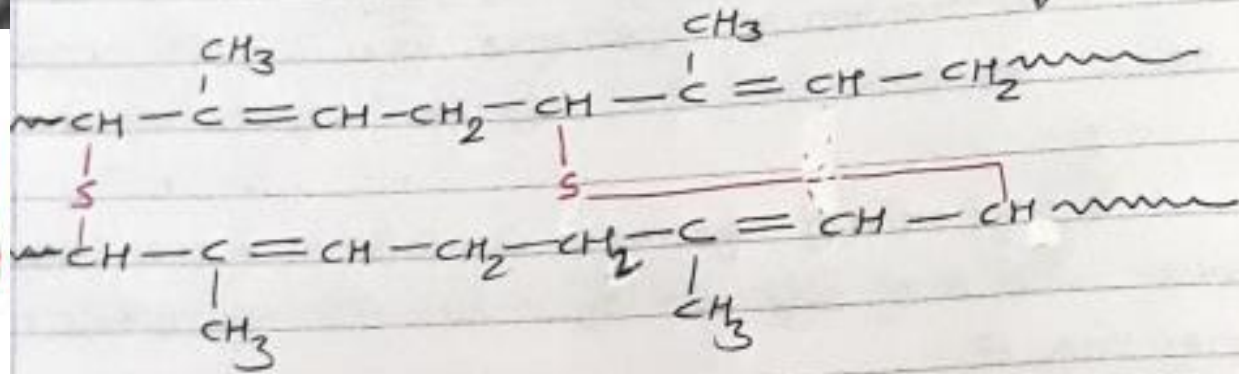
(Naturally Rubber)

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





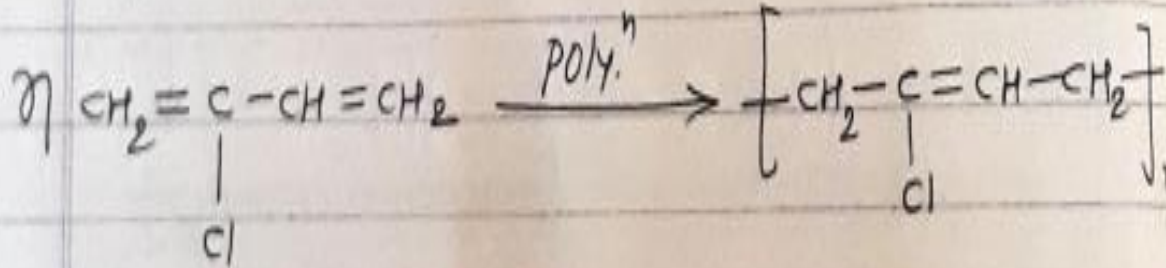
S 24632
 Δ
 373-415K



Vulcanised Rubber

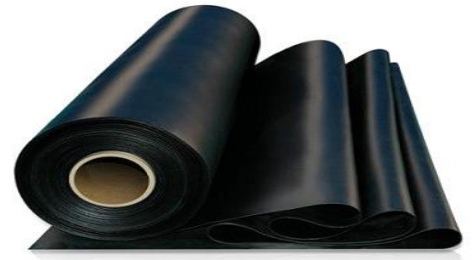
તો જ પુમાલો,

કલારોપિયુ જ પોલિમરાઈકરેશન કરવાથી પોલિકલારોપિયુ બને છે જે કોટેલીક્ર લાગતાંમ; કુદરતી રક્તકક્તાં મુલકા મુદ્દાદમ્મા વામ પરંતુ oil, Gasoline માં અકસોદકતાની લાગતે અક્રિયાતા છે



chloroprene

polychloroprene
(Neoprene)



Electrophilic Addition in Conjugated Diene or 1:4 Addition

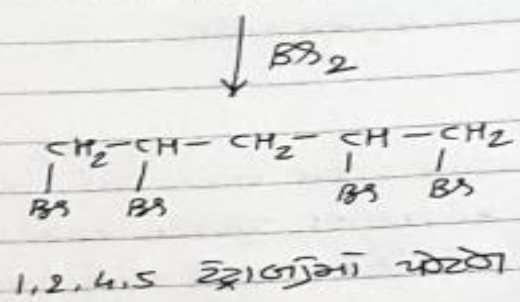
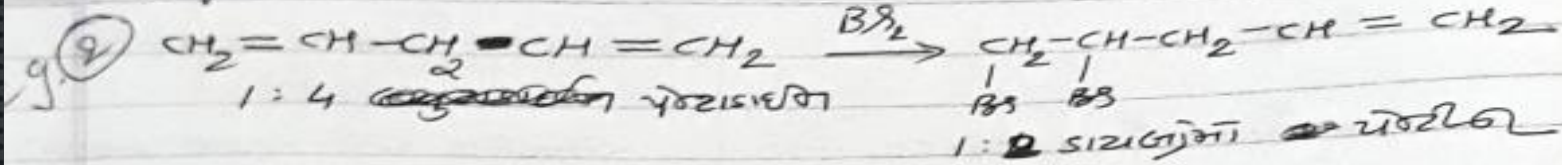


1:4 Addition in Conjugated Diene :

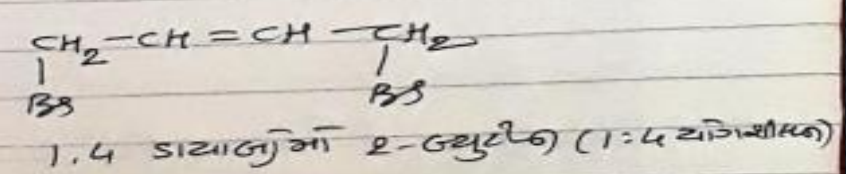
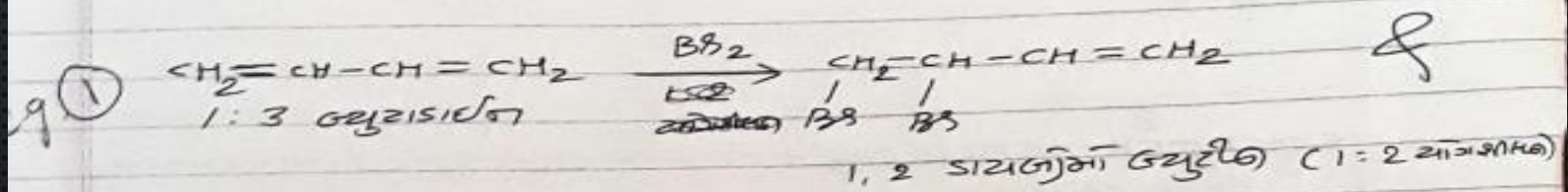
કોન્જુગેટેડ સાઇન (અકોનવિટ દ્વિબંધ ધરાવતા) માં
ઇન્-અનુરાગી યોગશીલન OR 1:4 યોગશીલન :

અકોનવિટ દ્વિબંધ ધરાવતા સાઇનની ^{પોટા} (બ્રાન્ચિંગ) Br_2 સાથે યોગશીલ
પ્રક્રિયા કરતાં 1 & 4 થા સ્થાને આવેલા દ્વિબંધ
આગળ Br_2 ક્રમશઃ ઉમેરાય છે & નીચાજ તરફ
ટ્રાન્સફોર્મ આપે છે. આ પ્રક્રિયાને 1:4 યોગશીલન
પ્રક્રિયા કહી શકાય છે.

c-9.

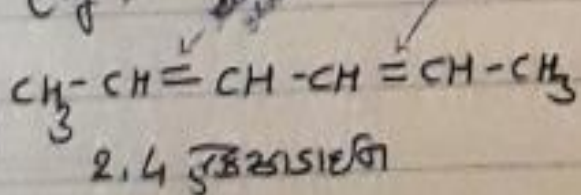


નોંધપાત્ર,

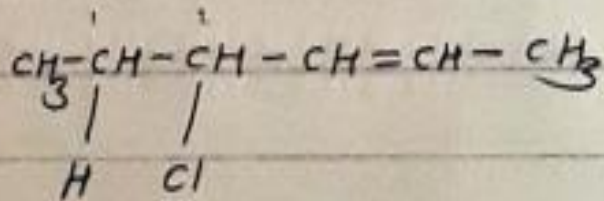


Step-11 का उदाहरण

eg.

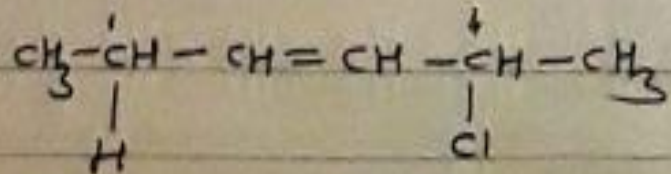


HCl



4-डबलबन्ध, 2 डबलबन्ध (1:2 नियम)

+

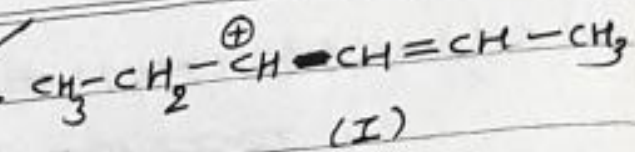
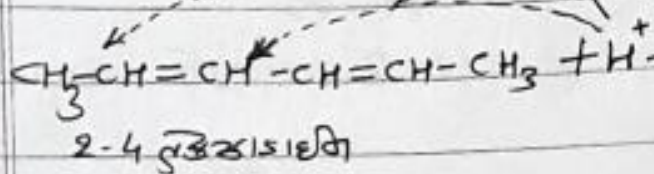


3-डबलबन्ध, 3 डबलबन्ध (1:4 नियम)

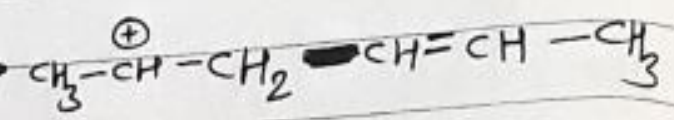
(15)

Mechanism: ~~2,4~~ 2,4-Addition:

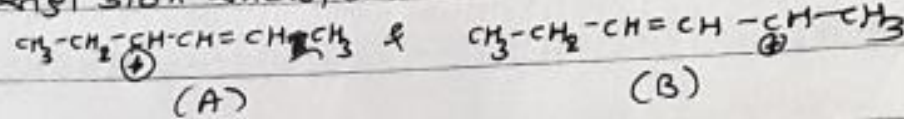
Step-I



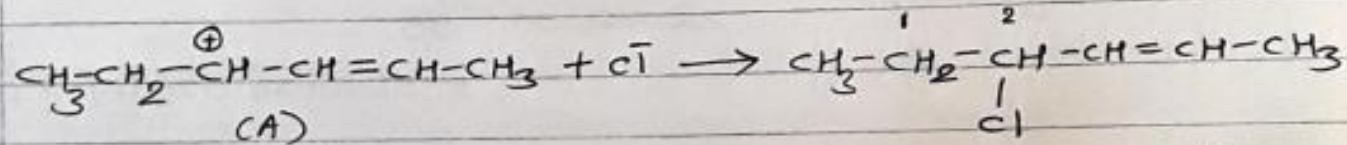
अलायलिक डाला. सायन (स्थान)



साम प्रथम तलकामां डोणयुगले डालामां गजले अडे एडे
 सांगलील युक्ति याए ए & स्थान अलायलिक डाला. सायन
 जाल ए. अली डाला. सायन (I) नां जे स्थानां शरु ए.

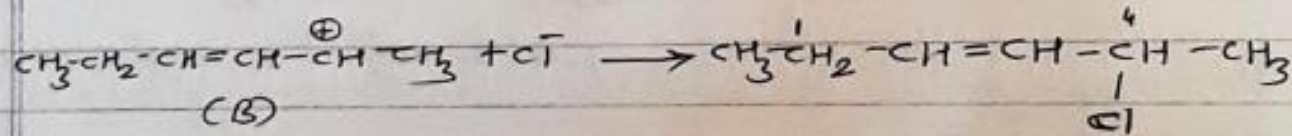


Step-II



(1:2 યોગશીલન)

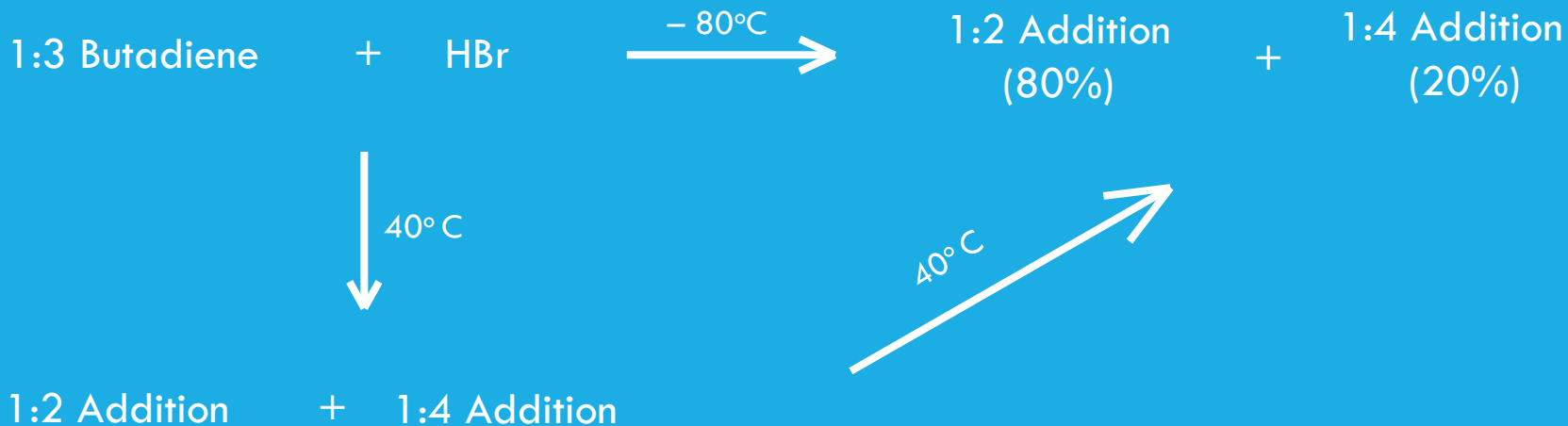
+



(1:4 યોગશીલન)

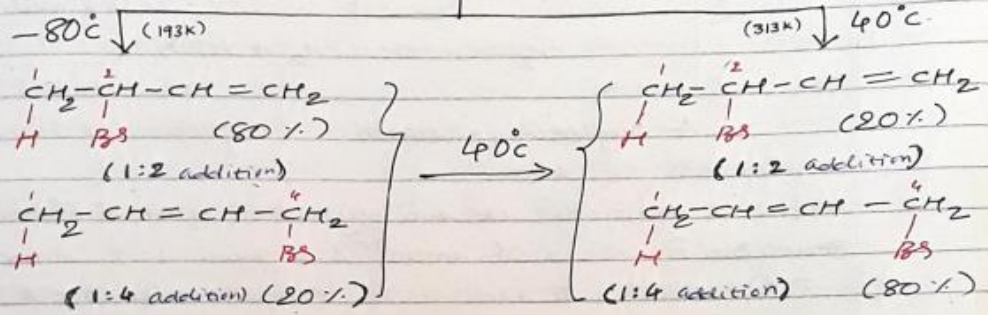
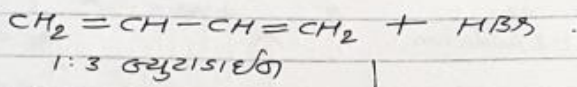
દ્વિતીય તબક્કામાં કાર્બો-આયન (A) & (B) ની Cl⁻ સાથે પ્રક્રિયા થતાં 1:2 કે 1:4 યોગશીલન પ્રક્રિયા થાય છે & આથી 1:2 યોગશીલન કે 1:4 યોગશીલન નીપજ મળે છે.

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



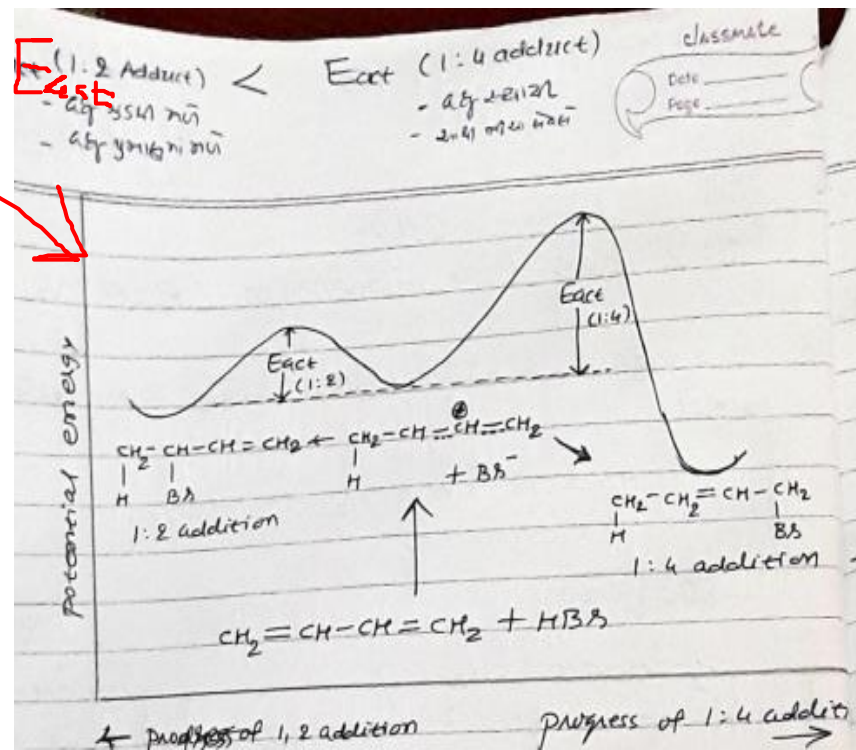
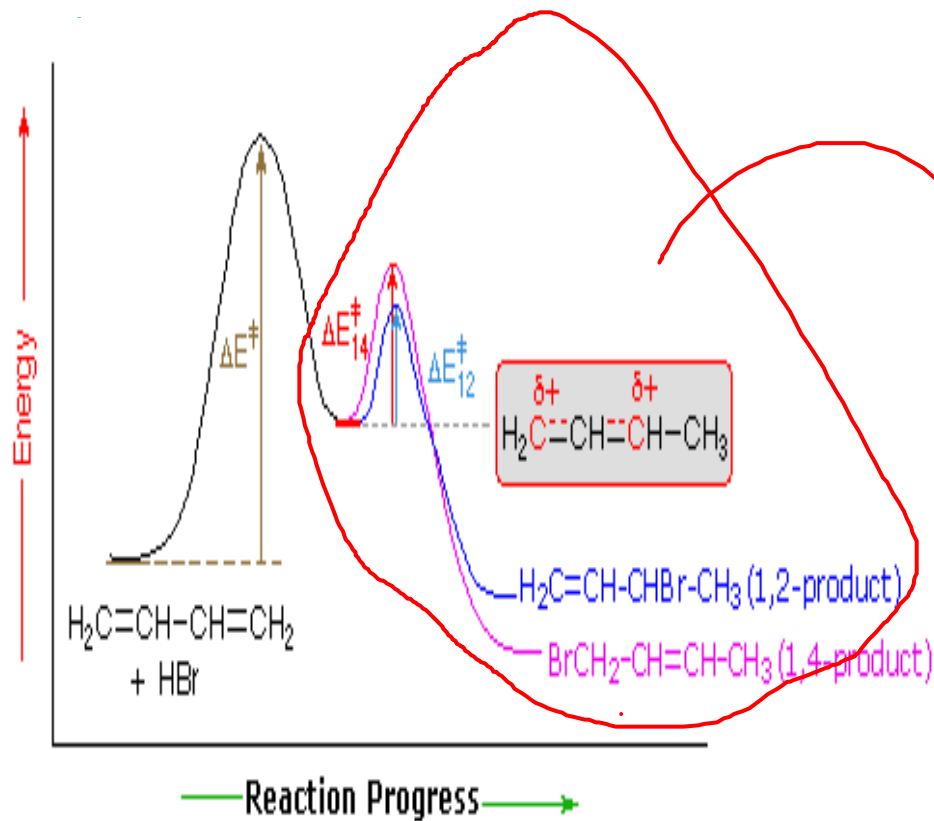
1:2 and 1:4 addition (Rate Vs. Equilibrium)

1:2 and 1:4 addition of HBr to 1,3-butadiene



→ At low temperature (193K) 1:3 addition of HBr to 1,3-butadiene gives 80% 1:2 and 20% 1:4 products. At 40°C (313K) 1:3 addition gives 20% 1:2 and 80% 1:4 products. This shows that at low temperature, the reaction is under kinetic control (1:2 addition is faster), while at high temperature, it is under thermodynamic control (1:4 addition is more stable).

→ At -80°C, 1:4 addition is favored (80%) because the transition state for 1:4 addition is lower in energy. At 40°C, 1:2 addition is favored (80%) because the reaction is reversible and the 1:2 product is more stable.

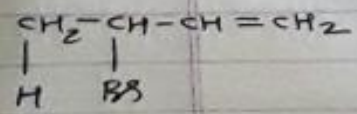
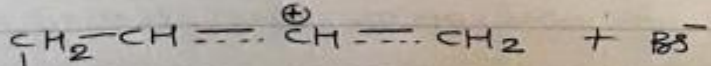
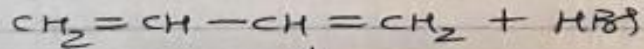


આલેકન પરથી કઈ શકાય છે,

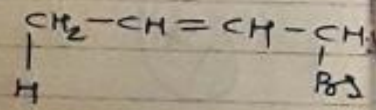
અહીં 1:3 બ્રુકાસાઈલની HBr સાથે પ્રક્રિયા થવાથી પ્રથમ કાર્બોકેટિયમ આયન ઉત્પન્ન થાય છે. આ કાર્બો-આયન 1:4 કરતાં 1:2 નીપજ ઝડપે મળે છે. આથી 1:4 કરતાં 1:2 નીપજની સક્રિયકરણ શક્તિ (E) આલેકી હોય છે. આમ આમાં પ્રથમ 1:2 નીપજ કરતાં 1:4 નીપજ વધુ સ્થાયી છે. આમ તેને આલેક નીચા લેવેલે દર્શાવેલ છે.

ઉપર દર્શાવેલા શ્રેણી 1:2 & 1:4 નીપજો (એલાઈલ બ્રુકાસાઈલ) સરળતાથી આયનોકરણ પામી સમાન કાર્બો-આયન ઉત્પન્ન કરે છે. આથી 1:1 વધી 1:4 નીપજ આ કાર્બો-આયન દ્વારા સંકુલના સ્થિતિ ગ્રહણ કરે

✓ અહીં 1:2 નીપજ ઝડપેથી મળે છે & ઝડપથી આયનોકરણ પામે છે. જ્યારે 1:4 નીપજ ઘનતર મળે છે & ઘનતર આયનોકરણ પામે છે. આમ કોલા T વધુ સ્થાયી (1:4) નીપજ મળે છે અર્થાત્ 1:2 નીપજ આ 1:4 નીપજ કરતાં ઝડપેથી મળે છે



1:2 નીપજ



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/watch?v=EbLLEbt9>

<https://youtu.be/EbLLEbt96Cs6Cs>

Stereo Selective and Stereo Specific Reactions :

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

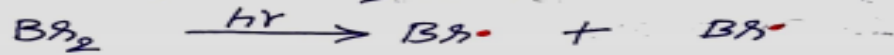
<https://youtu.be/rAKjN99FlhU>

<https://youtu.be/VClr6T2NhLo>

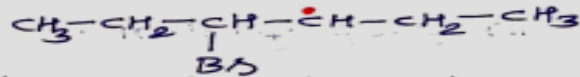
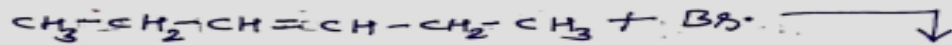
Free Radical Addition Reaction of 3-hexene with Br_2 :



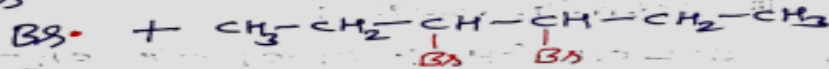
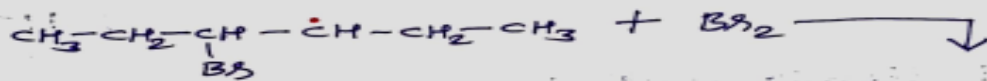
(i) Initiation : यज्ञः :



(ii) Propagation : यज्ञः :

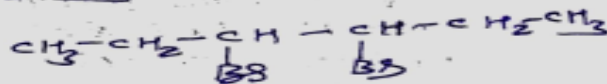
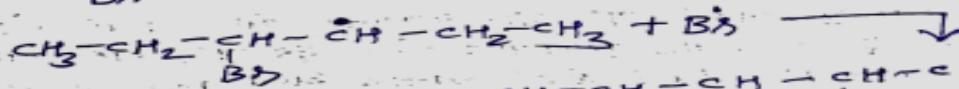


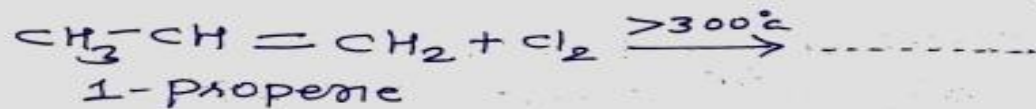
New free radical



3,4 dibromo hexane

(iii) Termination : अंतः :

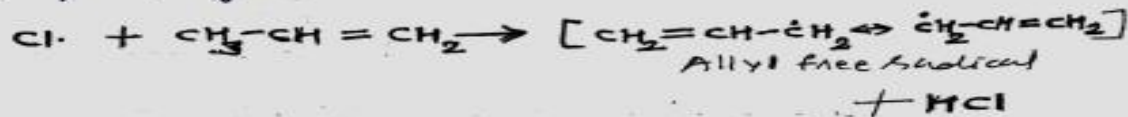




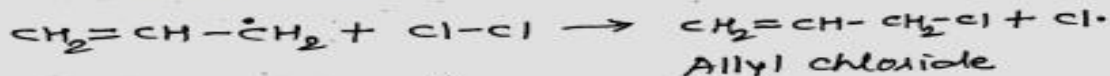
(i) Initiation:



(ii) Propagation:



(iii) Termination:



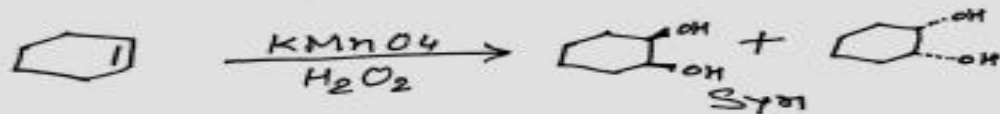
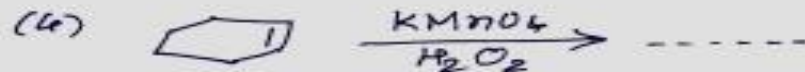
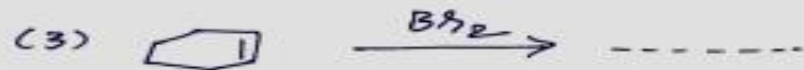
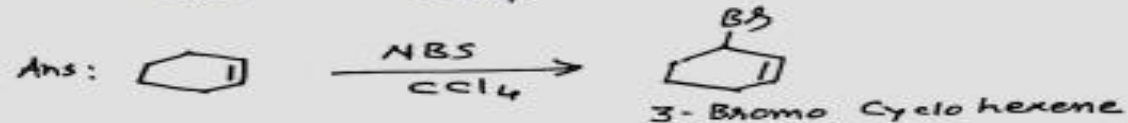
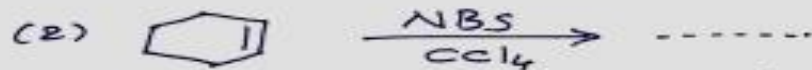
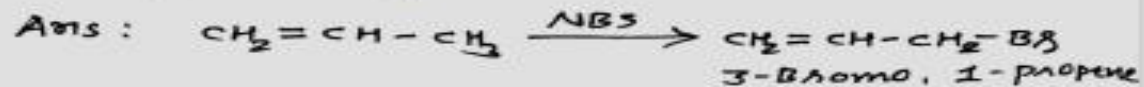
→ કોચા તાપમાને પ્રોપિલેનના Cl₂ સાથેની પ્રક્રિયા થી એલાઇલ ક્લોરાઇડ બને છે. આ પ્રક્રિયા addition નજીક પરંતુ - substitution પ્રકારની છે.

→ આ પ્રક્રિયામાં π બંધને ધરાવતા પ્રોપિલેનમાં Cl[•] ઉમેરાય છે & વ્યારનાદ પ્રતિવાર્તી રીતે ફર પહોં થઈ જાય છે.

આથી π બંધને કોઈ સસર થતી નથી & આથી π વિભાજન નહીં પરંતુ વિસ્થાપન પ્રક્રિયા થવાથી

એલાઇલ ક્લોરાઇડ બને છે તરીકે મળે છે.

• प्रश्न पूर्यो 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



Dr. Z.M. Gadhawala (Gold Medalist)
Associate Professor & Ph.D. Guide
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zmgadhawala@yahoo.co.in



THANK
YOU!