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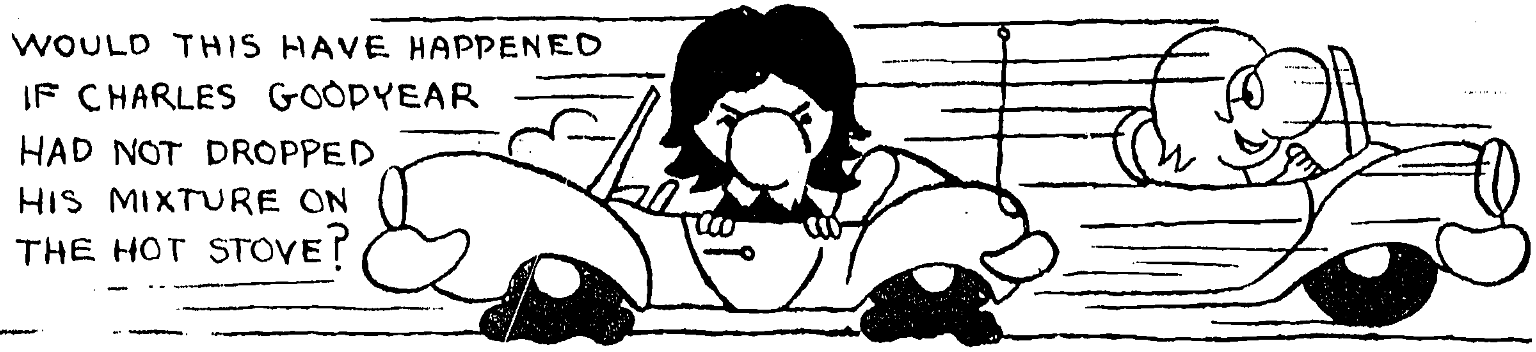
ABSTRACT

This booklet, one of a series of 17 developed at Prince George's Community College, Largo, Maryland, provides an individualized, self-paced undergraduate organic chemistry instruction module designed to augment any course in organic chemistry but particularly those taught using the text "Organic Chemistry" by Morrison and Boyd. The entire series of modules covers the first 13 chapters of the Morrison-Boyd text in great detail. Each module has been provided with from one to three audiotapes, available from Prince George's Community College, to provide students additional explanations of particular concepts. Each module includes a self-evaluation exercise, a reference guide, worksheets to be completed with the audiotapes, answer sheets for the worksheets, a progress evaluation, an answer sheet for the progress evaluation, an answer sheet for the self-evaluation exercise, an introduction to the topic covered by the module, and student performance objectives for the module. The topic of this module is dienes. (SL)



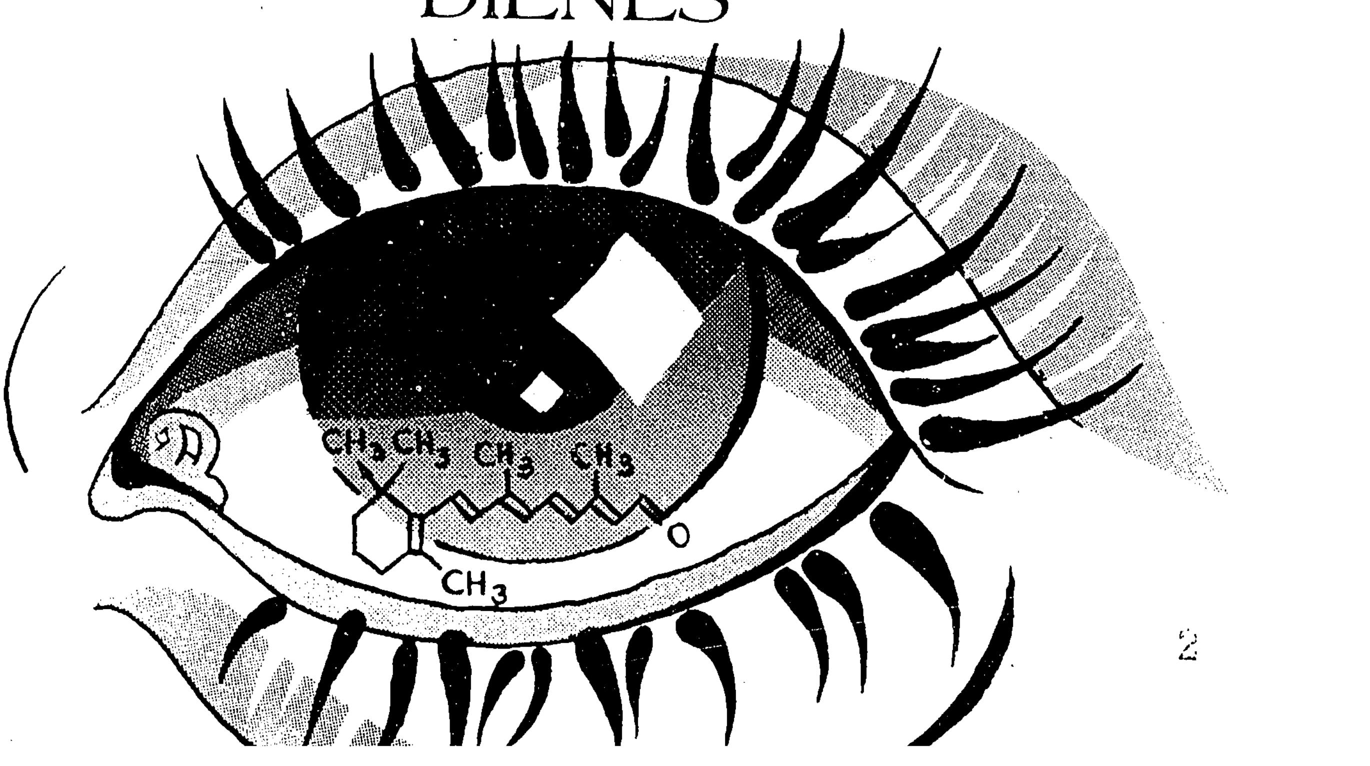
ORGANIC CHEMISTRY

V. Zdravkovich

13

Self
Instructional
Package


DIENES



Self Instructional Sequence in

ORGANIC CHEMISTRY

DIENES

INTRODUCTION

The tree known as Hevea brasiliensis is a native of the Amazon Valley and is a vital factor in the Brazilian economy. Early Spanish explorers found that South and Central American natives used the substance obtained from this tree to waterproof household utensils and to make balls for their games. In 1876 seventy thousand seeds were brought to England. The young trees were shipped to various English colonies in the Far East. The substance obtained from the Hevea brasiliensis became increasingly important. Its godfather, Joseph Priestley (1733-1804) used it to rub out pencil marks and named it rubber.

The search for the ways to synthesize rubber was initiated. The first synthetic rubber lacked the qualities of the natural rubber. In 1839, Charles Goodyear accidentally dropped one of the mixtures he used to experiment with on a hot stove, thus discovering the process that he called VULCANIZATION.

Can you describe the chemistry that took place when Charles Goodyear dropped his mixture on a hot stove?

Do you know the formula of rubber?

Do you know the reaction utilized in the preparation of rubber?

(Complete this unit and you will have the correct answers)

DIENES

Definitions

The student will be able to define, explain and illustrate with appropriate examples the following terms: ALLENE, CUMULATED DIENE, CONJUGATED DIENE, ISOLATED DIENE, VULCANIZATION, ISOPRENE RULE, RUBBER, GUTTA-PERCHA.

Reactions

The student will be able to write the balanced reactions for the hydrogenation, hydration, hydrohalogenation.

The student will be able to write the balanced reaction for the peroxide catalyzed additions of HBr, CX_4, CHX_3.

The student will be able to predict the products obtained as a result of the ozonolysis of different dienes.

The student will be able to identify the original diene from the ozonolysis products.

The student will be able to write the reactions for the different polymerization reactions.

Mechanisms

The student will be able to write the step by step mechanism for the carbonium ion addition and polymerization reactions of dienes.

The student will be able to write the step by step mechanism for the free radical addition and polymerization reactions of dienes.

The student will be able to explain the difference between the relative percentages of the 1,2 and 1,4 addition products obtained in the different addition reactions.

Multi-step synthetic schemes

The student will be able to devise a multi-step synthetic scheme for the synthesis of a diene from ethane or any other small alkane.

The student will be able to identify the intermediate compounds formed in a given multi-step synthetic scheme.

DIENES

Identify the following statements as True or False by placing a capital T or F on the line to the left.

1. _____ Trans 2-pentene has higher heat of hydrogenation than cis 2-pentene.

2. _____ Cumulated dienes are more stable than conjugated dienes.

3. _____ Conjugated dienes have higher heat of hydrogenation than cumulated dienes.

4. _____ A 1,2 addition to a conjugated diene happens faster than a 1,4 addition.

5. _____ A 1,4 addition product is more stable than a 1,2 addition product.

6. _____ A 1,2 addition requires larger energy of activation than a 1,4 addition.

7. _____ Isolated dienes undergo a 1,2 and a 1,4 addition.

8. _____ Alkenes are more reactive toward hydrohalogenation than dienes.

9. _____ Natural rubber is a cis polyisoprene.

10. _____ Isoprene rule is the recognition of the isoprene units in a given molecule.

11. _____ 1,3-butadiene can be prepared by heating of butene to about 200°C (cracking).

12. _____ Vulcanization is formation of sulfur bridges between polyisoprene chains.

Blacken out the correct answer or answers in the following questions:

13. In a reaction of 2-methyl-1,3-pentadiene with hydrogen bromide the following products are obtained:

    a) 4-bromo-4-methyl-2-pentene
    b) 3-bromo-2-methyl-1-pentene
    c) 4-bromo-2-methyl-2-pentene
    d) 1-bromo-2-methyl-2-pentene

SIP No. 13
Form B - Self Evaluation Exercise

14. In a reaction of 1,3-butadiene with hydrogen bromide in presence of peroxide the following products are obtained:

a) 1-bromo-2-butene
b) 3-bromo-1-butene
c) 4-bromo-1-butene
d) 2-bromo-2-butene

15. The resonance structures of the intermediate species in the free radical addition to 1,3-butadiene are:

a) $CH_3-\underset{\bullet}{C}H-CH=CH_2$

b) $CH_3-CH=CH-\overset{\bullet}{C}H_2$

c) $\overset{\bullet}{C}H_2-CH_2-CH=CH_2$

d) $CH_3-CH\overset{\bullet}{\overbrace{\cdots CH \cdots}}CH_2$

16. The resonance structures of the intermediate species in the carbonium ion addition to 2-methyl-1,3-butadiene (isoprene) are:

a) $\overset{+}{C}H_2-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-CH=CH_2$

b) $CH_3-\underset{+}{\overset{CH_3}{\overset{|}{C}}}-CH=CH_2$

c) $CH_3-\overset{CH_3}{\overset{|}{C}}=CH-\overset{+}{C}H_2$

d) $CH_3-\overset{CH_3}{\overset{|}{C}}\underbrace{\cdots CH \cdots}_{+}CH_2$

17. Reaction of 2,4-hexadiene with carbontetrachloride in presence of peroxide yields:

a) 1,1,1,3-tetrachloro-4-heptene
b) 4,7,7,7-tetrachloro-2-heptene
c) 1,1,1,5-tetrachloro-2-methyl-2-hexene
d) 4,6,6,6-tetrachloro-5-methyl-2-hexene

18. 1,4-butanediol $CH_2OH\ CH_2\ CH_2\ CH_2OH$ when heated in presence of acid yields:

a) 1-butene
b) 1,2-butadiene
c) 2-butene
d) 1,3-butadiene

19. The heats liberated when two isomeric dienes were hydrogenated are: diene A - 60.8 kcal/mole diene B - 56 kcal/mole. The statements one can make about these two dienes are:

a) diene A is more stable than diene B
b) diene A possesses more energy than diene B
c) on an energy diagram diene B occupies lower energy level than diene A
d) diene B is more stable than diene A

20. When isoprene (2-methyl-1,3-butadiene) is hydrogenated the expected heat of hydrogenation is 58 kcal/mole The observed heat of hydrogenation is 53.4 kcal/mole. The lower than expected heat of hydrogenation is due to:

a) hyperconjugation
b) delocalization of π electrons
c) resonance stabilization
d) overlap of all the p orbitals in the isoprene molecule

Self Instructional Package No. 13
Form C - Reference Guide

DIENES

The Reference Guide should be used in conjunction with Form B or the Self Evaluation Exercise. The references give the correlation between the questions in Form B and the available material in the textbook and in the form of tapes.

Questions 1, 2, 3, 19, 20	Chapter 8, Sections 16, 17, 18, 19
Questions 4, 5, 6	Chapter 8, Section 22
Question 7	Chapter 8, Sections 14, 15
Question 9, 12	Chapter 8, Section 25
Question 10	Chapter 8, Section 26
Questions 11, 18	Chapter 8, Section 15
Questions 13, 16	Chapter 8, Sections 20, 21
Questions 14, 15, 17	Chapter 8, Sections 23, 24

Additional explanations and examples for all questions are provided in Tape 1 with the accompanying work sheet and answer sheet.

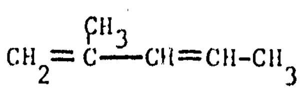
See plastic Nature working to this end
The single atoms each to the other tend
Attract, attracted to, the next in place
Form'd and impell'd its neighbor to embrace. ---*Alexander Pope*

Self Instructional Package No. 13
Tape 1 - Work Sheet

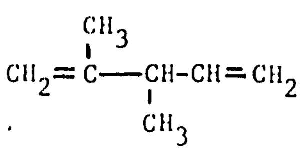
DIENES

Example No. 1

$CH_2=C=CH-CH_2$ 1,2-butadiene



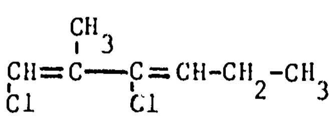
2-methyl-1,3-pentadiene

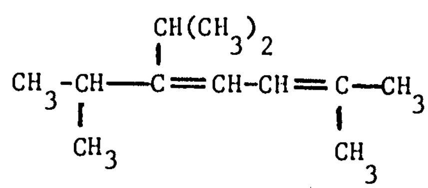


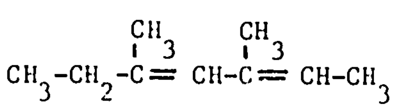
2,3-dimethyl-1,4-pentadiene

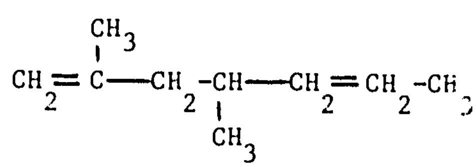
Assignment No. 1

Assign the correct IUPAC names to the following compounds:

a) 

c) 

b) 

d) 

Assignment No. 2 - Draw the structures which correspond to the following IUPAC names:

a) 2-bromo-3,4-dimethyl-2,5-octadiene

b) 7-methyl-6-ethyl- -octadiene

c) 2,3-hexadiene

d) 1,7-octadiene

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Example No. 2 - Classification of dienes

I. - Isolated Dienes $R-CH=CH-CH_2-CH=CH\ R$ ()

$CH_2=CH-CH_2-CH=CH_2$	$CH_3-CH=CH-CH_2-CH=CH_2$	$CH_2=CH-CH_2-CH_2-CH=CH_2$
1,4-pentadiene	2,5-hexadiene	1,5-hexadiene

II. - Cumulated Dienes or Allenes $R-CH=C=CH-R$ (= =)

$CH_2=C=CH_2$	$CH_2=C=CH-CH_3$	$CH_3-CH=C=CH-CH_3$
1,2-propodiene ALLENE	1,2-butadiene	2,3-pentadiene

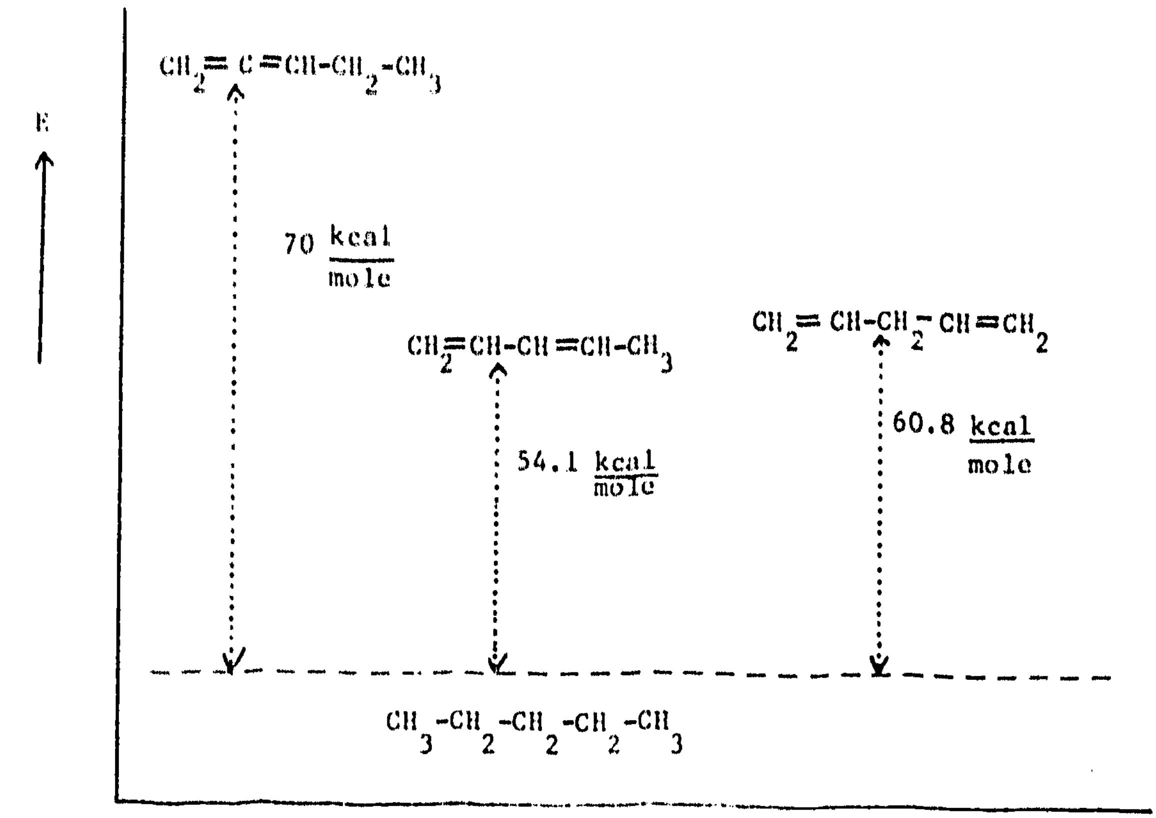
III. - Conjugated Dienes $R-CH=CH-CH=CH-R$ ()

$CH_2=CH-CH=CH_2$	$CH_3-CH=CH-CH=CH-CH_3$	$CH_2=CH-CH=CH-CH_2-CH_3$
1,3-butadiene	2,4-hexadiene	1,3-hexadiene

Example No. 3

	ΔH of Hydrogenation kcal/mole	
1,2-pentadiene (cumulated)	70	(Max.)
1,3-pentadiene (conjugated)	54.1	(Min.)
1,4-pentadiene (isolated)	60.8	

Example No. 3 (continued)



Example No. 4

		Heat of hydrogenation
monosubstituted alkene	$CH_2=CHR$	30 kcal/mole
disubstituted alkene	$CH_2=CR_2$ or $RCH=CHR$	28 kcal/mole
trisubstituted alkene	$RCH=CR_2$	27 kcal/mole

SIP No. 13
Tape 1 - Work Sheet

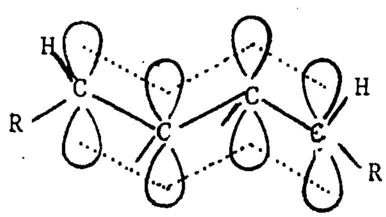
Example No. 4 (continued)

Table No. 1

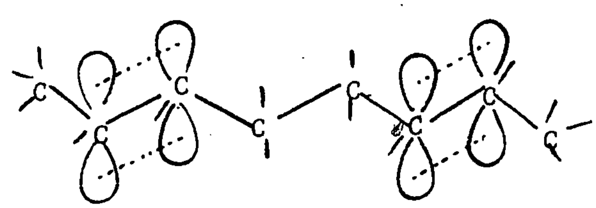
Compound	expected Heat of hydrogenation ΔH_1 kcal/mole	observed Heat of hydrogenation ΔH_2 kcal/mole	difference in kcal/mole ΔH_{1-2}
$CH_2=CH-CH=CH_2$	30 + 30 = 60	57.1	2.9
$CH_2=CH-CH=CH-CH_3$	30 + 28 = 58	54.1	3.9
$CH_2=C(CH_3)-CH=CH_2$	28 + 30 = 58	53.4	4.6

Example No. 5

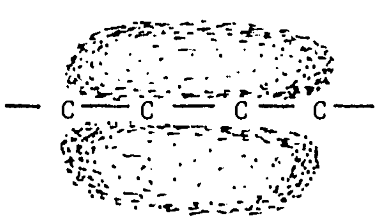
Orbital picture of dienes

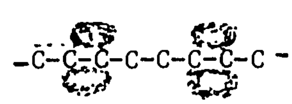


Conjugated dienes



cumulated dienes





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Example No. 5 (continued)

H_{1-2} = Delocalization Energy

Valence - Bond Structures:

I		II	
-C=C-C=C-	⟷	-Ċ-C=C-Ċ- (dotted bond between C1 and C4)	Resonance structures of 1,3-butadiene
1 2 3 4		1 2 3 4	

1,3-butadiene is the resonance hybrid of I and II

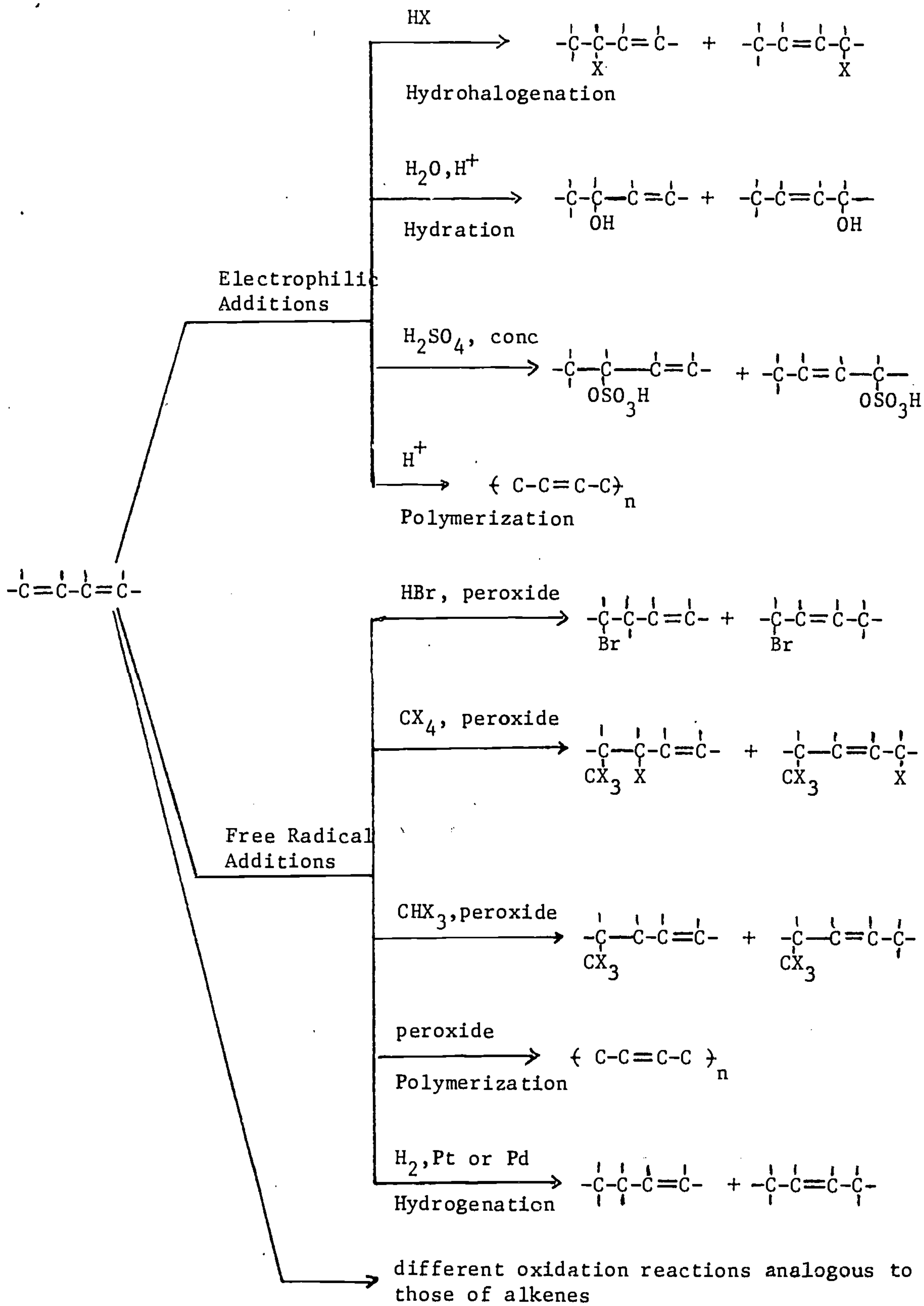
(1.34Å) C=C < C_{2-3} = 1.48Å < C-C (1.53Å)
in 1,3 butadiene

ΔH_{1-2} = Resonance Energy

Example No. 6

Table No. 2	Length [Å]	Hybridization
-C—C-	1.53	$Sp^3 - Sp^3$
=C—C-	1.50	$Sp^2 - Sp^3$
≡C—C-	1.46	$Sp - Sp^3$
(=C—C=	1.48A	$Sp^2 - Sp^2$)

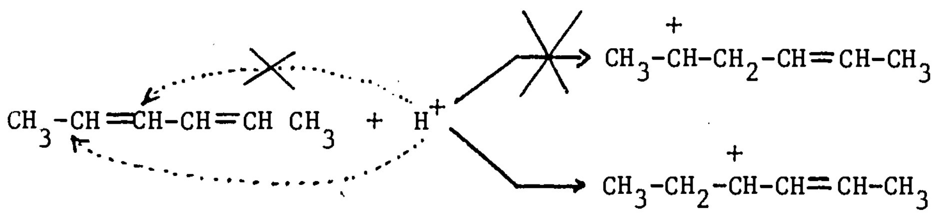
↓ Increase in "S" character of the σ bond


HX
Hydrohalogenation
H2O,H+
Hydration
Electrophilic Additions
H2SO4, conc
H+
Polymerization
HBr, peroxide
CX4, peroxide
Free Radical Additions
CHX3,peroxide
peroxide
Polymerization
H2,Pt or Pd
Hydrogenation
different oxidation reactions analogous to those of alkenes

Example No. 8

Electrophilic addition of HX to 2,4-hexadiene

Step 1



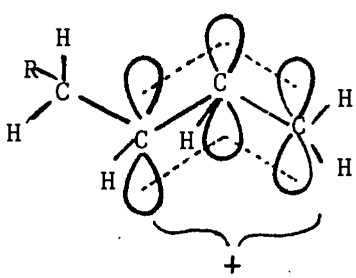
Allyl Carbonium Ion (much more stable)

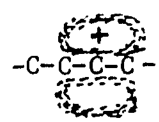
Step 2 - expected

$$CH_3-CH_2-\overset{+}{C}H-CH=CH-CH_3 + X^- \longrightarrow CH_3-CH_2-\underset{X}{C}H-CH=CH_2-CH_3$$

1,2 Addition Product

Orbital Picture of the Allyl Carbonium Ion





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SIP No. 13
Tape 1 - Work Sheet

Example No. 8 (continued)

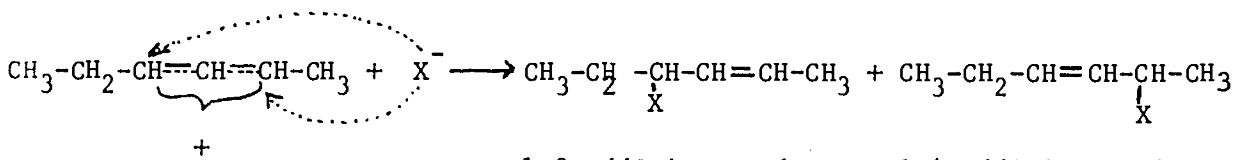
Resonance Structures of the Allyl Carbonium Ion

$CH_3CH_2-\overset{+}{C}H-CH=CH-CH_3 \longleftrightarrow CH_3CH_2-CH=CH-\overset{+}{C}H-CH_3 \longleftrightarrow CH_3CH_2-CH\overset{+}{\cdots}CH\cdots CH-CH_3$

I II III

Allyl carbonium ion formed in Step 1 is the resonance hybrid of Structures I, II and III.

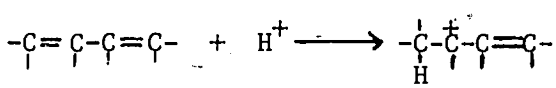
Step 2



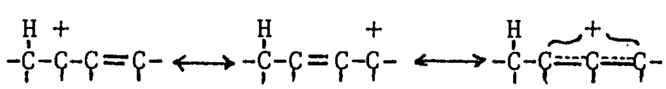
1,2-addition product 1,4-addition product

Example No. 9 - Electrophilic addition of HA to a conjugated diene

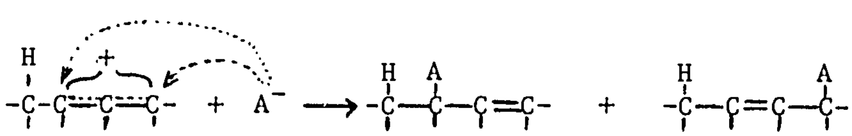
Step 1 - Formation of the allyl carbonium ion



Step 2a - Resonance stabilization of the allyl carbonium ion



Step 2' - Reaction of the allyl carbonium ion with the nucleophile



1,2-addition product 1,4-addition product

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SIP No. 13
Tape 1 - Work Sheet

Assignment No. 3

Write the step by step mechanism for the acid catalyzed hydration of 2-methyl-1,3-butadiene. Name all the products.

Assignment No. 4

Identify (draw the structures and name) the chief product or products in each of the following reactions.

a) 1,3-butadiene $\xrightarrow{H_2,Pt,Pd}$

b) 1,4-pentadiene $\xrightarrow{H_2O,H^+}$

c) 2-methyl-1,3-butadiene $\xrightarrow{Br_2,CCl_4}$

d) 1,3-pentadiene $\xrightarrow{HCl}$

e) 2,3-dimethyl-1,3-butadiene $\xrightarrow{H_2,Pt \text{ or } Pd}$

f) 2-methyl-1,4-hexadiene $\xrightarrow{HBr}$

SIP No. 13
Tape 1 - Work Sheet

Assignment No. 5

A hydrocarbon of formula C_9H_{16} absorbs two moles of H_2 upon catalytic hydrogenation. Upon ozonolysis this hydrocarbon yeilds:

$CH_3-\underset{H}{C}=O$ $\quad\quad$ $O=\underset{H}{C}-CH_2-\underset{H}{C}=O$ $\quad\quad$ $CH_3CH_2-\underset{CH_3}{C}=O$

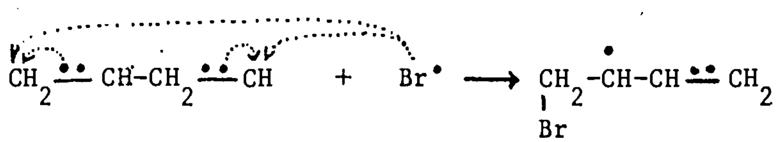
Draw the structure and name the original hydrocarbon.

Example No. 10 - Free Radical Addition of HBr to 1,3-butadiene

$$ROOR \longrightarrow RO^{\bullet} \quad or \quad FR^{\bullet}$$

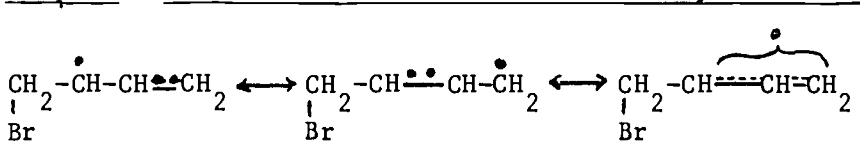
$$FR^{\bullet} + HBr \longrightarrow FRH + Br^{\bullet}$$

Step 1 - Formation of the allyl free radical



Allyl free radical

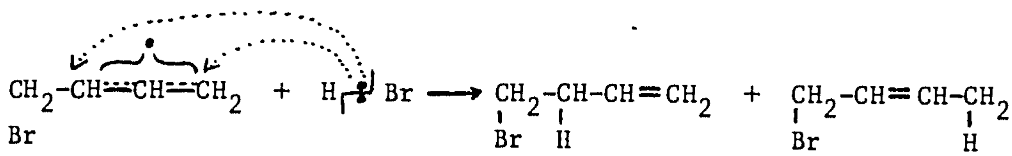
Step 2a - Resonance stabilization of the allyl free radical



SIP No. 13
Tape 1 - Work Sheet

Example No. 10 (continued)

Step 2 - Formation of the products



1,2-addition product 1,4-addition product

Assignment No. 6

Write the step by step mechanism for the peroxide catalyzed addition of carbontetrabromide to 2,4-hexadiene.

Assignment No. 7

Which compound of each pair listed below would you expect to be more reactive toward addition of $BrCCl_3$ in presence of peroxide?

a) 1,3-butadiene 1-butene

b) 1,3-butadiene 2-methyl-1,3-butadiene

c) 1,3-butadiene 1,4-pentadiene

d) 1,3-butadiene 1,3-hexadiene

SIP No. 13
Tape 1 - Work Sheet

Assignment No. 8

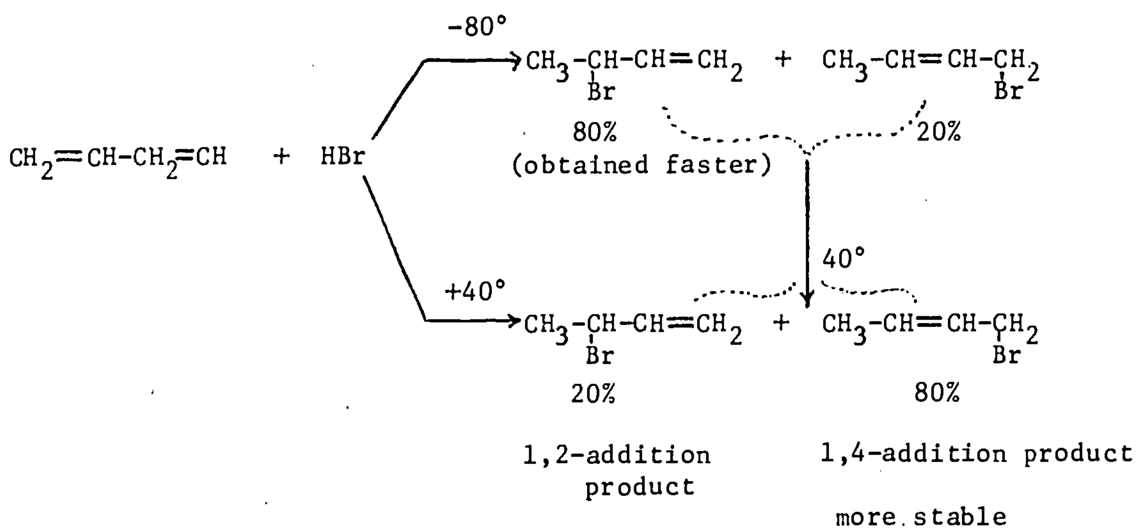
Confused Clyde was asked to complete a number of reactions and identify the products. The reactions as well as his answer are given below. Rectify his state of confusion.

a) 1,4-pentadiene $\xrightarrow{H_2O,\ H^+}$ $CH_3\text{-}CH(OH)\text{-}CH_2\text{-}CH{=}CH_2$ + $CH_3\text{-}CH{=}CH\text{-}CH(OH)\text{-}CH_3$

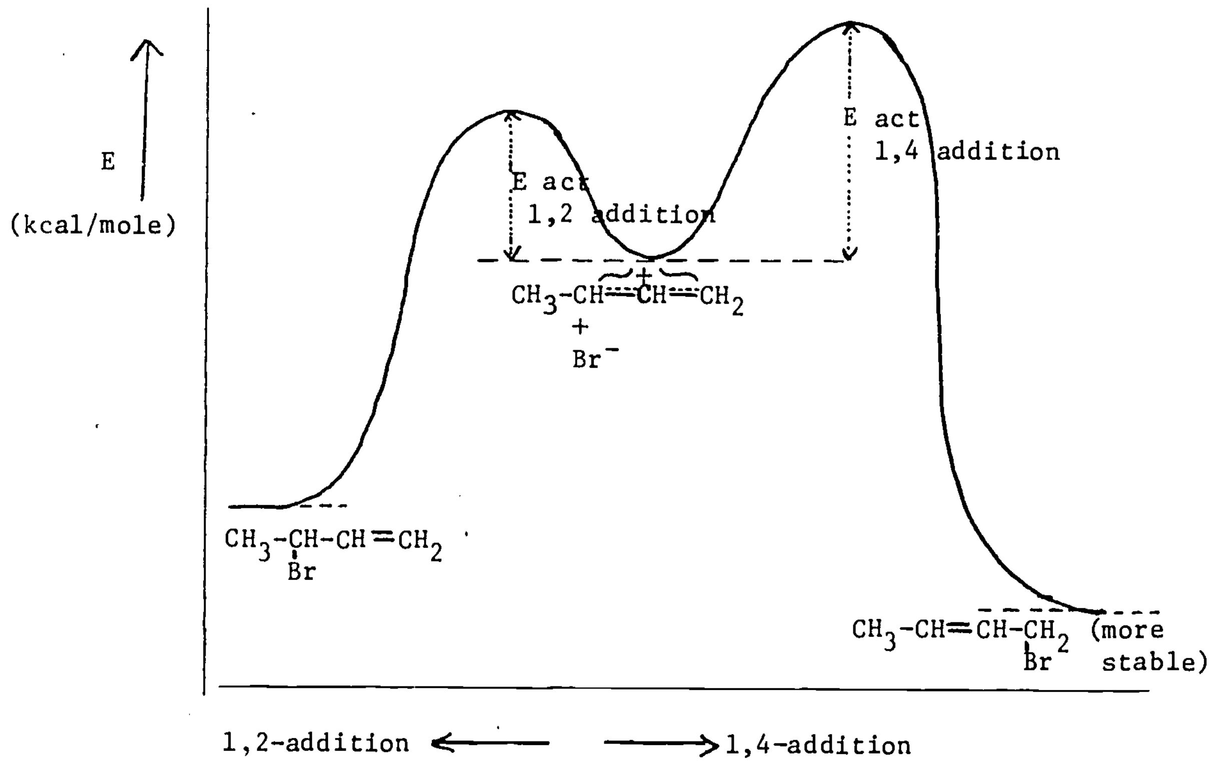
b) 1,3-butadiene $\xrightarrow{HBr,\ ROOR}$ $CH_3\text{-}CH(Br)\text{-}CH{=}CH_2$ + $CH_3\text{-}CH{=}CH\text{-}CH_2Br$

c) 2-methyl-1,4-pentadiene $\xrightarrow{H_2,\ Pt}$ $CH_3\text{-}CH_2\text{-}CH_2\text{-}C(CH_3){=}CH_2$ + $CH_3\text{-}CH{=}CH\text{-}CH(CH_3)\text{-}CH_3$

Example No. 11



Example No. 12 - Energy diagram of the reaction of the allyl carbonium ion with the bromide anion



Example No. 13 - Polymerization Reactions

$$n\ CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{\text{Acid or Peroxide}} {-}(CH_2{-}CH{=}CH{-}CH_2){-}_n$$

polybutadiene

$$n\ CH_2{=}C(Cl){-}CH{=}CH_2 \longrightarrow {-}(CH_2{-}C(Cl){=}CH{-}CH_2){-}$$

chloroprene (2-chloro-1,3-butadiene) → polychloroprene

$$n\ CH_2{=}C(CH_3){-}CH{=}CH_2 \longrightarrow {-}(CH_2{-}C(CH_3){=}CH{-}CH_2){-}_n$$

isoprene (2-methyl-1,3-butadiene) → polyisoprene

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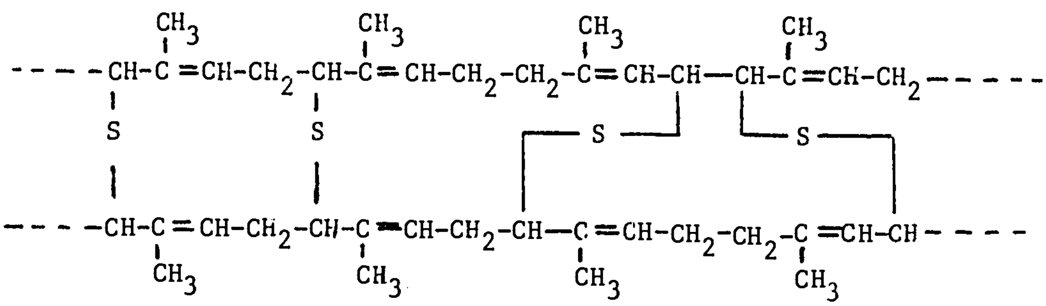
Example No. 14

Monomer	Trade Name	Uses
1,3-butadiene	Polybutadiene	Golf ball covers, substitute for gutta percha
1,3-butadiene and styrene ($CH_2=CH(C_6H_5)$)	GRS* (cold rubber)	tread of the heavy duty truck tires
1,3-butadiene and acrylonitrile ($CH=CH(CN)$)	Buna N ** (nitrile rubber)	fuel base; lining in the fuel tanks, underground storage tanks
2-chloro-1,3-butadine (chloroprene)	Neoprene	rubber substitute
2-methyl-1,3-butadiene (isoprene)	Ameripol (natural rubber)	rubber articles
isobutylene and isoprene or isobutylene alone	Butyl rubber	tires, inner tubes, etc.
ethylene and propylene	EPR Ethylene-Propylene Rubber	rubber substitute
ethylene	Polyethylene	films, containers, pipes, etc
vinyl chloride ($H_2C=CH(Cl)$)	Polyvinylchloride	film, piping, fibers
tetrafluoroethylene	Teflon	nonreactive surface coatings, valves, gaskets
propylene	Polypropylene	fibers, molded objects
styrene ($H_2C=CH(C_6H_5)$)	Polystyrene	packing materials
$F_2C=C(F)(Cl)$	KCl-F	valves, gaskets

*GRS means Government Rubber-Styrene type, a notation introduced during World War II

**Originally developed in Germany during World War II

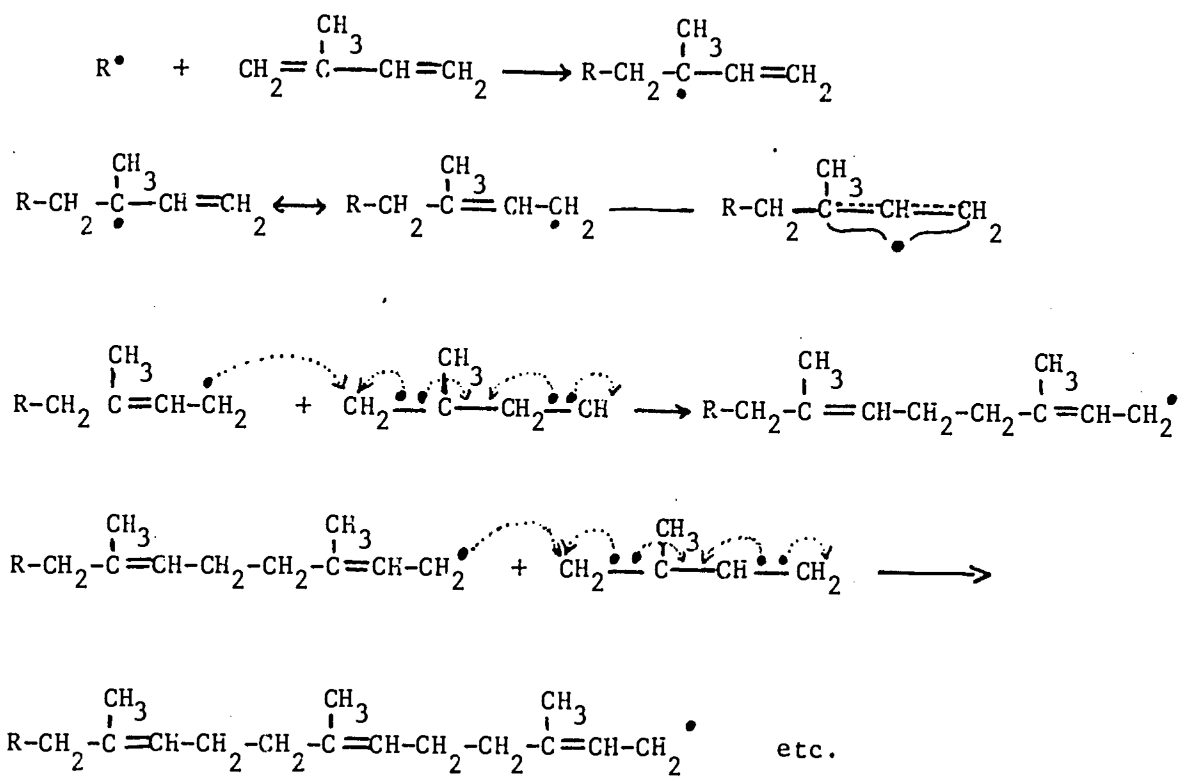
Example No. 15 - Vulcanization



Vulcanization is the formation of sulfur bridges between different polymer chains utilizing the allylic carbons.

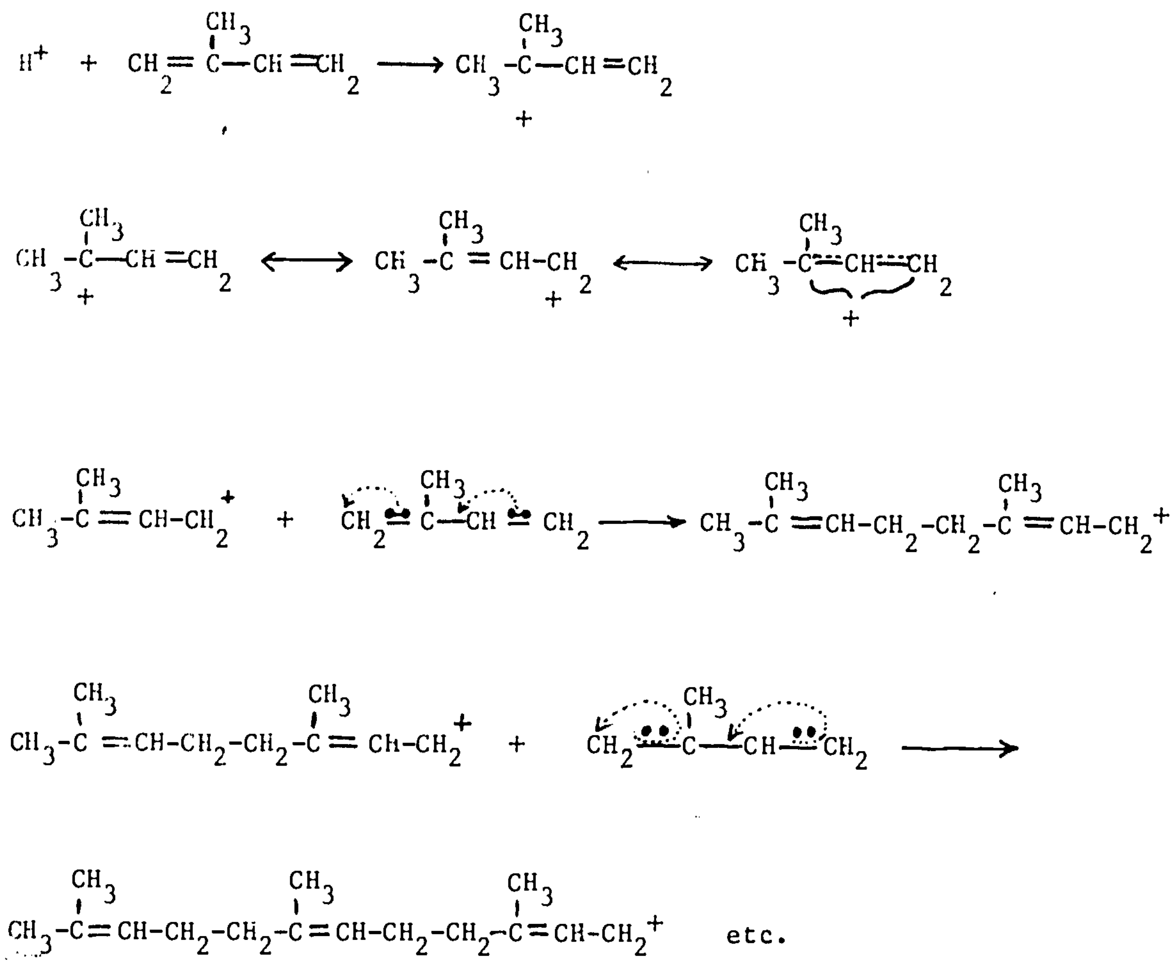
Example No. 16 - Free radical polymerization of isoprene

$ROOR \longrightarrow RO^{\bullet}$ or $R^{\bullet}$

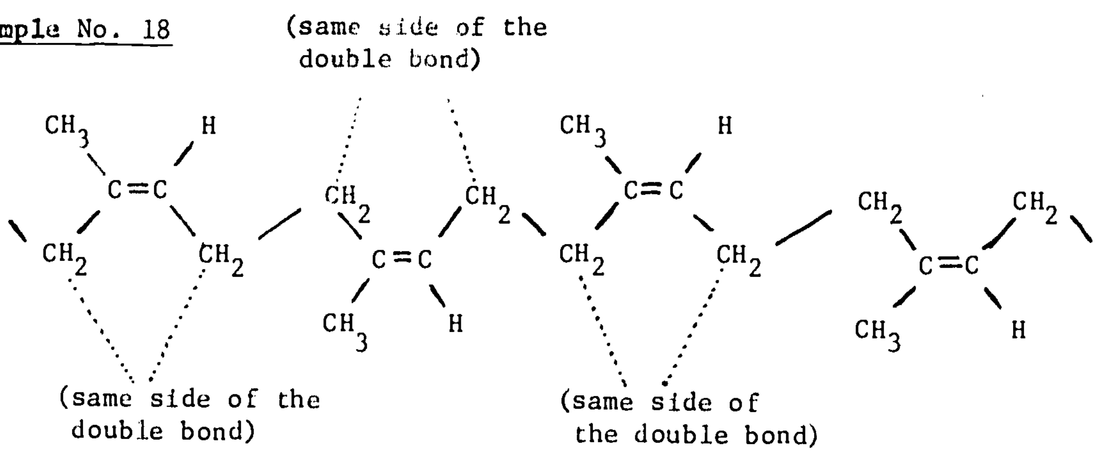


SIP No. 13
Tape 1 - Work Sheet

Example No. 17 - Cationic polymerization of isoprene

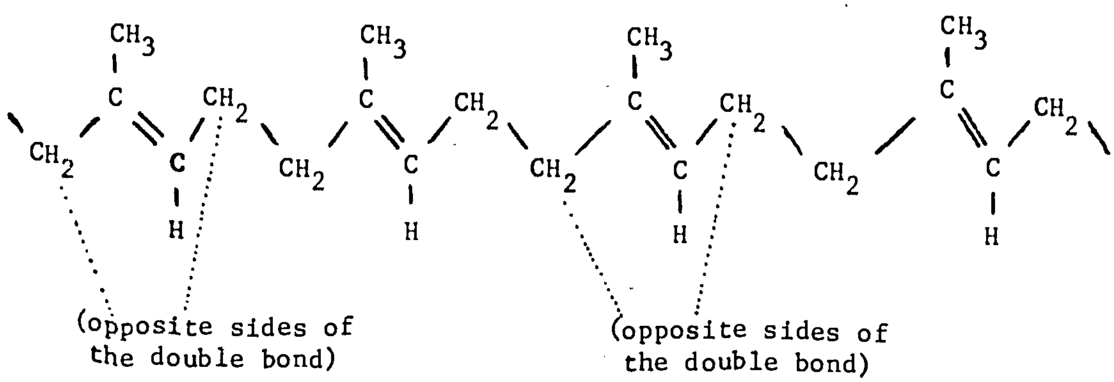


Example No. 18



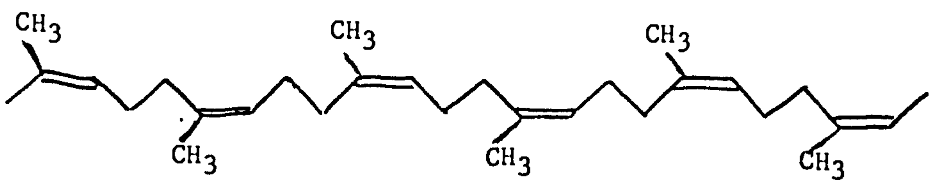
Natural rubber or Hevea rubber - all cis configurations

Example No. 18 (continued)

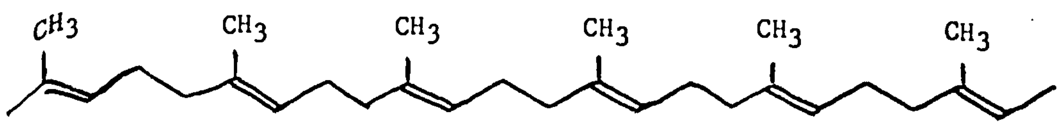


Gutta - Percha - all trans configurations

Schematic representation of the configuration of chains in natural rubber

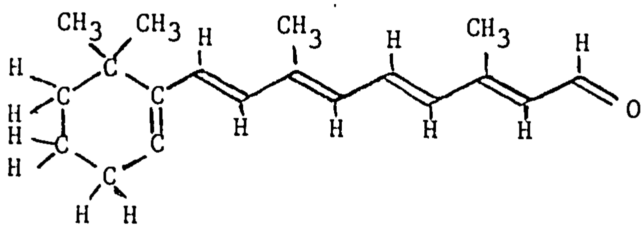


Schematic representation of the configuration of chains in gutta percha

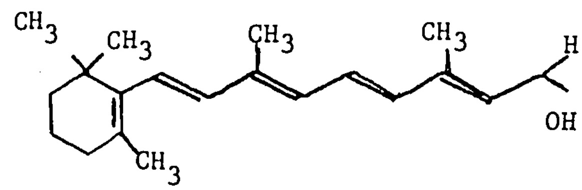


Assignment No. 9

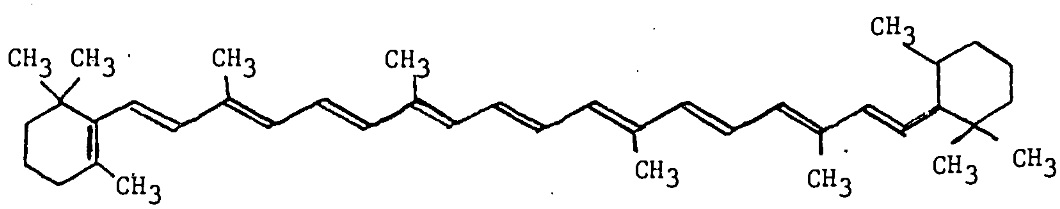
Identify the isoprene units in the biologically active compounds below:



Retinal - a key molecule in the chemistry of vision



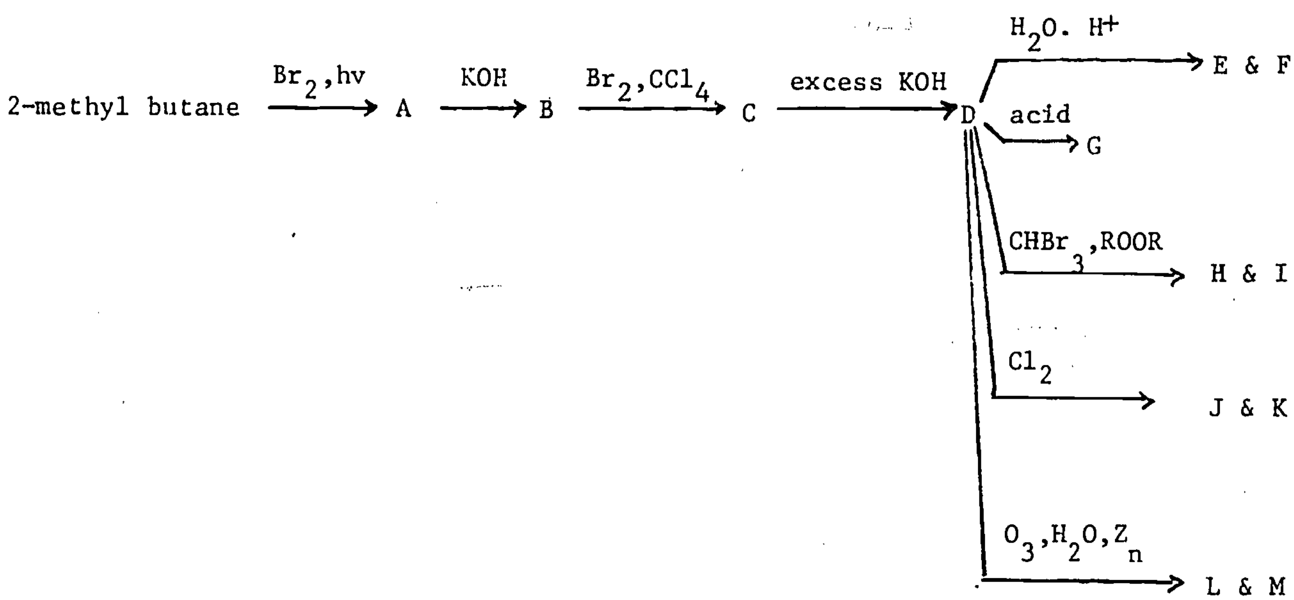
Vitamin A



B-Carotene - the pigment which causes carrots to be orange-colored.

Assignment No. 10

Identify compounds A through M in the multi-step synthetic scheme below.



SIP No. 13
Tape 1 - Work Sheet

Assignment No. 11

Outline all steps in the laboratory synthesis of:

a) 1,3-butadiene and b) 3-methyl-2-butene-1-ol from ethane.

Self Instructional Package No. 13
Tape 1 - Answer Sheet

DIENES

Assignment No. 1

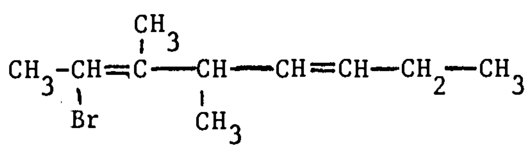
a) 1,3-dichloro-2-methyl-1,3-hexadiene

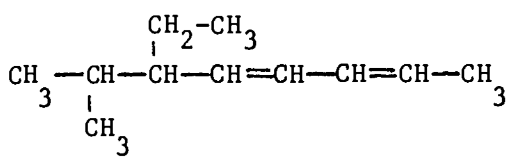
b) 3,5-dimethyl-2,4-heptadiene

c) 2,6-dimethyl-5-isopropyl-2,4-heptadiene

d) 2,4-dimethyl-1,5-heptadiene

Assignment No. 2

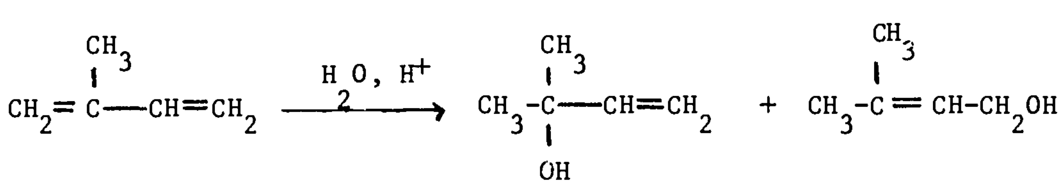
a) 

b) 

c) $CH_3-CH=C=CH-CH_2-CH_3$

d) $CH_2=CH-CH_2-CH_2-CH_2-CH_2-CH=CH_2$

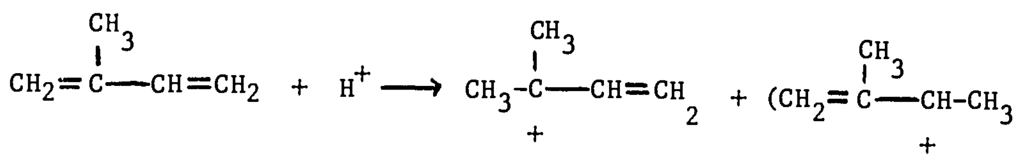
Assignment No. 3



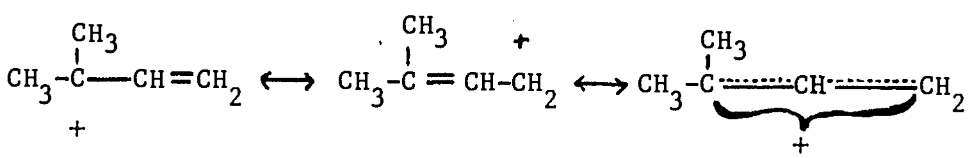
SIP No. 13
Tape 1 - Answer Sheet

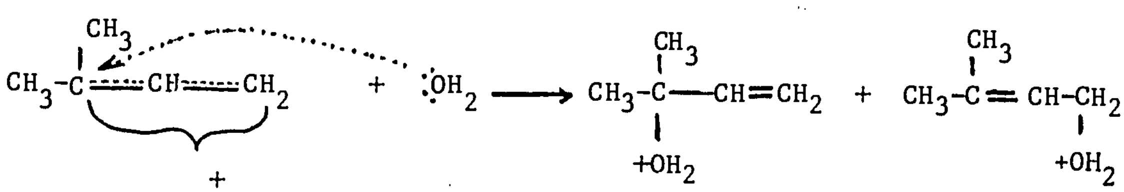
Assignment No. 3 (continued)

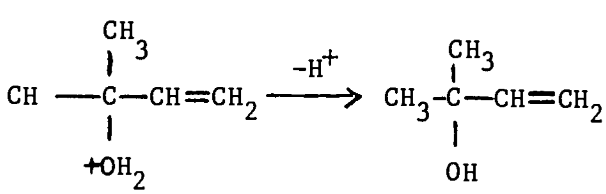
Mechanism:



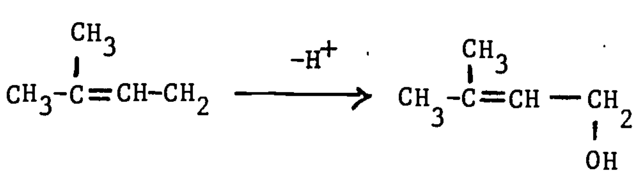
main product very low %







1,2 addition product



1,4 addition product

SIP No. 13
Tape 1 - Answer Sheet

Assignment No. 4

a) $CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{H_2,\ Pt\ or\ Pd} CH_3{-}CH_2{-}CH{=}CH_2 + CH_3{-}CH{=}CH{-}CH_3$

1-butene 2-butene

b) $CH_2{=}CH{-}CH_2{-}CH{=}CH_2 \xrightarrow{H_2O,\ H} CH_3{-}CH(OH){-}CH_2{-}CH{=}CH_2$

4-pentene-2-ol

c) $CH_2{=}C(CH_3){-}CH{=}CH_2 \xrightarrow{Br_2,\ CCl_4} CH_2(Br){-}C(Br)(CH_3){-}CH{=}CH_2 + CH_2(Br){-}C(CH_3){=}CH{-}CH_2(Br)$

3,4-dibromo-3-methyl-1-butene 1,4-dibromo-2-methyl-2-butene

$+ CH_2{=}C(CH_3){-}CH(Br){-}CH_2(Br)$ 3,4-dibromo-2-methyl-1-butene

lower %

d) $CH_2{=}CH{-}CH{=}CH{-}CH_3 \xrightarrow{HCl} CH_2{=}CH{-}CH(Cl){-}CH_2{-}CH_3 + CH_2(Cl){-}CH{=}CH{-}CH_2{-}CH_3$

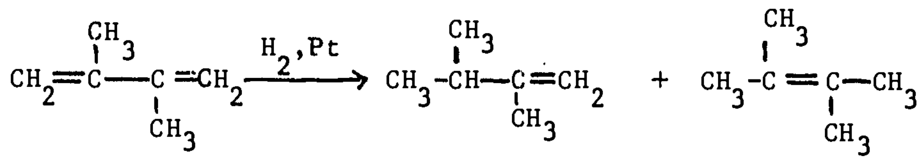
3-chloro-1-pentene 1-chloro-2-pentene

$+ CH_3{-}CH{=}CH{-}CH(Cl){-}CH_3$

4-chloro-2-pentene

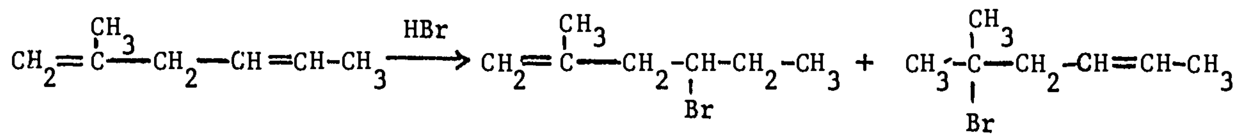
SIP No. 13
Tape 1 - Answer Sheet

Assignment No. 4 (continued)

e) 

2,3-dimethyl-1-butene

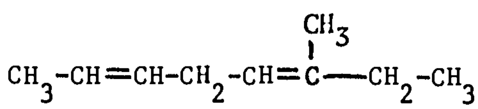
2,3-dimethyl-2-butene

f) 

4-bromo-2-methyl-1-hexene

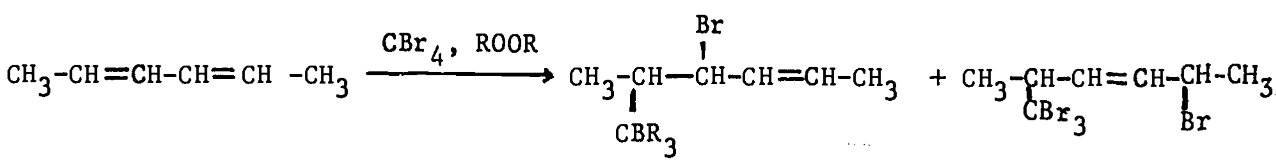
5-bromo-5-methyl-2-hexene

Assignment No. 5



6-methyl-2,5-octadiene

Assignment No. 6



Chain initiation -

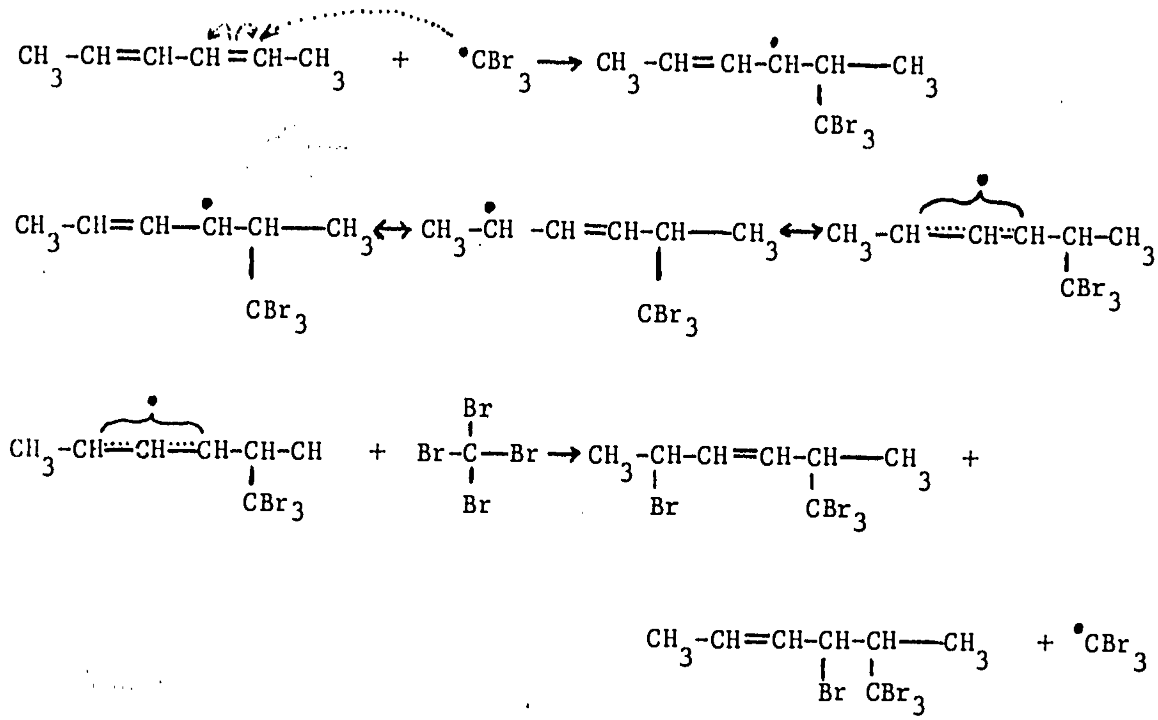
$$ROOR \xrightarrow{hv} RO^{\bullet}$$

$$RO^{\bullet} + Br{\bullet\bullet}CBr_3 \longrightarrow ROBr + {}^{\bullet}CBr_3$$

SIP No. 13
Tape 1 - Answer Sheet

Assignment No. 6 (continued)

Chain propagation -



Assignment No. 7

a) 1,3-butadiene

b) 2-methyl-1,3-butadiene

c) 1,3-butadiene

d) 1,3-hexadiene

Assignment No. 8

correct reactions:

a) $CH_2{=}CH{-}CH_2{-}CH{=}CH_2 \xrightarrow{H_2O,\ H^+} CH_3{-}\underset{\displaystyle OH}{CH}{-}CH_2{-}CH{=}CH_2$

SIP No. 13
Tape 1 - Answer Sheet

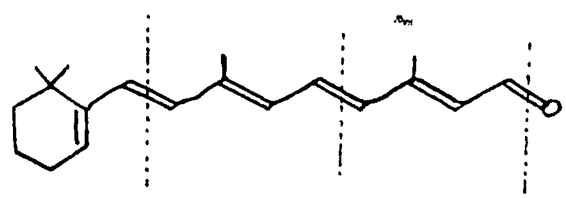
Assignment No. 8 (continued)

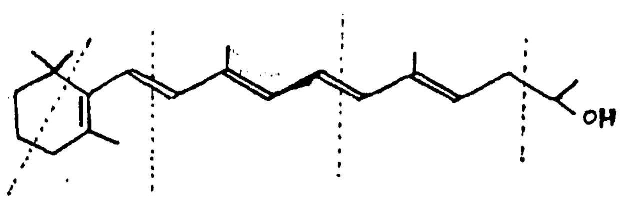
b) $CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{HBr,\ ROOR} \underset{Br}{CH_2}{-}CH_2{-}CH{=}CH_2 + CH_3{-}CH{=}CH{-}\underset{Br}{CH_2}$

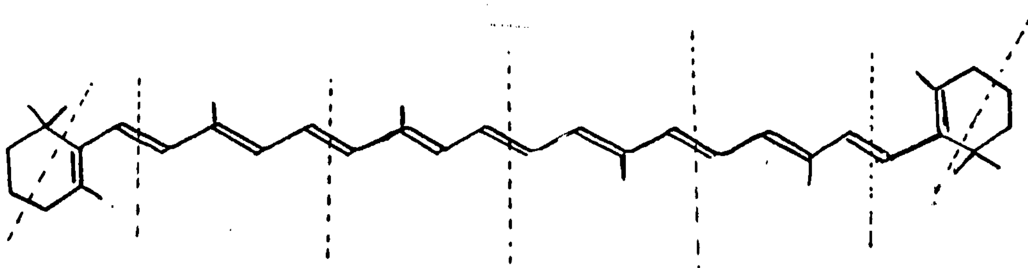
4-bromo-1-butene   1-bromo-2-butene

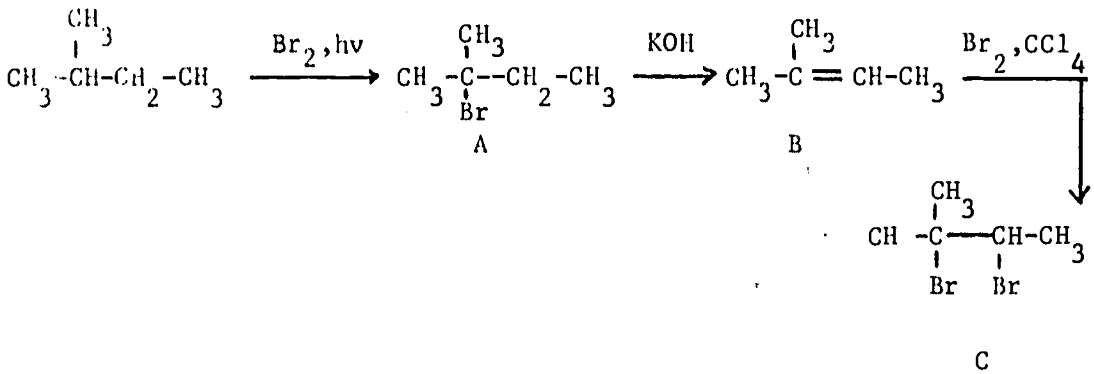
c) $CH_2{=}CH{-}CH_2{-}\overset{CH_3}{C}{=}CH_2 \xrightarrow{H_2,Pt} CH_3{-}CH_2{-}CH_2{-}\overset{CH_3}{C}{=}CH_2 + CH_2{=}CH{-}CH_2{-}\overset{CH_3}{CH}{-}CH_3$

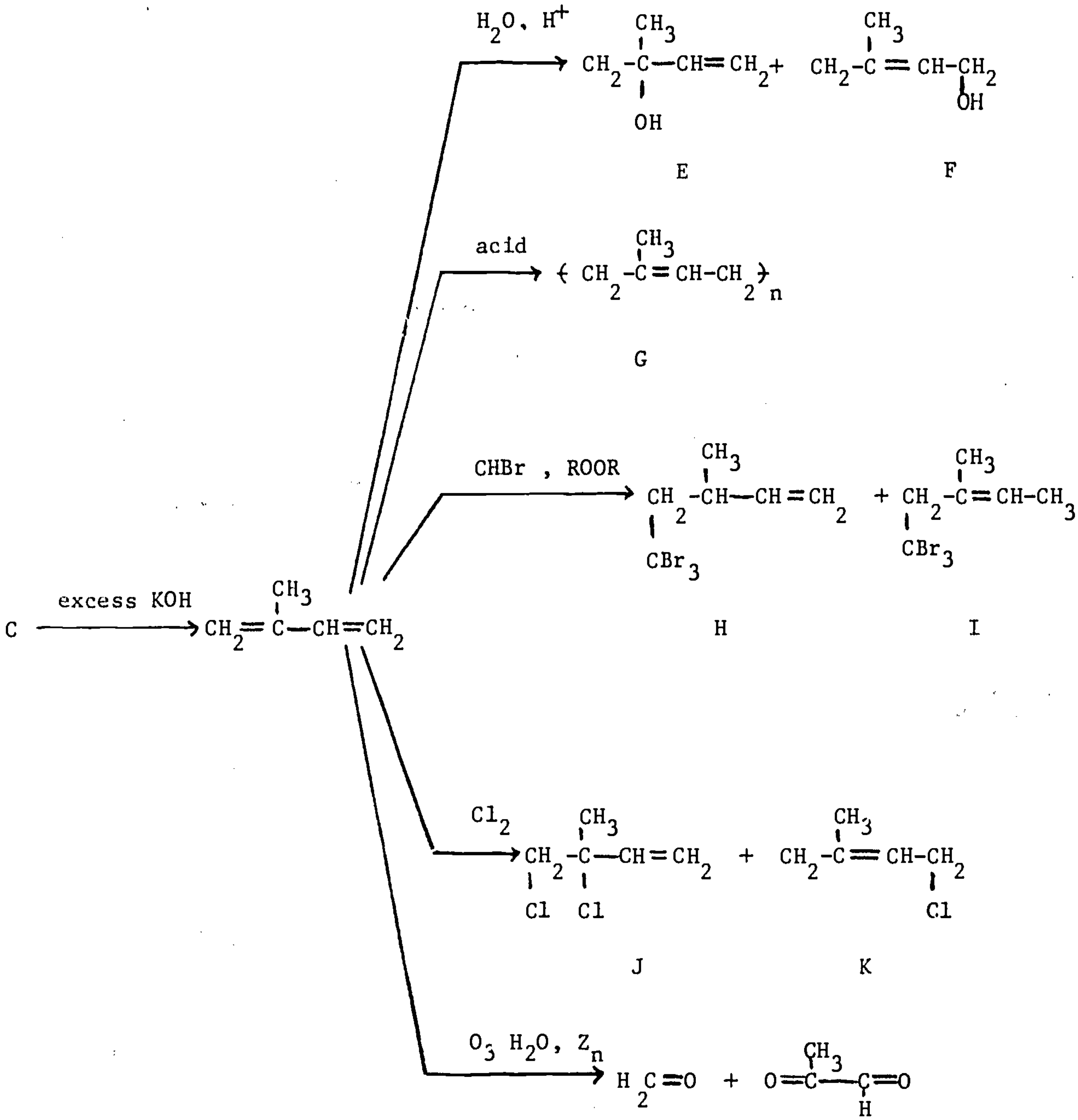
Assignment No. 9







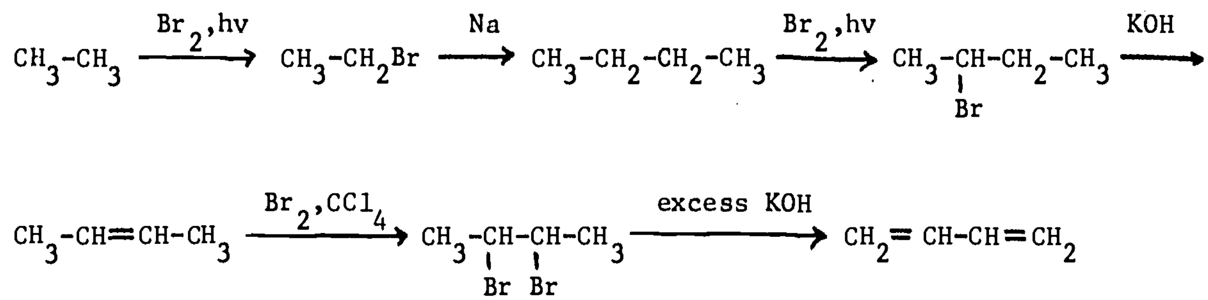

Br2,hv
KOH
Br2,CCl4
A
B
C


excess KOH
H2O, H+
acid
CHBr , ROOR
Cl2
O3 H2O, Zn
E
F
G
H
I
J
K

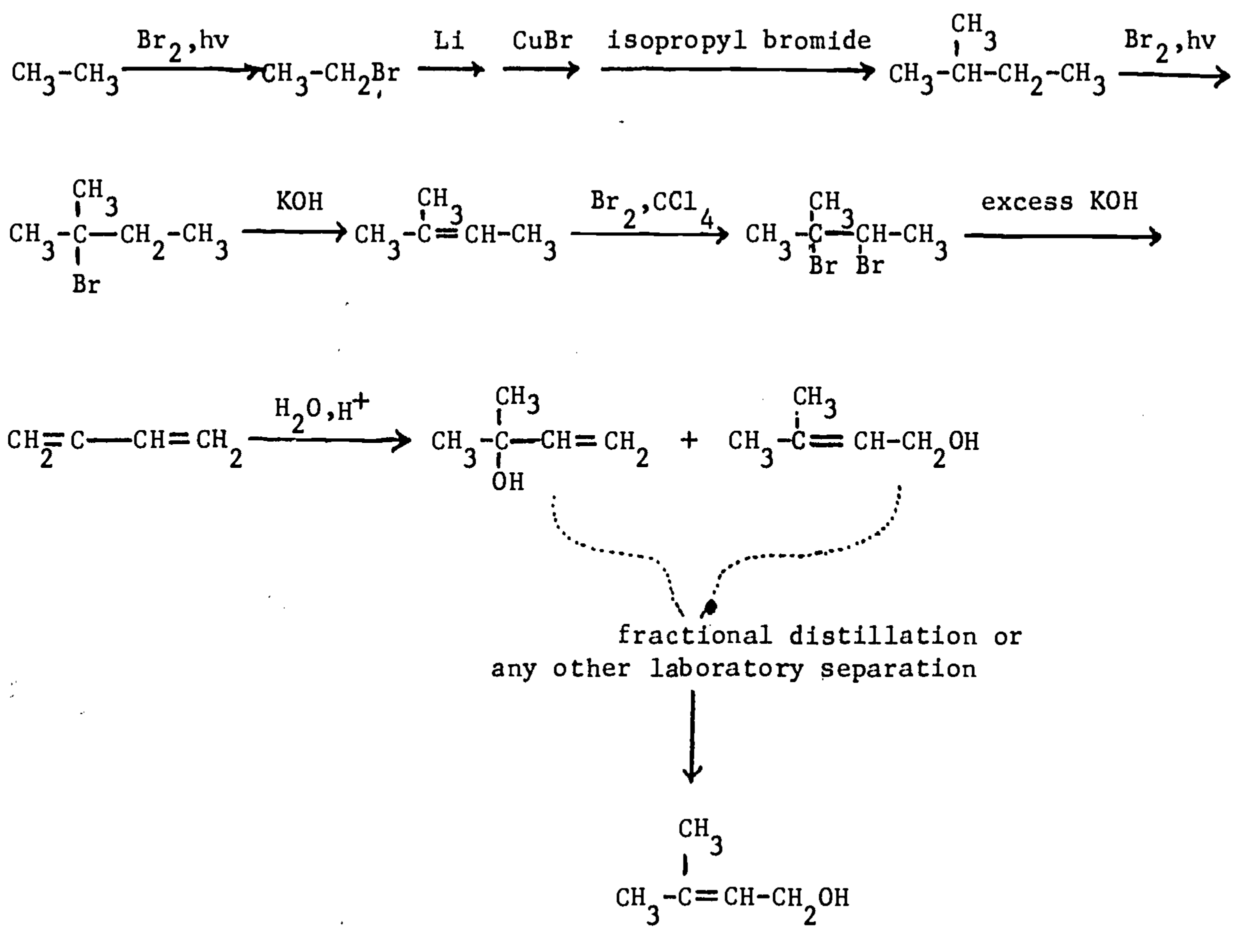
SIP No. 13
Tape 1 - Answer Sheet

Assignment No. 11

a)



b)



DIENES

Identify the statements below as True or False by placing a capital T or a capital F on the line to the left.

1. _____ Dienes are more reactive toward addition reactions than alkenes.

2. _____ The greater stability of conjugated dienes results from the delocalization of π electrons.

3. _____ 1,2-addition product has greater stability than the 1,4-addition product.

4. _____ 1,4-addition has higher energy of activation than the 1,2-addition.

5. _____ p orbitals in 1,3-butadiene overlap and form a uniform cloud of electron density above and below the carbon plane.

6. _____ Isolated dienes undergo both the 1,2 and the 1,4 addition.

7. _____ 2,6-heptadiene has lower heat of hydrogenation than 2,4-heptadiene.

8. _____ Gutta-percha is a trans-polyisoprene.

9. _____ Cationic polymerization results in the formation of polymer with all units possessing a cis arrangement.

10. _____ Free radical polymerization results in the formation of a polymer with all units possessing a trans arrangement.

Blacken out the correct answer or answers in each question.

11. In the reaction of 1,3-butadiene with bromoform in presence of peroxide the following products are obtained:

    a) 4,4,4-tribromo-3-methyl-1-butene

    b) 5,5,5-tribromo-1-pentene

    c) 5,5,5-tribromo-2-pentene

    d) 1,1,1-tribromo-2-methyl-2-butene

12. Partial hydrogenation of isoprene (2-methyl-1,3-butadiene) in presence of platinum yields:

    a) 3-methyl-1-butene
    b) 2-methyl-1-butene
    c) 2-methyl-2-butene
    d) 2-butene

13. Ozonolysis of 2,4-heptadiene will yield the following products:

    a) $CH - \overset{O}{\overset{\|}{C}}H$

    b) $H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$

    c) $H-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H$

    d) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$

14. The resonance structures of the intermediate formed in a carbonium ion addition to 1,3-pentadiene are:

    a) $CH_3-\overset{+}{C}H-CH=CH-CH_3$

    b) $\overset{+}{C}H_2-CH_2-CH=CH-CH_3$

    c) $CH_3-CH=CH-\overset{+}{C}H-CH_3$

    d) $CH_3-CH \cdots CH \cdots CH-CH_3$ (with + delocalized, shown by dotted arc)

15. The major products obtained in the reaction of 2-methyl-2,5-hexadiene with HBr are:

    a) 5-bromo-5-methyl-1-hexene

    b) 5-bromo-2-methyl-2-hexene

    c) 4-bromo-5-methyl-1-hexene

    d) 5-bromo-2-methyl-3-hexene

16. The lower than expected heat of hydrogenation in the conjugated dienes is often referred to as the:

    a) hyperconjugation energy

    b) delocalization energy

    c) resonance stabilization energy

    d) orbital energy

Self Instructional Package No. 13
Form B[1] - Answer Sheet

DIENES

1.	F	13.	a, b, c, d
2.	F	14.	a, c
3.	F	15.	a, b, d
4.	T	16.	b, c, d
5.	T	17.	c, d
6.	F	18.	d
7.	F	19.	b, c, d
8.	F	20.	b, c, d
9.	T		
10.	T		
11.	T		
12.	T		

Self Instructional Package No. 13
Form D^1 - Answer Sheet

DIENES

1. T
2. T
3. F
4. T
5. T
6. F
7. F
8. T
9. F
10. F
11. b, c
12. a, b, c
13. a, b, d
14. a, c, d
15. a, b
16. b , c

41