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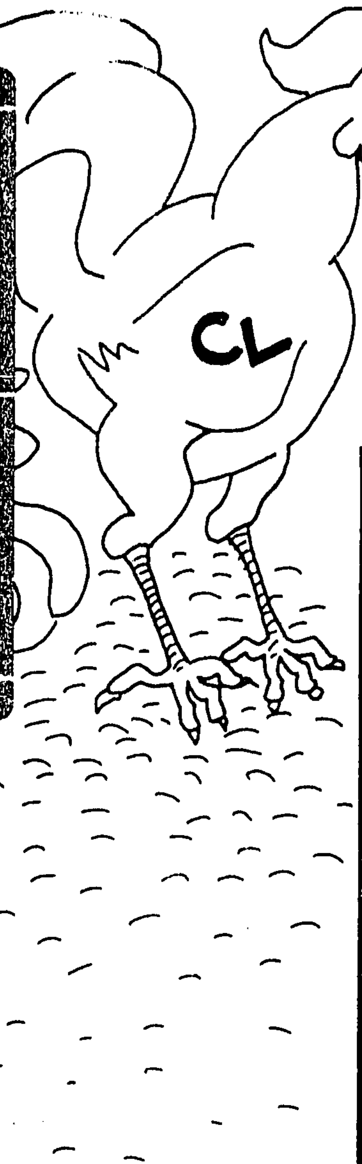
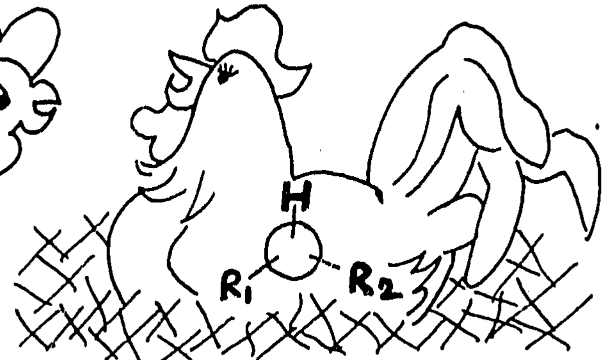
ABSTRACT

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 stereochemistry 2. (SL)



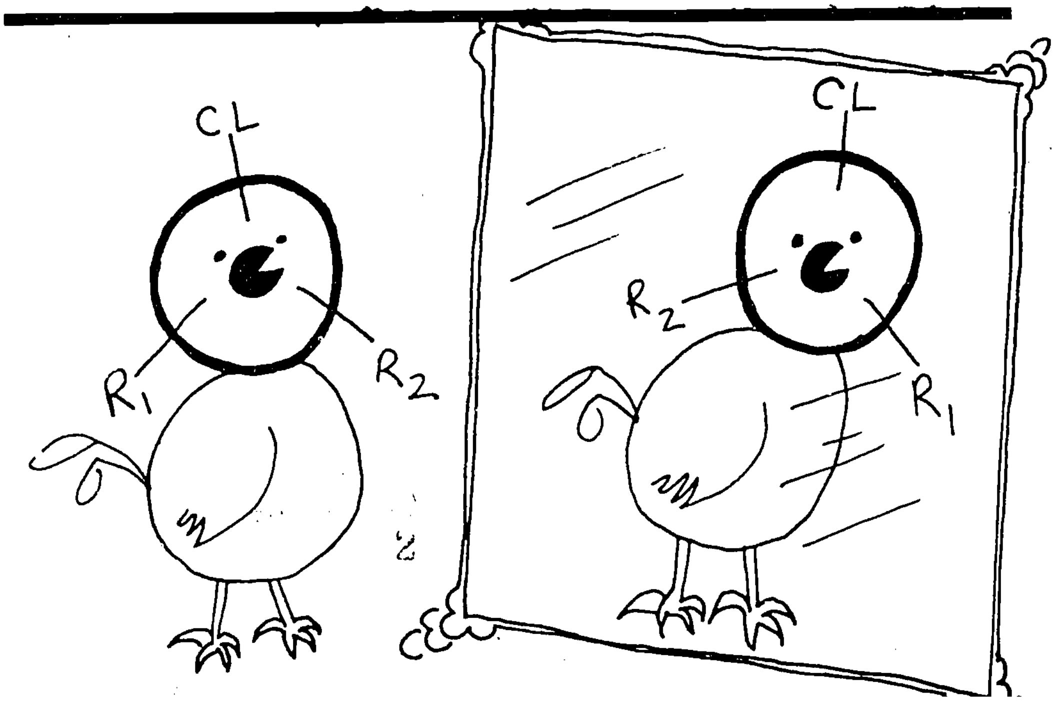

# ORGANIC CHEMISTRY

*V. Zdravkovich*

II

**S**elf
**I**nstructional
**P**ackage


# STEREOCHEMISTRY 2



Self Instructional Sequence in

# ORGANIC CHEMISTRY

# STEREOCHEMISTRY II

*"The sacred fire kindled by the grand maitre is still burning. Long may this flame be fed within the temple where now rests in eternal sleep that hero of science whose greatest ambition was to be able in his last hour to pronounce the words, so simple in their form so boundless in their aspiration:*

*"J'ai fait ce que j'ai pu."* *1

These words were delivered in honor of a famous scientist and a great man, Jan Louis Pasteur, buried in the chapel of the Institut Pasteur in Paris.

As a graduate student at the Ecole normale superieure, a school which trained teachers for the state secondary schools, Pasteur founded the modern stereochemistry. His teacher, a famous crystallographer, Mitcherlich, reported in 1844 that the salts of paratartaric acid (racemic acid) and tartaric acid have identical chemical and physical properties and yet paratartarates are optically inactive while tartarates are dextrorotatory. In search of a logical explanation for this phenomena, Pasteur spent some time in experimental research. He obtained well formed crystals of paratartaric acid, noticed the presence of hemihedral faces and furthermore realized that some were oriented to the right and some to the left. Using an ordinary lense and a pair of tweezers, Pasteur hand-picked and separated these crystals into two groups. The solution of one group rotated the light to the right like the tartaric acid itself and the solution of the other group rotated the light to the left. Pasteur prepared nineteen different tartarates (salts of tartaric acid) and discovered the existence of hemihedral faces and optical antipodes in each case. He demonstrated that racemic tartaric acid can be separated into a dextrorotatory and a levorotatory tartaric acid which when mixed together yield again the optically inactive racemic acid.

*"These findings aroused tremendous interest at the Academic des Sciences. Biot was commissioned to arrange for a repetition of the experiment under his own scrupulous supervision. He furnished Pasteur with a sample of racemic acid, which had been found to be inactive to polarized light, as well as samples of sodium carbonate and ammonia water, and requested him to prepare the sodium ammonium double salt. This was done in Biot's presence in one of the rooms at the College. Ten days later, when the solution had deposited 30-40 grams of crystals, Pasteur was again summoned to Biot's laboratory to select the dextro and levorotatory crystals, placing them to Biot's right and left, respectively. Biot then prepared the carefully weighed solutions and called Pasteur back into the laboratory just before making the examination in the polarimeter. The more interesting solution, which was to cause rotation to the left, was tried first. The rotation was to the left. Visibly moved, the illustrious old man embraced Pasteur and in a trembling voice said: "My dear boy, I have loved the sciences so much all my life that this makes my heart pound."* *2

This was the first resolution ever performed. In a remarkable lucid interpretation of this phenomena, Pasteur concluded that the explanation can be found within the structure of the molecules themselves and that the molecules must be dissymetric and behave like mirror images of each other. Thus he provided the scientist with the lead which led to the present concepts of molecular structure and stereochemistry.

Pasteur did not perform only the first chemical resolution of a racemic acid, he also performed the first biological resolution of the racemic tartaric acid by using a fungus Penicillium glaucum.

To talk about Pasteur in connection with stereochemistry alone, however important to an organic chemist, is a sad understatement. His contributions to the fields of fermentation, wine-making, beer making, and silk industry are remarkable. But perhaps his most important contribution to the world is his pioneer work on immunization and infectious diseases. Pasteur is not only a founder of the modern stereochemistry, he is also a founder of the modern medicine.

## STEREOCHEMISTRY II

Definitions -

The student will be able to define or describe and illustrate with appropriate examples when applicable the following terms: RESOLUTION, STEREOSPECIFIC reaction, Stereoselective reaction, Conformational isomer, Configurational isomer, Enantiomer, Diastereoisomer, Syn-addition, Trans-addition.

Problems -

The student will be able to identify the products obtained in the conversion of an achiral molecule into a chiral molecule as optically active or inactive.

The student will be able to draw the configurations of the stereoisomers and to predict their relative optical activity or the lack of it in the:

a) reaction of an optically inactive compound in which a chiral center is generated.

b) reaction of an enantiomer in which no bond to the chiral center is cleaved and no new chiral center is generated.

c) reaction of an enantiomer in which a new chiral center is generated but no bond to the chiral center is cleaved.

d) addition reactions of cis or trans (Z or E) alkenes.

The student will be able to outline all the steps employed in a successful resolution.

The student will be able to correlate the configurations of the reactants and the products by examining the reaction which took place.

The student will be able to explain the fact that meso compound is obtained in larger yield than the other diastereosiomer in the reactions in which it is produced.

Self Instructional Package No. 11
Form B - Self Evaluation Exercise

# STEREOCHEMISTRY II

Identify the questions below as True or False by placing a capital T or F in the space to the left.

1. _____ An optically inactive reactant always hields an optically inactive product.

2. _____ An optically active compound always yields an optically active product.

3. _____ Resolution is a separation of racemic mixture into its components.

4. _____ When a second chiral center is generated in a chemical reaction one of the products is always a meso compound.

5. _____ An enantiomer which possesses one chiral center and undergoes a chemical reaction in which no bond to the chiral center is broken and no new chiral center is generated will always retain its original configuration.

6. _____ A reaction of an enantiomer in which a bond to the chiral center is cleaved will always produce an optically active compound.

7. _____ The resolution is based on the formation of diastereoisomers which can then be separated by a simple laboratory technique.

8. _____ A reaction of a dextrorotatory enantiomer in which no bond to the chiral center is cleaved and no new chiral center is generated will yield a dextrorotatory enantiomer with the same configuration.

9. _____ Addition of peroxyformic acid to an alkene in which a diol is formed is a typical syn addition.

10. _____ Bromination of butane yields a racemic mixture of 2-bromobutane due to the flat, planar shape of the intermediate free radical.

11. _____ In a reaction of an enantiomer which results in a formation of a meso compound and another diastereoisomer, the meso compound is obtained predominantly.

12. _____ A stereospecific reaction is a reaction that yields predominantly one stereoisomer.

13. _____ A stereoselective reaction is a reaction in which stereochemically different reactants give stereochemically different products.

14. _____ In a syn addition the two portions of the reagent add to the same face or the same side of the alkene.

15. _____ An alkene undergoes a syn addition with a cold aqueous solution of $KM_nO_4$.

16. The following statements about a reaction of an optically inactive compound in which a chirol center is generated are correct:

a) the product is optically inactive.
b) the product is optically active.
c) the product is an enantiomer.
d) the product is a racemic mixture.

17. The light induced bromination of pentane will produce:

a) ($\pm$) 3-bromo pentane

b) ($\pm$) 2-bromo pentane

c) ($\pm$) 1-bromo pentane

d) 3-bromo pentane

18. The addition of HCl to 1-pentene will produce:

a) ($\pm$) 2-chloropentane

b) ($\pm$) 3-chloropentane

c) optically inactive mixture of chloropentanes

d) optically active product.

19. The addition of HBr to ($\pm$) 3-bromo-1-butene will produce:

a) a meso 2,3-dibromo butane

b) an optically inactive mixture of dibromobutanes

c) ($\pm$) 2,3-dibromo butane

d) (+) 2,3-dibromobutane

The following three questions apply to the reaction below:

$$(\pm)\ \text{2-chloro butane} \xrightarrow{Cl_2,hv}$$

20. When the products were separate! by careful fractional distillation the number of fractions obtained was:

a) 2 b) 3 c) 4 d) 5

21. The fractions isolated and identified had following characteristic properties:

a) all of them were optically inactive

b) one was optically active

c) two possessed two chiral centers

d) three could be further resolved into two enantiomers

22. The fractions when separated and analyzed were identified as:

a) 2,2-dibromo butane

b) 1,3-dibromo butane

c) meso-2,3-dibromobutane

d) (+) 2,3-dibromobutane

23. Select the reactions which can safely be used to relate the configurations:

a) (+) $CH_3$ CHBr $CH_2OH$ $\xrightarrow{KM_nO_4}$ CH CHBr COOH

b) (-) $CH_3$ $CH_2$ CH(OH) $CH_3$ $\xrightarrow{PBr_3}$ $CH_3$ $CH_2$ CHBr $CH_3$

c) (+) $CH_3$ $CH(CH_3)$ CHBr $CH_2CH_3$ $\xrightarrow{NaCN}$ $CH_3$ $CH(CH_3)$ CH(CN) $CH_2$ $CH_3$

d) (-) $CH_3$ CH $(CH_3)$ CH(OH) $CH_2Br$ $\xrightarrow{NaCN}$ $CH_3$ $CH(CH_3)$ CH(OH) $CH_2CN$

24. The addition of bromine to (S) 3-bromo-1-butene results in the formation of:

a) S,R 1,2,3-tribromo butane

b) R,S 1,2,3-tribromo-butane

c) R,R 1,2,3-tribromo butane

d) S,S 1,2,3-tribromo butane

25. In the addition of bromine to (S) 3-bromo-1-butene:

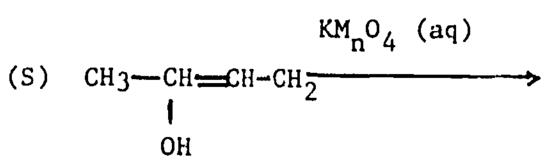
a) all products are optically active.

b) all products are optically inactive.

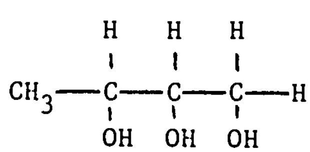
c) one product is optically active and one is optically inactive.

d) two products are optically active and one product is optically inactive.

The next two questions apply to the reaction below:




26. The reaction above results in the formation of:

a)


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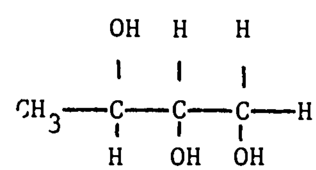
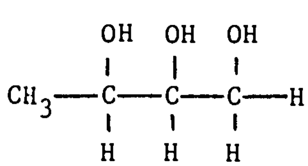
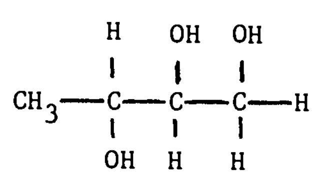


b)


d)


27. In the reaction above:

a) all products are optically active.

b) all products are optically inactive.

c) one product is optically active and the other is opticall inactive.

d) two products are optically active and one is optically inactive.

28. An addition of bromine to cis-3-hexene results in:

a) meso 3,4-dibromo hexane

b) (±) 3,4-dibromo hexane

c) optically inactive products

d) optically active products

29. An addition of bromine to trans 2-pentene results in:

a) meso 2,3-dibromo pentane

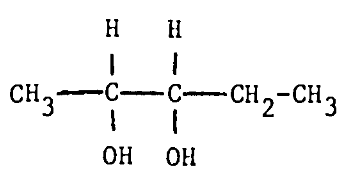
b) (±) 2,3-dibromo pentane

c) optically inactive products

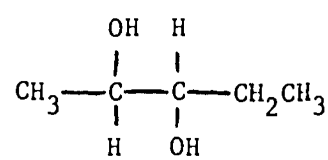
d) optically active products

30. An addition of aqueous $KM_nO_4$ to cis-2-pentene results in:

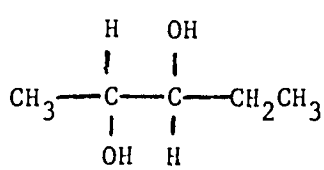
a)



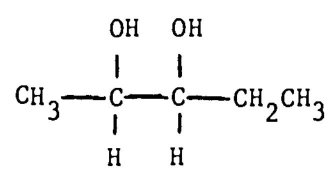

c)




b)




d)




11

Self Instructional Package No. 11
Form C - Reference Guide

# STEREOCHEMISTRY II

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, 16, 17, 18 | Chapter 7, Section 3 | Morrison & Boyd |
| Questions 3, 7 | Chapter 7, Section 9 | Organic Chemistry |
| Questions 4, 19, 20, 21, 22, 24, 25, 26, 27 | Chapter 7, Sections 7, 8 | |
| Questions 5, 8, 9, 23 | Chapter 7, Sections 4, 5 | |
| Questions 6, 10 | Chapter 7, Section 10 | |
| Question 11 | Chapter 7, Section 8 | |
| Questions 12, 13, 14, 15, 30 | Chapter 7, Section 11 | |
| Questions 28, 29 | Chapter 7, Section 12 | |

Further explanation and examples for all questions can be found in Tape 1 - Stereochemistry II.

For questions 9, 15, and 30, additional explanation and examples can be found in SIP 10 - Tape 2 - Alkenes II - Hydrogenation, Polymerization, Oxidation.

Self Instructional Package No. 11
Tape 1 - Work Sheet

## STEREOCHEMISTRY II

Example No. 1 - Review definitions

STRUCTURAL ISOMERS - species which have the same molecular formula but different structure

STEREOISOMERS - species which have the same molecular formula and the same structure but different arrangement of atoms in space. (different configuration)

CONFORMATIONAL - stereoisomers which can be interconverted into each other due to the free rotation around the carbon-carbon single bond. (cannot be separated)

CONFIGURATIONAL ISOMERS - stereoisomers which can be interconverted into each other only if a bond is cleaved. (can be separated)

ENANTIOMERS - nonsuperimposable mirror image isomers. They are optically active when separated.

DIASTEREOISOMERS - nonsuperimposable stereoisomers which are not mirror images of each other (can be optically active.)

GEOMETRIC ISOMERS - diastereoisomers which owe their existence to the hindered rotation around the carbon-carbon double bond.

Example No. 2 - Reactions of the stereoisomers to be discussed in this tape

I - Reactions of achiral molecules in which a chiral center is generated.

Result: optically inactive reactant always yields an optically inactive product. (racemic mixture)

II - Reactions of chiral molecules in which no bond to the chiral center is cleaved and no new chiral center is generated.

Result: retention of configuration around the chiral center.

III - Reactions of chiral molecules in which new chiral center is generated.

Result: retention of configuration around the chiral center and formation of products resulting from the attack on the opposite sides where the new chiral center is generated.

IV - Resolution of racemic mixture.

V - Reactions of chiral molecules in which a bond to the chiral center is cleaved.

VI - Stereospecific addition reactions of different alkenes.

Example No. 3 - Reaction Type I

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \xrightarrow{Br_2,\text{ light}} (\pm)\ CH_3\text{-}\overset{*}{C}H(Br)\text{-}CH_2\text{-}CH_3$$

Achiral molecule
(optically inactive)

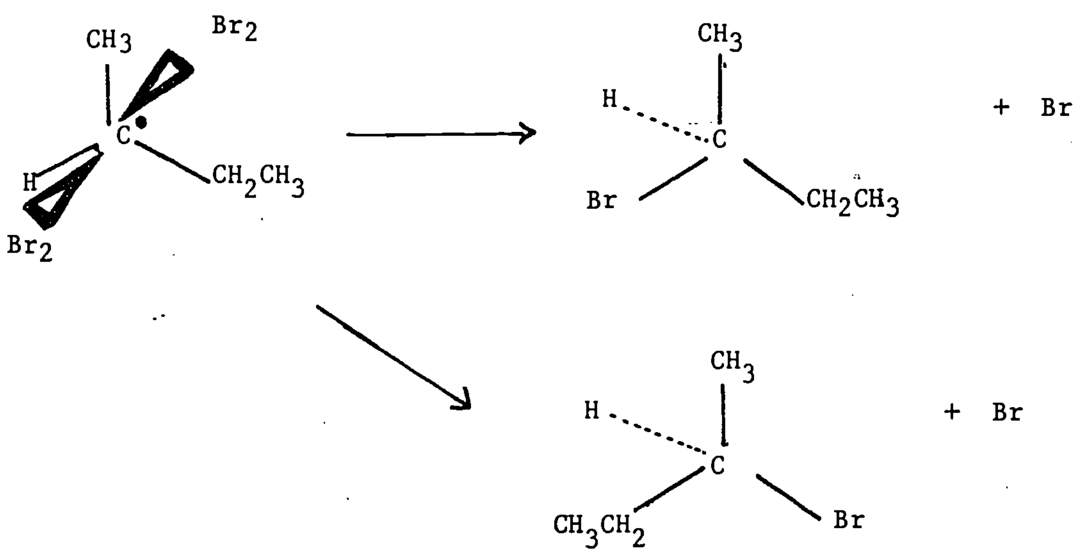
Racemic mixture
(optically inactive)

Mechanism -

$$Br_2 \xrightarrow{\text{light}} 2\ Br^{\bullet}$$

$$CH_3\ CH_2\ CH_2\ CH_3 + Br^{\bullet} \longrightarrow CH_3\ \dot{C}H\ CH_2\ CH_3 + HBr$$

$$CH_3\ \dot{C}H\ CH_2\ CH_3 + Br_2 \longrightarrow CH_3\ CH(Br)\ CH_2\ CH_3 + Br^{\bullet}$$



SIP No. 11
Tape 1 - Work Sheet

Example 4 - Reaction Type I

$$CH_2{=}CH\text{-}CH_2\text{-}CH_3 \xrightarrow{HBr} (\pm)\ CH_3\text{-}\overset{*}{C}H(Br)\text{-}CH_2\text{-}CH_3$$

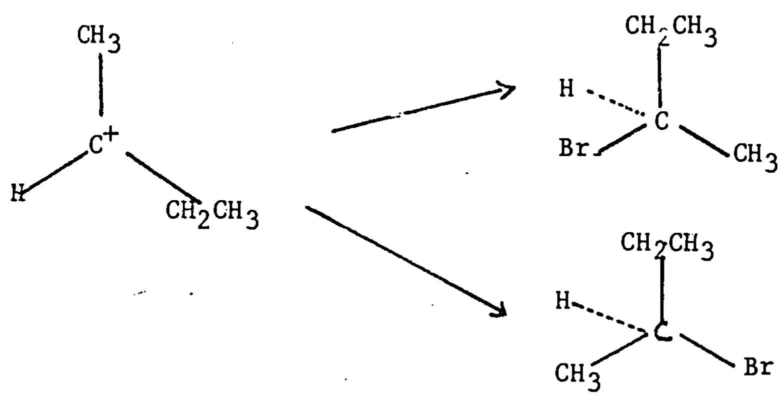
Achiral molecule
(optically inactive)

Racemic mixture
(optically inactive)

Mechanism -

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

$$CH_3\text{-}\overset{+}{C}H\text{-}CH_2\text{-}CH_3 + Br^- \longrightarrow CH_3\text{-}CH(Br)\text{-}CH_2\text{-}CH_3$$




Assignment No. 1

a) Draw the structures and name the products in the reactions below.

b) Identify the chiral centers in the reactants (if any).

c) Identify the chiral centers in the products (if any).

d) Explain on the basis of the reaction mechanism why are the products in all reactions optically inactive.

1.) 1-pentene $\xrightarrow{H_2O, H^+}$

2.) 1-butene $\xrightarrow{KMnO_4, aq}$

3.) propane $\xrightarrow{Br_2, hv}$

SIP No. 11
Tape 1 - Work Sheet

## Assignment No. 2

Confused Clyde was asked to complete a number of reactions and identify the products as optically active or inactive. Clyde's answer is given below. Try to rectify his state of confusion.

a) 2-hexene $\xrightarrow{H_2O,H^+}$ $CH_3-CH_2-\underset{|}{\underset{OH}{CH}}-CH_2-CH_3$

3-pentanol - optically inactive

b) 2-methyl butane $\xrightarrow{Cl_2,hv}$ $CH-\overset{CH_3}{\underset{Cl}{C}}-CH-CH_3$

2-chloro-2-methyl butane- optically inactive

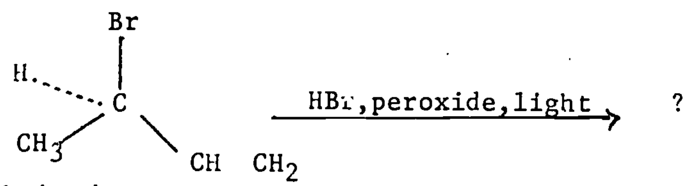
c) 3-methyl pentane $\xrightarrow{Cl_2,hv}$ $CH_3-CH_2-\overset{CH_3}{\underset{Cl}{C}}-CH_2-CH_3$

3-chloro-3-methyl pentane- optically inactive

SIP No. 11
Tape 1 - Work Sheet

Example No. 5 - Reaction Type II

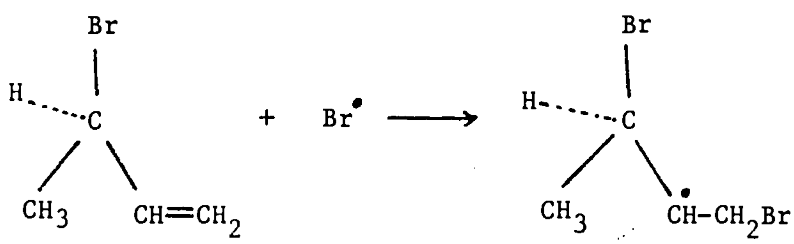
R-3-bromo-1-butene $\xrightarrow{\text{HBr, peroxide, light}}$ ?

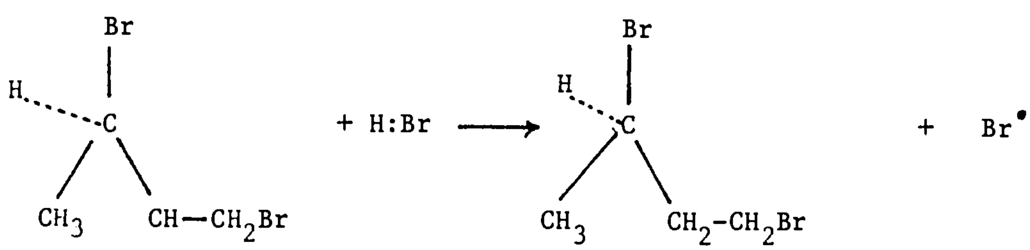



Mechanism -

$$ROOR \xrightarrow{\text{light}} 2\ RO^{\bullet} \quad \text{or} \quad FR^{\bullet}$$

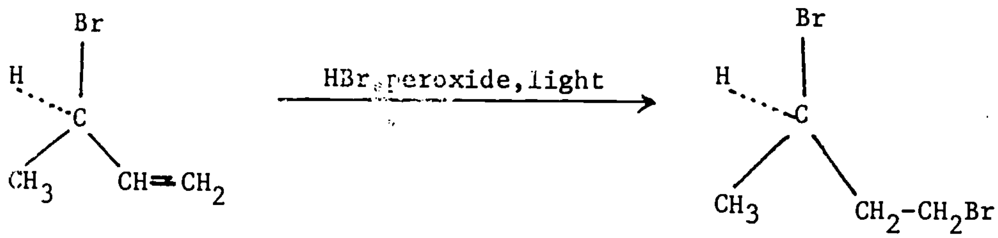
$$RO^{\bullet} + HBr \longrightarrow ROH + Br^{\bullet}$$



Example No. 5 - Reaction Type II (continued)

Overall reaction

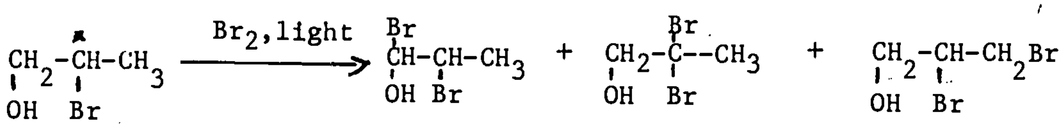



R-3-bromo-1-butene

R-1,3-dibromobutane

The configuration around the chiral center remains unchanged. Reaction proceeds with the RETENTION OF CONFIGURATION.

Example No. 6 - Reaction Type II




A B C

S-2-bromo 1-propanol

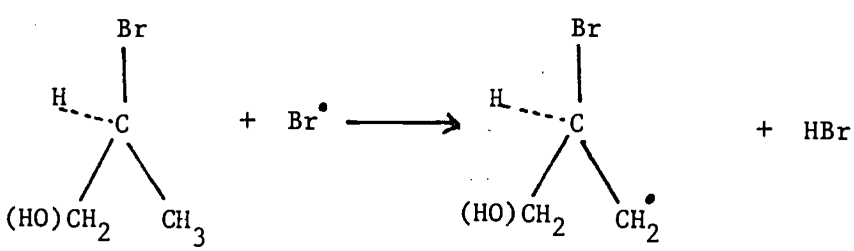
1,2-dibromo-1-propanol

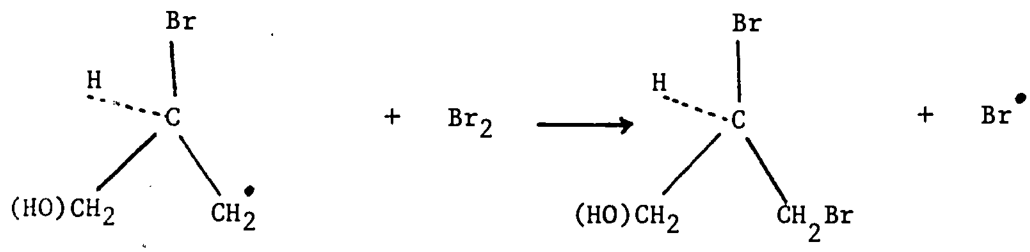
2,2-dibromo 1-propanol

2,3-dibromo 1-propanol

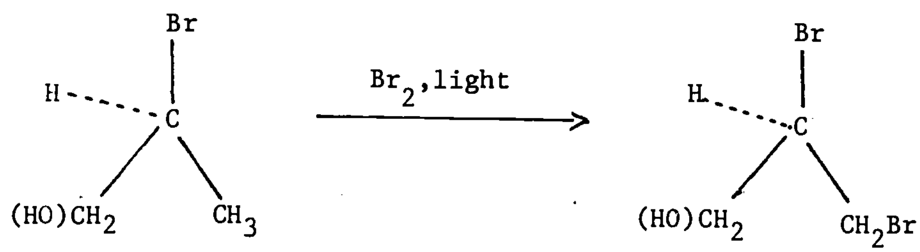
Mechanism for the formation of 2,3-dibromo-1-propanol

$$Br_2 \xrightarrow{\text{light}} 2\ Br^{\bullet}$$






Overall reaction:

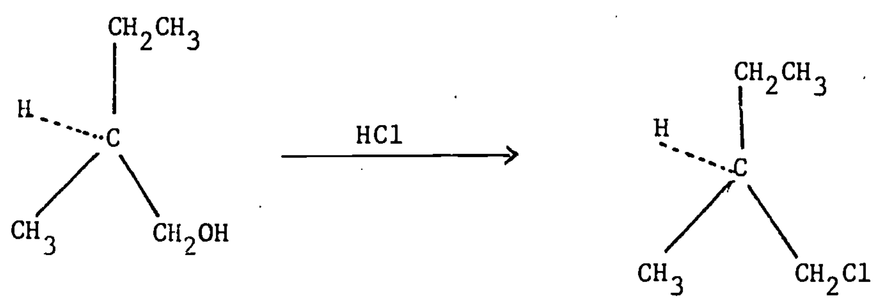



S-2-bromo-1-propanol          R-2,3-dibromo-1-propanol

Reaction proceeds with the retention of configuration..

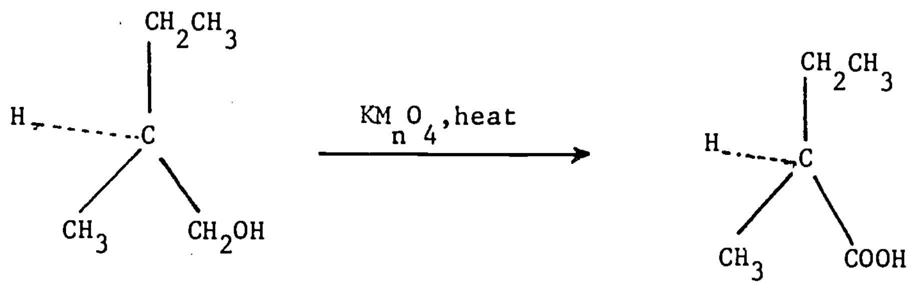
Example No. 7 - Reaction Type II - Statements

1. Retention of configuration does NOT mean retention of R and S specification.
2. Retention of configuration does NOT mean retention of the specific rotation (either sign or magnitude).




S(-) 2-methyl-1-butanol          S (+) 1-chloro-2-methyl butanol

Example No. 7 - Reaction Type II - Statements (continued)




S (-) 2-methyl-1-butanol — S (+) -2-methyl butanoic acid

3. When no bond to the chiral center is cleaved, the configuration of the product can be identified. The two configurations - that of the reactant and the product are correlated.

4. When no bond to the chiral center is cleaved and the reactant is an optically pure enantiomer, the product will be an optically pure enantiomer also.

Assignment No. 3

Which of the following reactions can safely be used to relate the configurations of the reactant and the product?

a) (+) $CH_3CHBrCH_2CH_3 \xrightarrow{NaOH} CH_3CH(OH)CH_2CH_3$

b) (-) $CH_3CH_2CH(OH)CH_2Br \xrightarrow{NaCN} CH_3CH_2CH(OH)CH_2CN$

c) (+) $CH_3CH_2CHCl\,CH_2CH_2OH \xrightarrow{KMnO_4} CH_3CH_2CHCl\,CH_2COOH$

d) (+) $CH_3CH_2CH(OH)CH_3 \xrightarrow{Na} CH_3CH_2CH(ONa)CH_3$

SIP No. 11
Tape 1 - Work Sheet

Assignment No. 4

Draw the structures, name and assign the R and S specifications where applicable to all the products in the reactions below. Identify the ones which are optically active.

a) R-3-chloro-2-methyl butane $\xrightarrow{Cl_2,\text{light}}$

b) S-3-bromo-1-pentene $\xrightarrow{\text{HBr, peroxide, light}}$

c) R-4-bromo-2-methyl-1-pentene $\xrightarrow{H_2O,\text{acid}}$

Example No. 8 - Reaction Type III

$$CH_3\ CHClCH_2\ CH_3 \xrightarrow{Cl_2, h\nu} CH_2Cl\ \overset{*}{C}HCl\ CH_2\ CH_3 + CH_3CCl_2\ CH_2\ CH_3$$

A — 1,2-dichlorobutane

B — 2,2-dichlorobutane

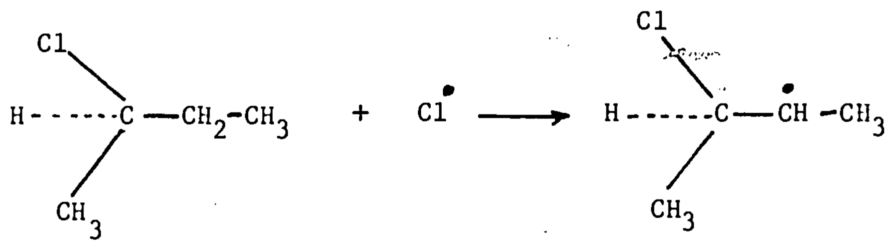
$$CH_3\ \overset{*}{C}HCl\ CH_2\ CH_2Cl \qquad CH_3\ \overset{*}{C}HCl\ \overset{*}{C}HCl\ CH_3$$

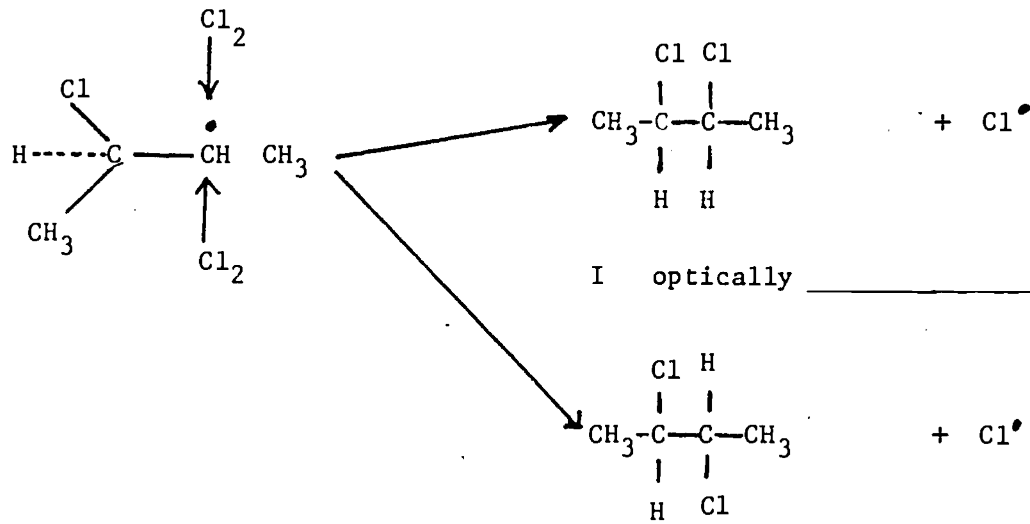
C — 1,3-dichlorobutane

D — 2,3-dichlorobutane

Mechanism - Formation of 2,3-dichlorobutane

$$Cl_2 \xrightarrow{h\nu} 2Cl^\bullet$$



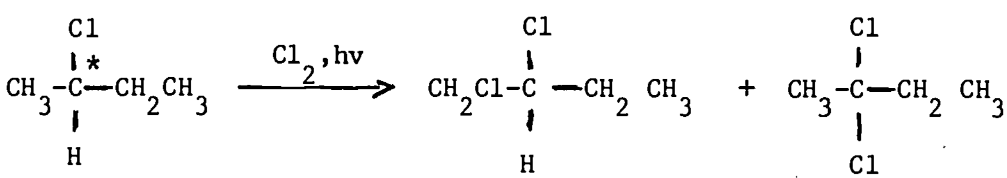


I optically ______________

II optically ______________

I and II relative to each other are ______________________________

<u>Overall reaction</u> -

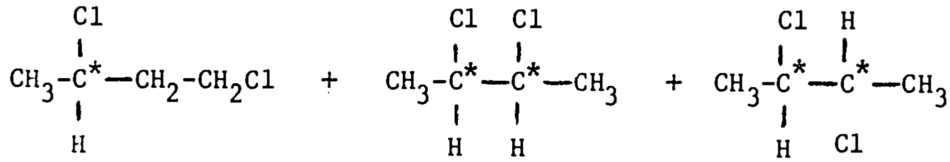


A optically __________

B optically __________

22

Overall reaction - (continued)

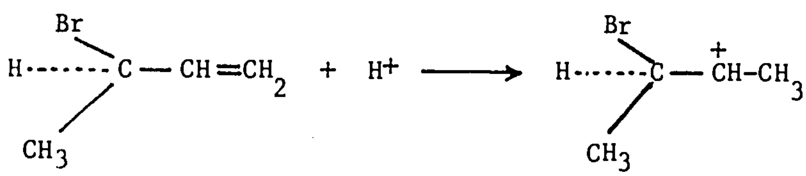


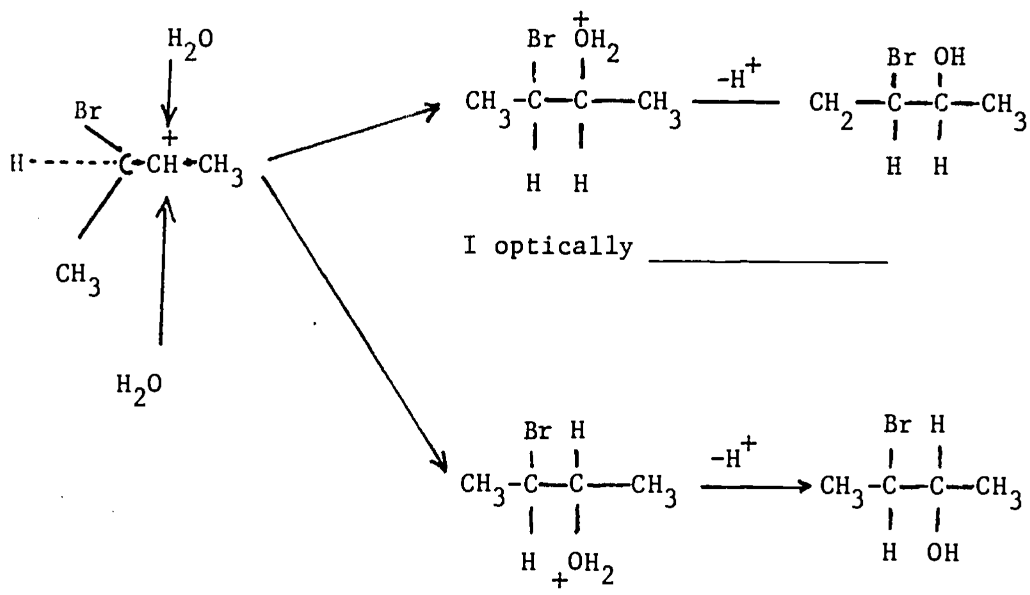
C  D  E

optically __________  optically __________  optically __________

Example No. 9 - Reaction Type III

$$CH_2{=}CH\text{-}\overset{*}{C}HBr\text{-}CH_3 \xrightarrow{H_2O,H} CH_3\text{-}\overset{*}{C}H(OH)\text{-}\overset{*}{C}HBr\text{-}CH_3$$





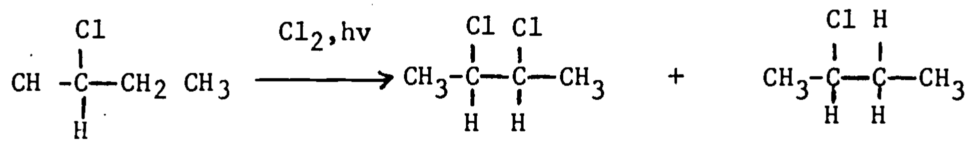
I optically ______________

II optically ______________

I and II relative to each other are ________________________

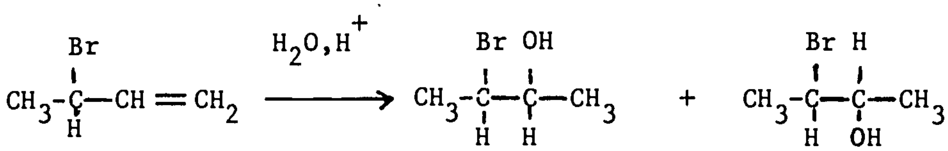
SIP No. 11
Tape 1 - Work Sheet

Example No. 10




I II

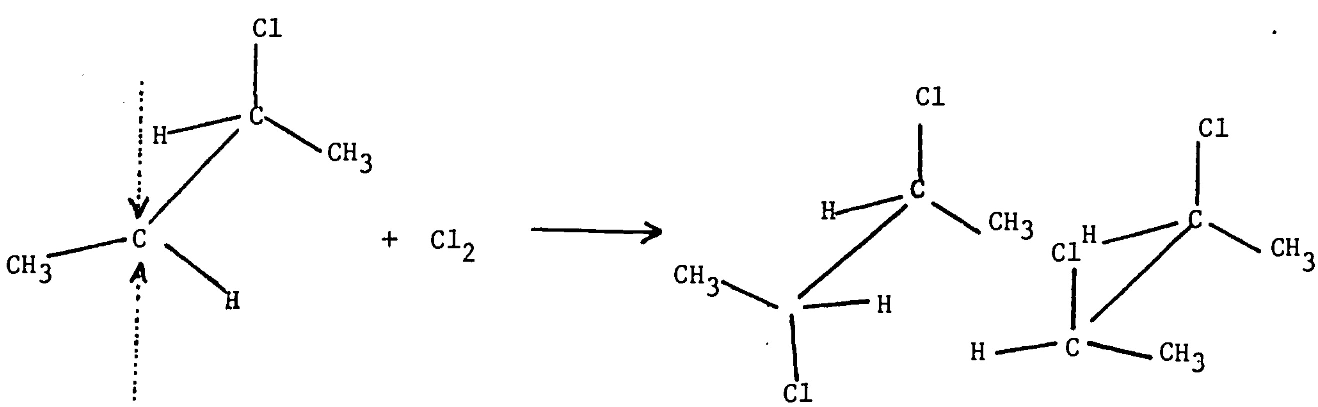
major product (~ 70%) (~ 30%)



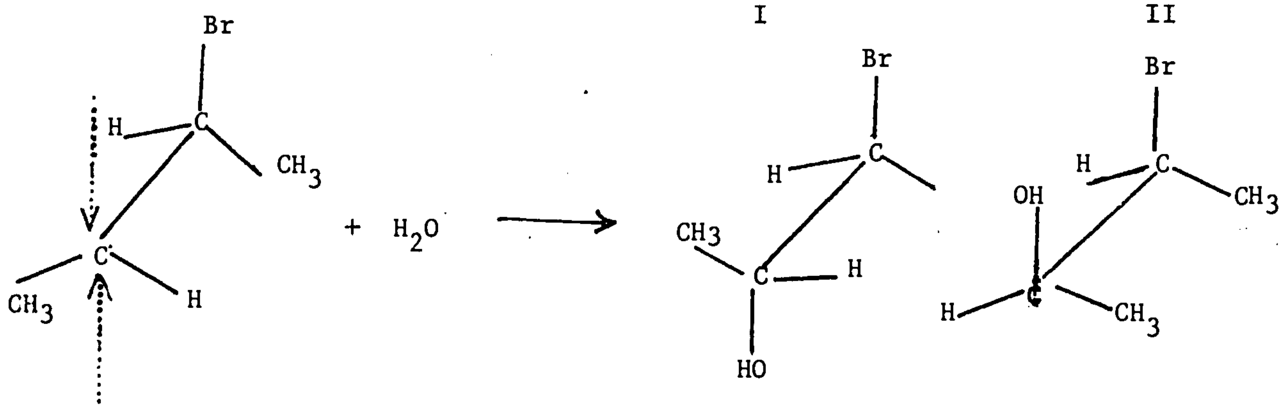

I II

major product

The reaction of the intermediates




I II



Assignment No. 5

Identify (Draw the configurations) all the fractions of the formula $C_5H_{10}Cl_2$ obtained in the free radical chlorination of R(-) 1-chloro-2-methyl butane. Account for optical activity or inactivity in each case.

Assignment No. 6

Draw the configurations and name all the products in the free radical chlorination of R-2-chloro-1-propanol. Identify each as optically active or inactive.

Assignment No. 7

Each of the following reactions is carried out and the products are separated by careful fractional distillation or recrystallization. For each reaction identify the number of fractions, draw the configurations of each fraction, and identify the optically active ones.

a) $R\text{-}CH_2{=}CH\text{-}CH(OH)\text{-}CH_3 \xrightarrow{KM_nO_4(aq)}$

b) (±) 2-chlorobutane $\xrightarrow{Cl_2,hv}$

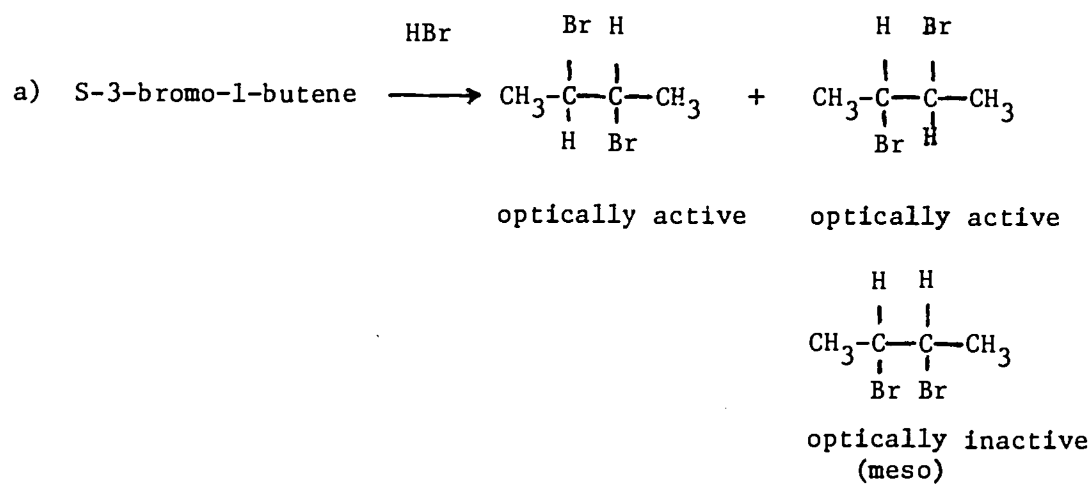
c) S-3-chloro-1-butene $\xrightarrow{HBr}$

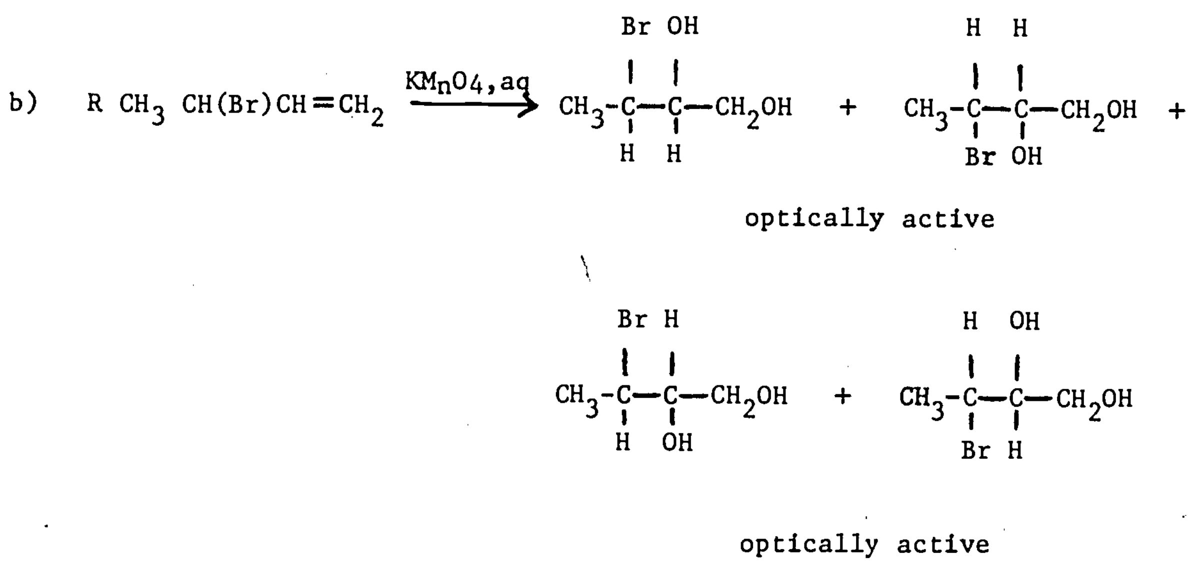
25

SIP No. 11
Tape 1 - Work Sheet

Assignment No. 8

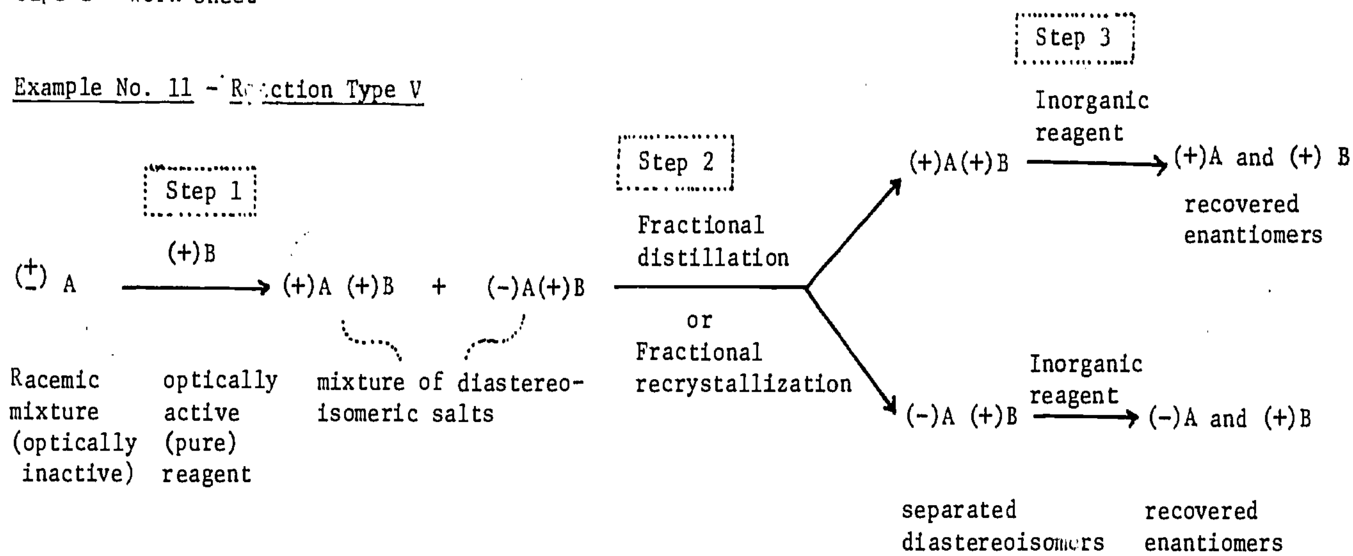
Inert Irma was asked to identify all the fractions in a number of reactions, to draw their configurations and identify the optically active ones. Her answers are given below. Supply any necessary corrections to her answers which are given below.



SIP No. 11
Tape 1 - Work Sheet

Example No. 11 - Reaction Type V




Step 1 - conversion of an optically inactive racemic mixture into a mixture of two diastereoisomers

Step 2 - separation of the diastereoisomers

Step 3 - recovery of the original enantiomers from each diastereoisomer

SIP No. 11
Tape 1 - Work Sheet

Assignment No. 9

When the racemic acid $CH_3\ CHCl\ \overset{O}{\overset{\|}{C}}-OH$ (2-chloro propanoic acid) is allowed to react with S-2-methyl-1-Butanol, a mixture of esters -

$$CH_3\ CHCl\ \underset{O}{\underset{\|}{C}}-O\ CH_2\ CH(CH_3)CH_2\ CH_3$$ is obtained.

Draw the configurations of the two esters formed in this reaction and outline all the steps in the resolution of this racemic acid. State all the reagents and procedural steps.

Assignment No. 10

When butane reacts with bromine in presence of light a racemic mixture of 2-bromo butanes is obtained. How does this prove the mechanism in which the methyl free radical is the intermediate species rather than one which consists of the following steps:

$$X^{\bullet} + RH \longrightarrow RX + H^{\bullet}$$

$$H^{\bullet} + X_2 \longrightarrow HX + X^{\bullet}$$

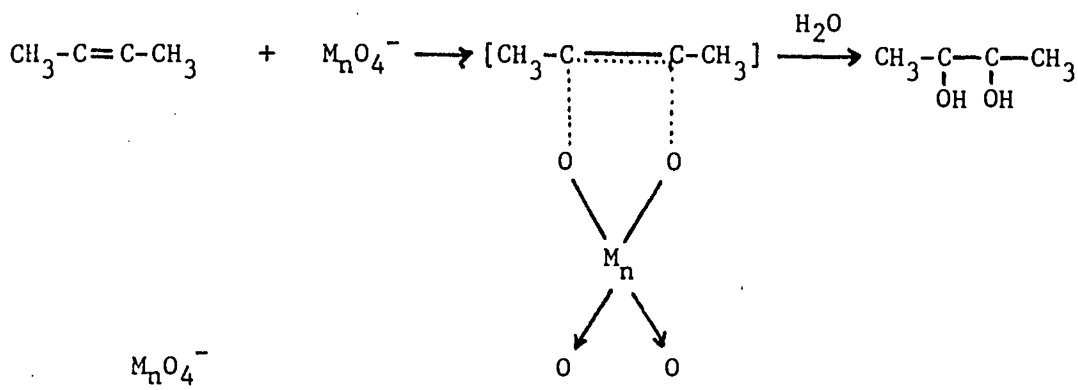
Example No. 12 - Reaction Type VI

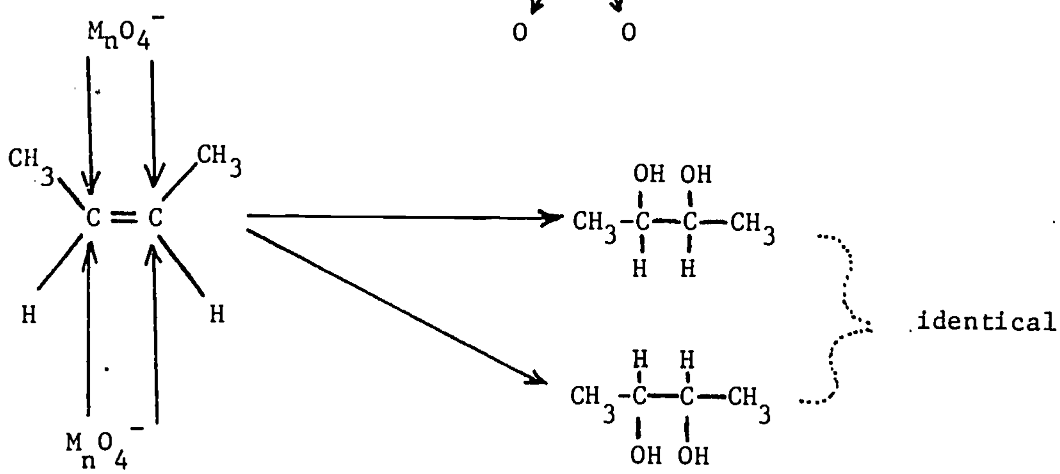
$$\text{2-butene} \xrightarrow{Br_2} CH_3\ CHBr\ CHBr\ CH_3$$

$$\text{2-butene} \xrightarrow{KMnO_4,aq} CH_3\ CH(OH)CH(OH)CH_3$$

$$\text{2-butene} \xrightarrow{\text{peroxy acid}} CH_3CH(OH)CH(OH)CH_3$$

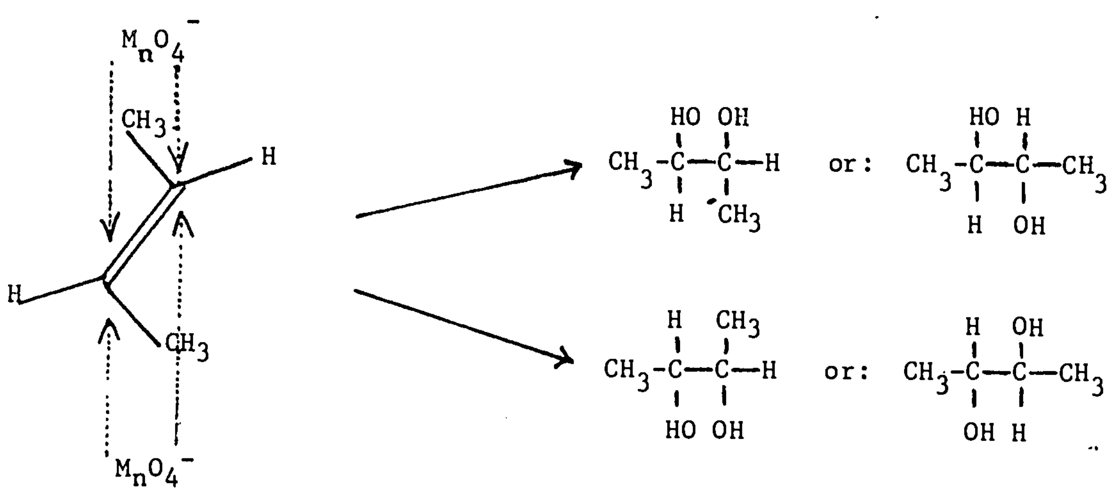
Example No. 13 - Reaction Type VII






cis-2-butene

meso-2,3-butane diol



trans-2-butene

racemic mixture of the two enantiomers

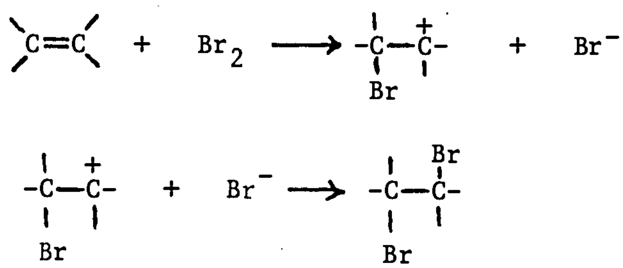
SIP No. 11
Tape 1 - Work Sheet

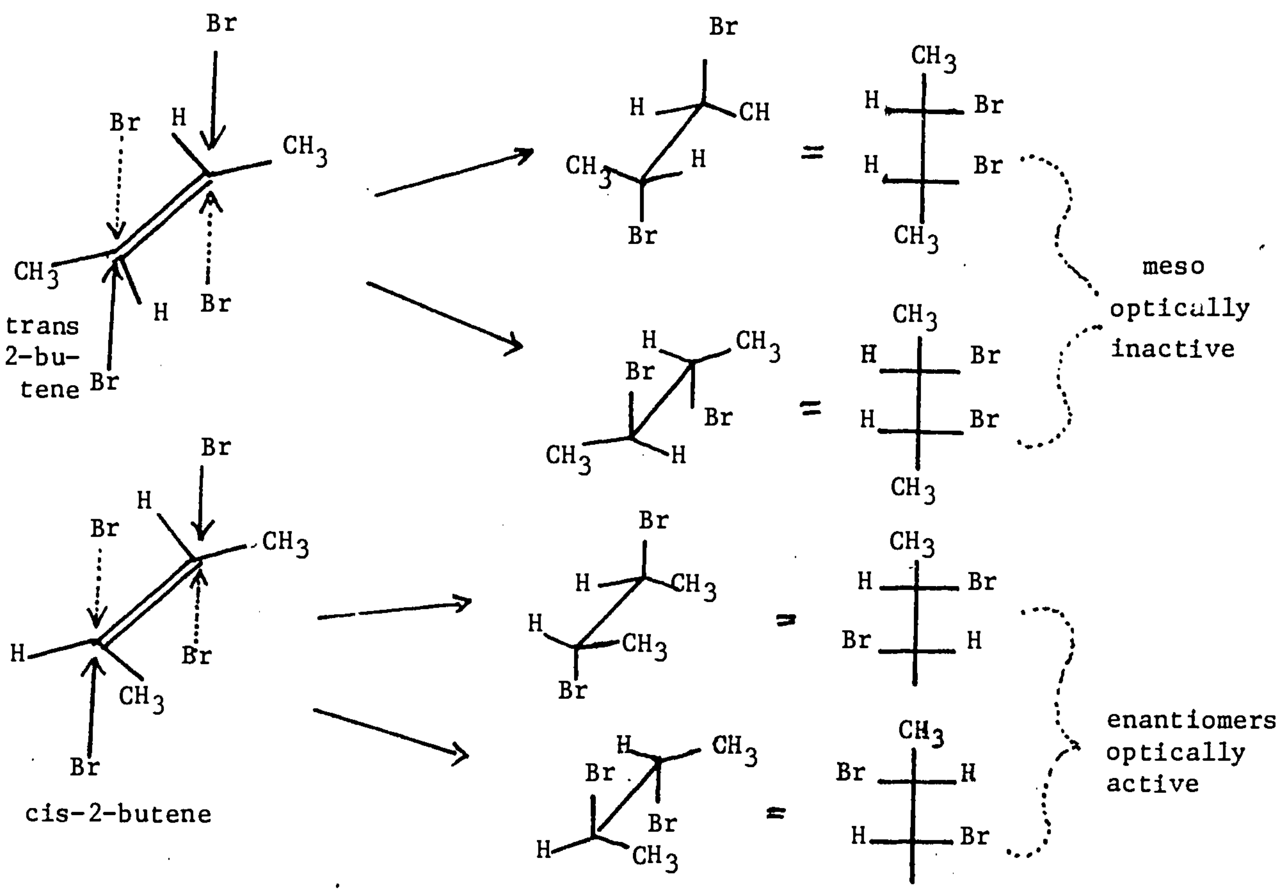
## Assignment No. 11

Draw the configurations of all the products obtained in the reaction of:
a) cis 2-pentene and b) trans-2-pentene with aqueous solution of $KM_nO_4$.
Identify the products as optically active or inactive.

## Example No. 14

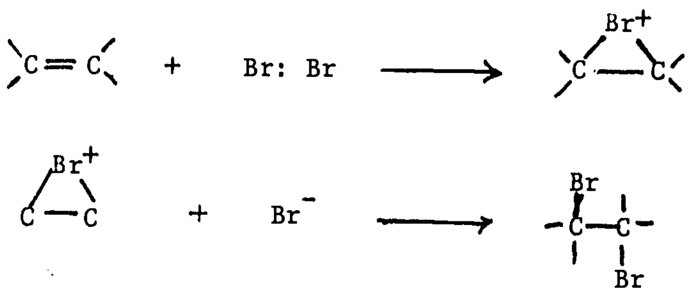
Mechanism -



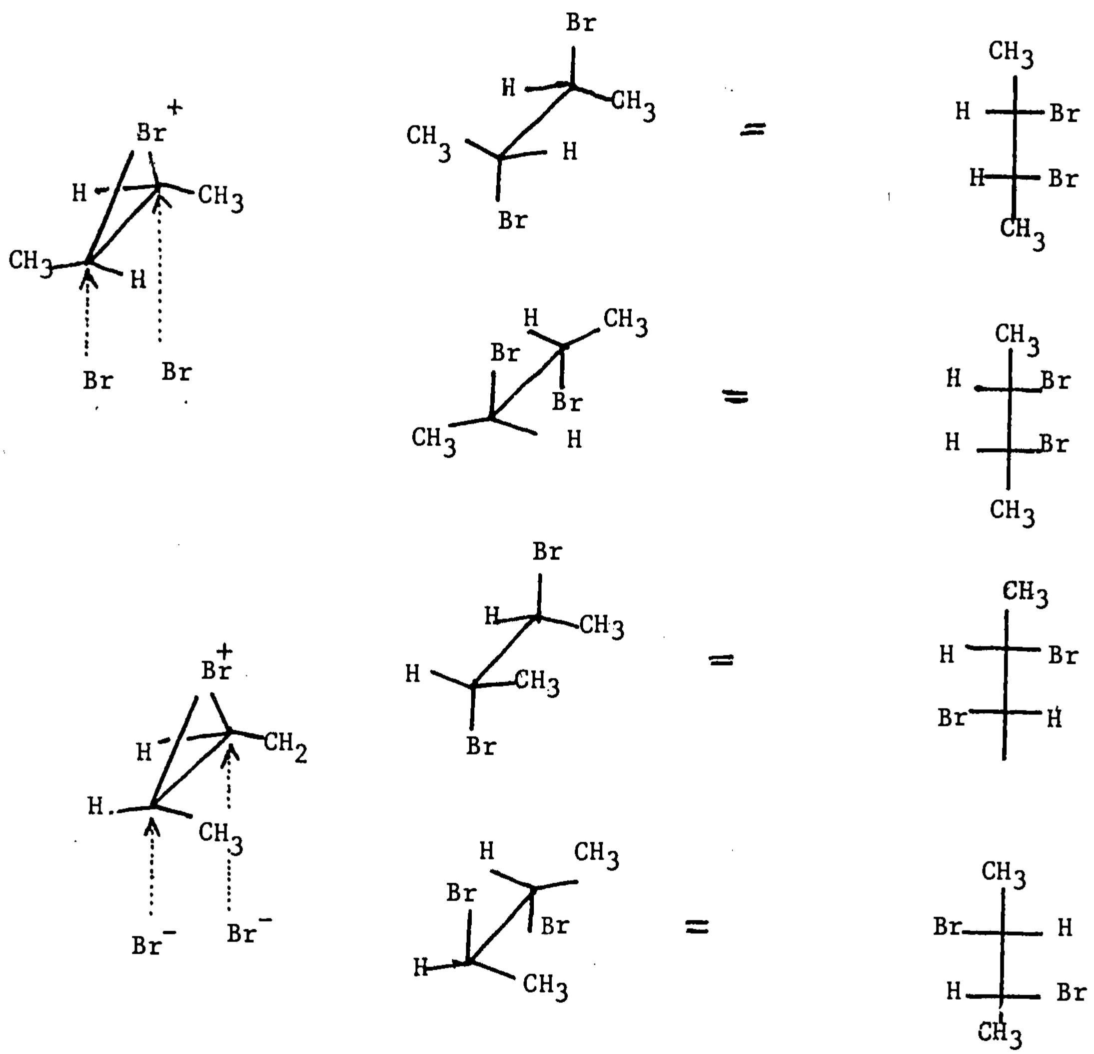


SIP No. 11
Tape 1 - Work Sheet

<u>Bromination mechanism proposed in 1937</u>:



Bromonium ion



Assignment No. 12

Draw the configurations of the compounds obtained in the following reactions:

a) trans-2-pentene $\xrightarrow{Br_2}$

b) cis-2-pentene $\xrightarrow{\text{peroxy acid, } H_2O}$

c) Z-isobutene (2-methyl propene) $\xrightarrow{KM_nO_4(aq)}$

d) 1-butene $\xrightarrow{KM_nO_4(aq)}$

Assignment No. 13

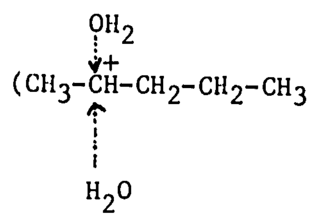
When cis-2-butene reacts with aqueous solution of $KM_nO_4$ a meso inactive 2,3-butane diol is obtained. When cis-2-butene reacts with peroxy acid a racemic mixture of 2,3-butane diol is obtained. When trans-2-butene reacts with peroxy acid a meso 2,3-butane diol is obtained. What is the stereochemistry of hydroxylation with peroxy acids?

## STEREOCHEMISTRY II

### Assignment No. 1

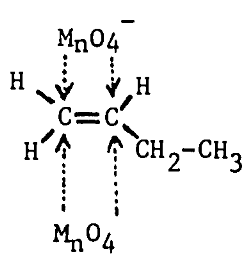
a) $CH_2{=}CH{-}CH_2{-}CH_2{-}CH_3 \xrightarrow{H_2O,H^+} (\pm)\ CH_3{-}\overset{*}{C}H(OH){-}CH_2{-}CH_2{-}CH_3$

2-pentanol



water can become attached to either side of the flat carbonium ion)

b) $CH{=}CH{-}CH_2{-}CH_3 \xrightarrow{KM_nO_4(aq)} (\pm)\ HOCH_2{-}CH(OH)_2\overset{*}{C}H_2{-}CH_3$



$M_nO_4^-$ can become attached to either side of the flat double bond

c) $CH_3\ CH_2\ CH_3 \xrightarrow{Br_2,hv} CH_3\ CHBr\ CH_3 + CH_3CH_2\ CH_2Br$

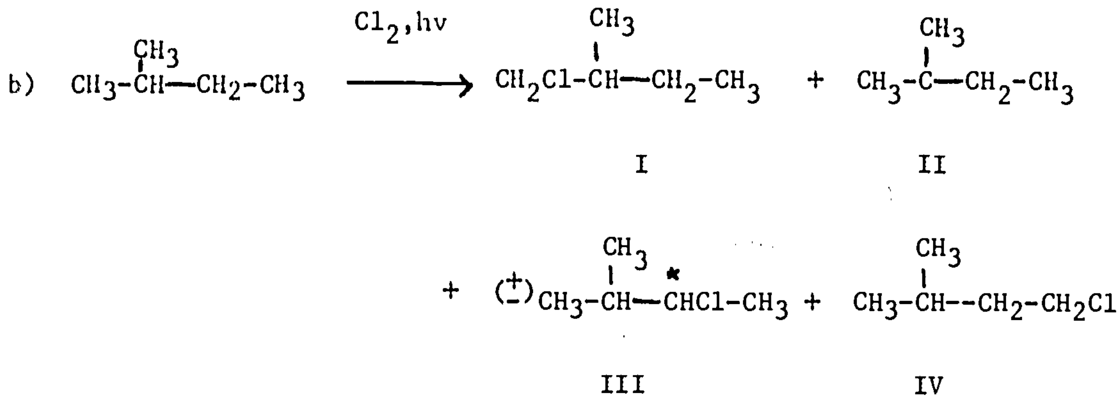
(no chiral center)

### Assignment No. 2

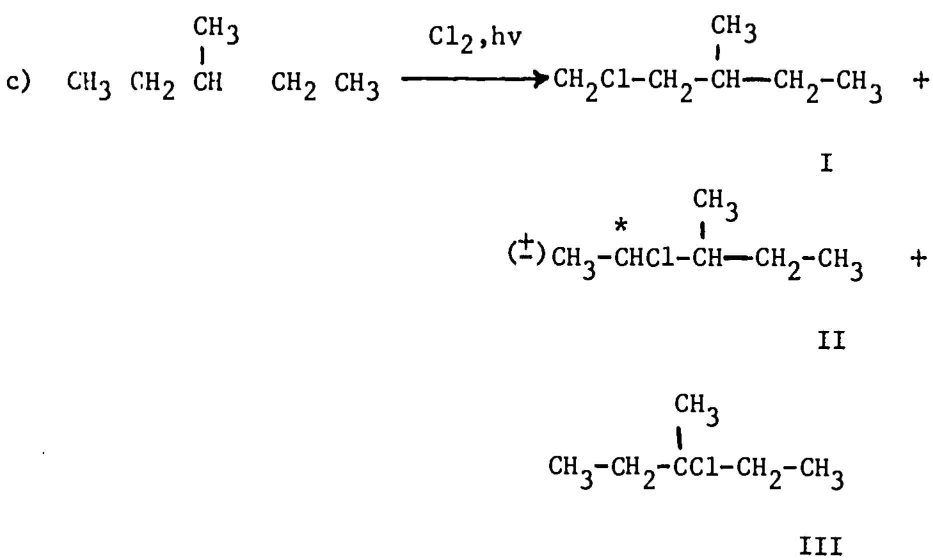
a) $CH_3{-}CH{=}CH{-}CH_2{-}CH_2{-}CH_3 \xrightarrow{H_2O,H^+} (\pm)\ CH_3{-}\overset{*}{C}HOH{-}CH_2{-}CH_2{-}CH_2\ CH_3 +$

$(\pm)\ CH_3{-}CH_2{-}\overset{*}{C}HOH{-}CH_2{-}CH_2{-}CH_3$

Assignment No. 2 (continued)




I, II, IV have no chiral centers.



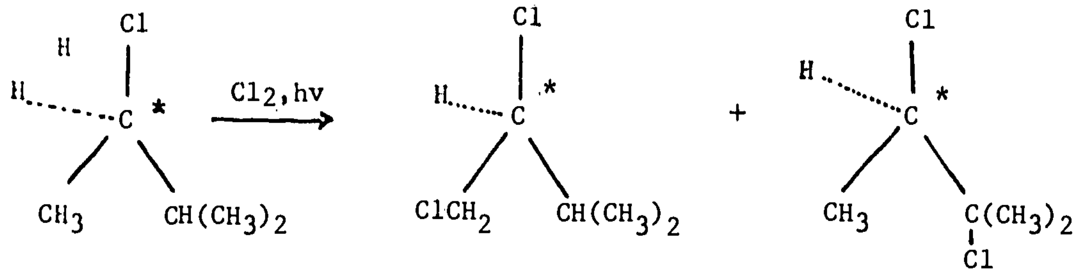

I and III contain no chiral center.

Assignment No. 3

b, c, d

Assignment No. 4

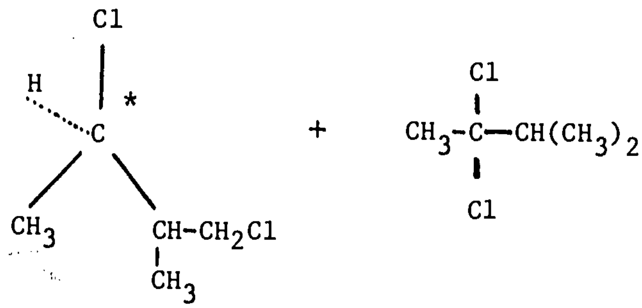
a)




R-2-chloro-2-methyl butane

S-1,2-dichloro-2-methyl butane
optically active

R-2,3-dichloro-2-methyl butane
optically active

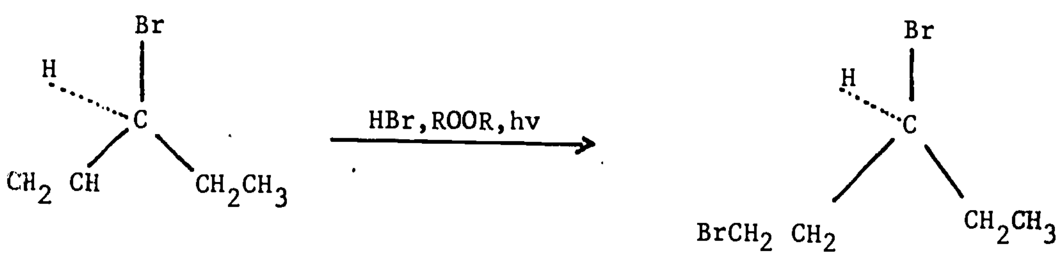


R-1,3-dichloro-2-methyl butane
optically active

no chiral center

optically inactive

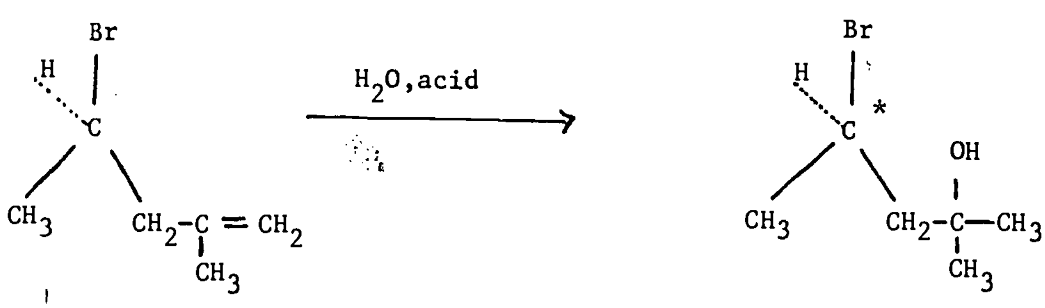
b)




S-3-bromo-1-pentene

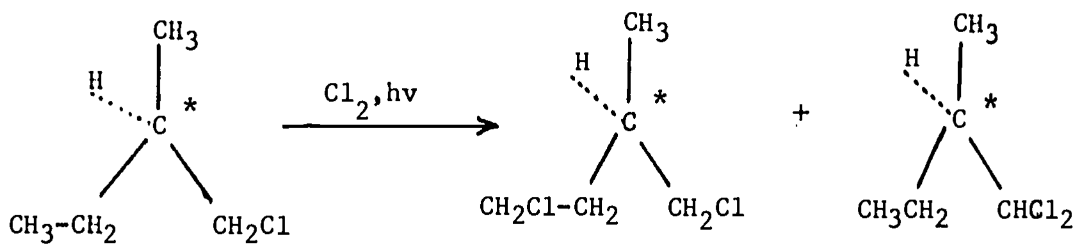
S-1,3-dibromopentane

c)




R-4-bromo-2-methyl-2-pentanol

Assignment No. 5

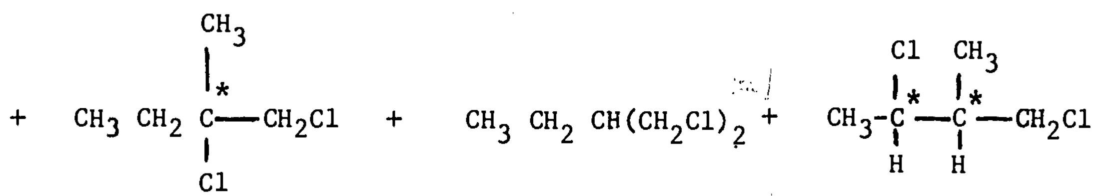


R(-)-1-chloro-2-methyl butane

R-1,4-dichloro-2-methyl butane

R-1,1-dichloro-2-methyl butane

optically active
(retention of configuration)



1,2-dichloro-2-methyl butane

probably optically active

(bond to the chiral center is cleaved)

1,3-dichloro-2-ethyl propane

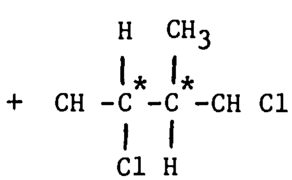
optically inactive

(no chiral center)

1,3-dichloro-2-methyl butane

optically active

(two chiral centers)



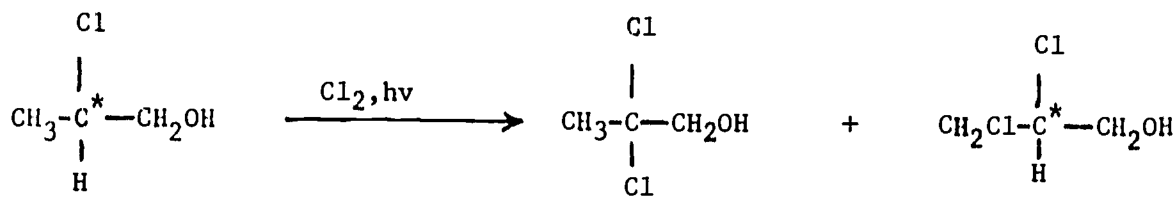
1,3-dichloro-2-methyl butane

(two chiral centers)

37

SIP No. 11
Tape 1 - Answer Sheet

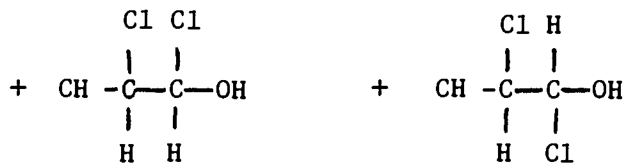
Assignment No. 6




R-2-chloro-1-propanol

2,2-dichloro-1-propanol
optically reactive

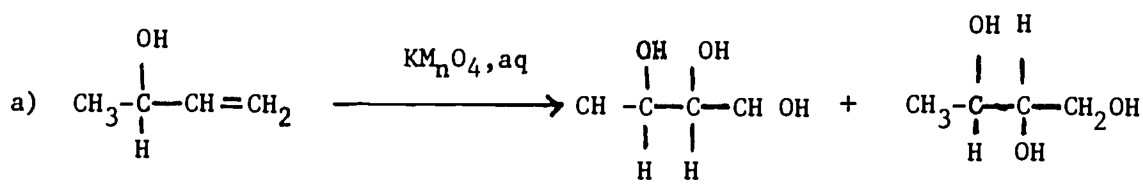
2,3-dichloro-1-propanol
optically active




1,2-dichloro-1-propanol
optically active

1,2-dichloro-1-propanol
optically active

Assignment No. 7




optically active
I

optically active
II

b) $(\pm)\ CH_3\text{-}\overset{*}{C}HCl\text{-}CH_2\text{-}CH_3 \xrightarrow{Cl_2,hv} CH_2Cl\text{-}\overset{*}{C}HCl\text{-}CH_2\text{-}CH_3$ +

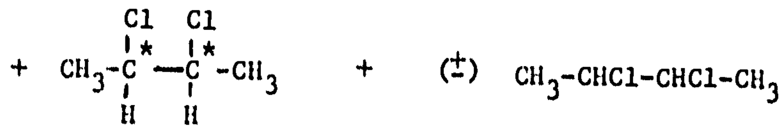
I

+ $(\pm)\ CH_3\ \overset{*}{C}HCl\ CH_2\ CH_2Cl$ + $CH_3\ C\ (Cl)_2\ CH_2\ CH_3$ +

II III

Assignment No. 7 (continued)

b)



IV V

All five fractions are optically inactive.

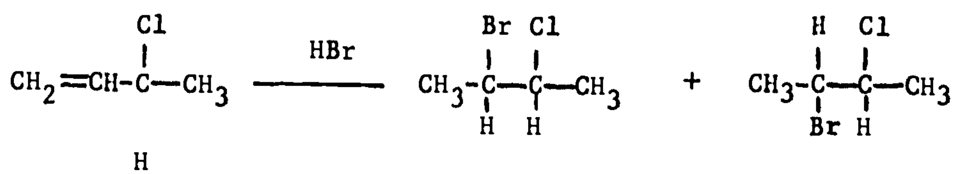
III - no chiral centers

IV - meso compound

V - racemic mixture (retention around the original chiral centers and the generation of a new one)

V, II - racemic mixtures (retention around the original chiral centers)

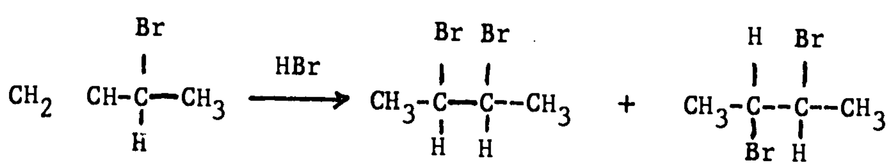
c)



I optically active

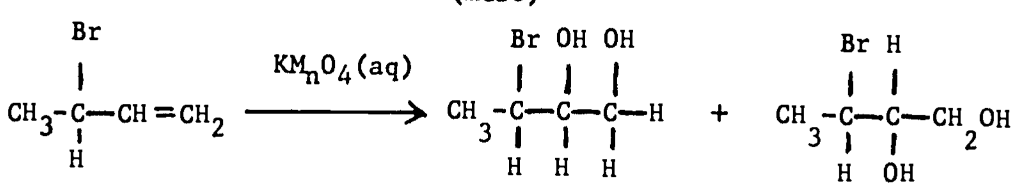
II optically active

Assignment No. 8



I optically inactive (meso)

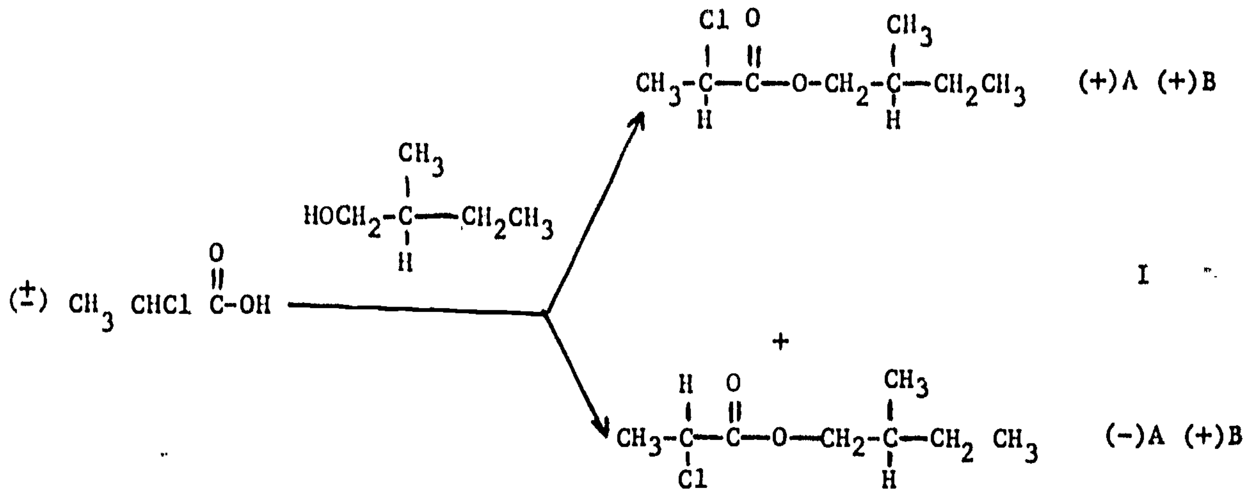
II optically active



I optically active

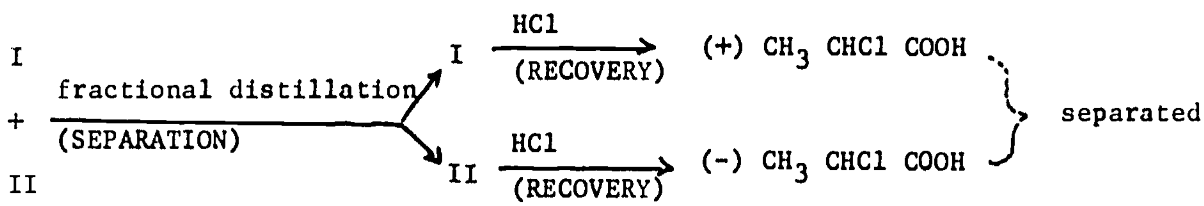
II optically active

Assignment No. 9



I

II



mixture of
the two
diastereoisomeric
esters

Assignment No. 10

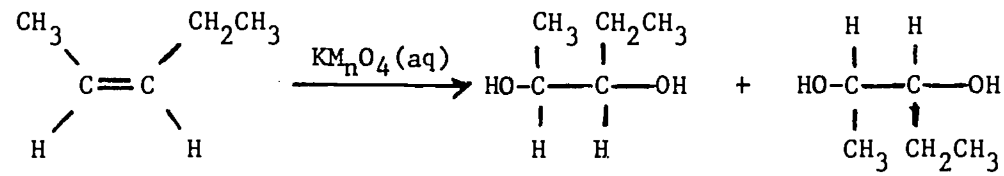
The intermediate sec. butyl free radical is flat. Bromine $Br_2$ can become attached to either side with equal probability yielding a racemic mixture.

In the other mechanism no definite prediction can be made - there is no alkyl intermediate species.

SIP No. 11
Tape 1 - Answer Sheet

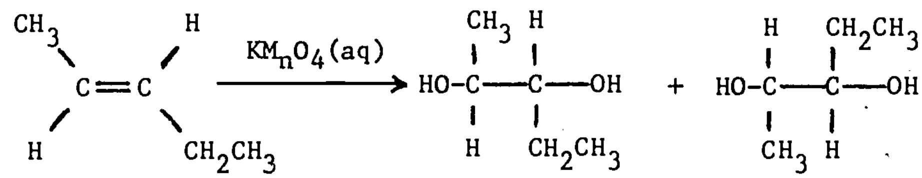
Assignment No. 11

a)




racemic mixture

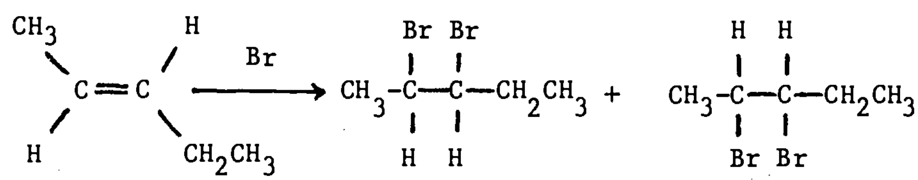
b)



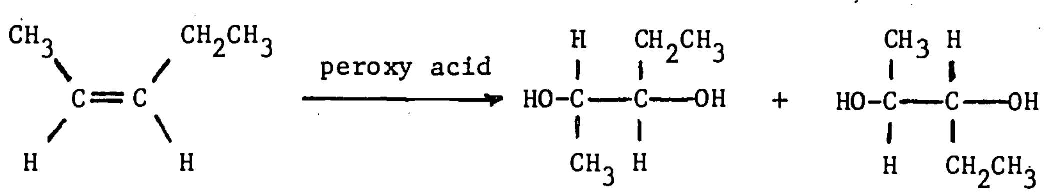

racemic mixture

Assignment No. 12

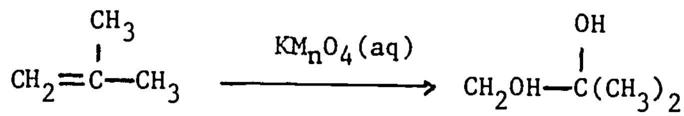
a)

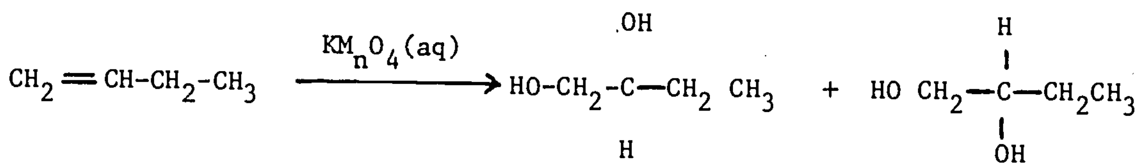



b)



Assignment No. 12 (continued)

c) 

d) 

Assignment No. 13

Anti addition - the two OH groups become attached to the opposite sides of the double bond.

Self Instructional Package No. 11
Form D - Progress Check Evaluation

## STEREOCHEMISTRY II

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

1. _____ A reaction of an optically inactive compound in which a chiral center is generated will produce an optically active product.

2. _____ The generation of a chiral center always involves formation of an optically active product.

3. _____ Reaction in which no bond to the chiral center is broken proceeds with retention of configuration.

4. _____ A meso compound is one of the products whenever a second chiral center is generated.

5. _____ A generation of a second chiral center is accompanied by the formation of racemic mixture.

6. _____ When a bond to the chiral center is broken the products are optically inactive.

7. _____ Aqueous solution of $KM_nO_4$ adds via syn addition to an alkene.

8. _____ An alkene undergoes a syn addition with bromine.

9. _____ Trans 2-butene produces meso 2,3-dibromo butane with bromine.

10. _____ (+) Enantiomer will produce a (+) product in a reaction in which no bond to the chiral center is broken and no new chiral center is generated.

11. _____ The R enantiomer will produce an R product in a reaction in which no bond to the chiral center is broken and no new chiral center is generated.

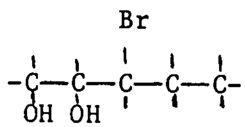
12. _____ Resolution is separation of two salts.

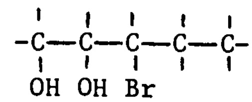
13. _____ The basis for resolution is the conversion of enantiomers into diastereoisomers.

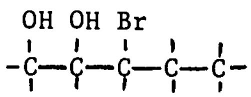
14. _____ Diastereoisomers can be separated by fractional distillation or fractional crystallization.

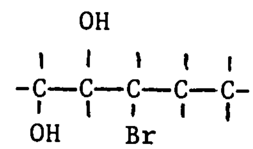
15. _____ The flat shape of the intermediate free radical in the halogenation of butane causes attack from both sides yielding a racemic mixture.

16. The reaction of S-3-bromo-1-pentene with aqueous solution of $KM_nO_4$ will produce the following:

a) 

c) 

b) 

d) 

17. The reaction of R-3-bromo-1-butene with HBr in the presence of peroxide will produce:

a) meso 2,3-dibromo butane

b) R,R-2,3-dibromo butane

c) R,R and S,S-2,3-dibromo butane

d) R-1,3-dibromo butane

18. Select the reactions below which can be used to relate the configurations of the products and the reactants.

a) (+) $CH_3\text{-}CH(OH)\ CH(CH_3)_2 \xrightarrow{PBr_3} CH_3\text{-}CHBr\text{-}CH(CH_3)_2$

b) (-) $CH_2OH\text{-}CHBrCH_2\ CH(CH_3)_2 \xrightarrow{KM_nO_4} HOOC\text{-}CHBr\ CH_2\ CH(CH_3)_2$

c) (+) $CH_3\text{-}CHOH\text{-}CHBr\text{-}CH(CH_3)_2 \xrightarrow{NaCN} CH_3\text{-}CH\ OH\text{-}CHCN\text{-}CH(CH_3)_2$

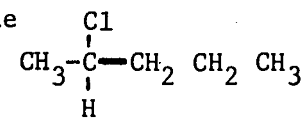
d) (+) 1,2-dichloropropane $\xrightarrow{Br_2, hv}$ 1,2,3-dibromo-3-chloro propane

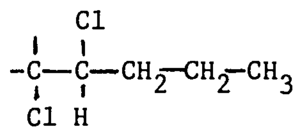
19. The chlorination of (+) 2-chloropentane in light will yield the following number of fractions:

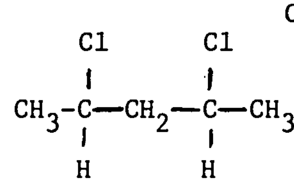
a) 1  b) 3  c) 5  d) 7

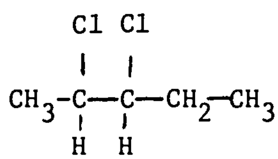
20. The number of optically active dichloropentane obtained in the chlorination of (+) 2-chloropentane is:

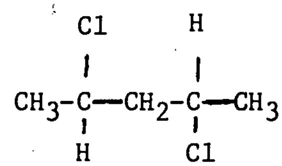
a) 2 b) 4 c) 5 d) 6

21. Some of the optically active dichloropentane obtained as the result of the light induced chlorination of (+) 2-chloropentane 

a) 

c) 

b) 

d) 

22. The addition of bromine to (+) 3,4-dibromo-1-butene will produce the following number of fractions:

a) 2 b) 3 c) 4 d) 6

23. The compounds produced in the addition of bromine to (+) 3,4-dibromo-1-butene will be:

a) all optically active

b) all optically inactive

c) one optically active and one optically inactive

d) two optically active and two optically inactive

24. The product obtained in the reaction of 1-butene with HBr will be:

a) optically active

b) optically inactive

c) (+) 2-bromobutane

d) ($\pm$) 2-bromobutane

25. An optically inactive compound undergoing a reaction in which a chiral center is generated will yield:

    a) an optically active product

    b) an optically inactive product

    c) a racemic mixture

    d) one of the enantiomer

26. The addition of $KM_nO_4$ to trans-2-butene will yield:

    a) a meso 2,3-butane diol

    b) (+) 2,3-butane diol

    c) ($\pm$) 2,3-butane diol

    d) an optically inactive product

27. The addition of peroxyformic acid to trans-2-butene will yield:

    a) a meso 2,3-butane diol

    b) (+) 2,3-butane diol

    c) ($\pm$) 2,3-butane diol

    d) an optically inactive product

28. The addition of bromine to cis-2-butene will yield:

    a) a meso 2,3-dibromo-butane

    b) (+) 2,3-dibromobutane

    c) ($\pm$) 2,3-dibromobutane

    d) an optically inactive product

## STEREOCHEMISTRY II

| | | | |
|---|---|---|---|
| 1. | T | 16. | a, d |
| 2. | F | 17. | b, d |
| 3. | T | 18. | a, c |
| 4. | F | 19. | a, b, c |
| 5. | T | 20. | d |
| 6. | F | 21. | a, c, d |
| 7. | T | 22. | a, b, c |
| 8. | F | 23. | a, d |
| 9. | F | 24. | a, b, d |
| 10. | T | 25. | c |
| 11. | T | 26. | a, d |
| 12. | F | 27. | a |
| 13. | F | 28. | b, c |
| 14. | T | 29. | b, c |
| 15. | T | 30. | a, d |

Self Instructional Package No. 11
Form D[1] - Progress Check Evaluation - Answers

## STEREOCHEMISTRY II

| | | | |
|---|---|---|---|
| 1. | F | 16. | a, b |
| 2. | F | 17. | d |
| 3. | T | 18. | b, d |
| 4. | F | 19. | d |
| 5. | F | 20. | c |
| 6. | F | 21. | a, b, d |
| 7. | T | 22. | a |
| 8. | F | 23. | c |
| 9. | T | 24. | b, d |
| 10. | F | 25. | b, c |
| 11. | F | 26. | c, d |
| 12. | F | 27. | a, d |
| 13. | T | 28. | c, d |
| 14. | T | | |
| 15. | T | | |