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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 alkanes-preparations. (SL)

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# ORGANIC CHEMISTRY

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*V. Zdravkovich*

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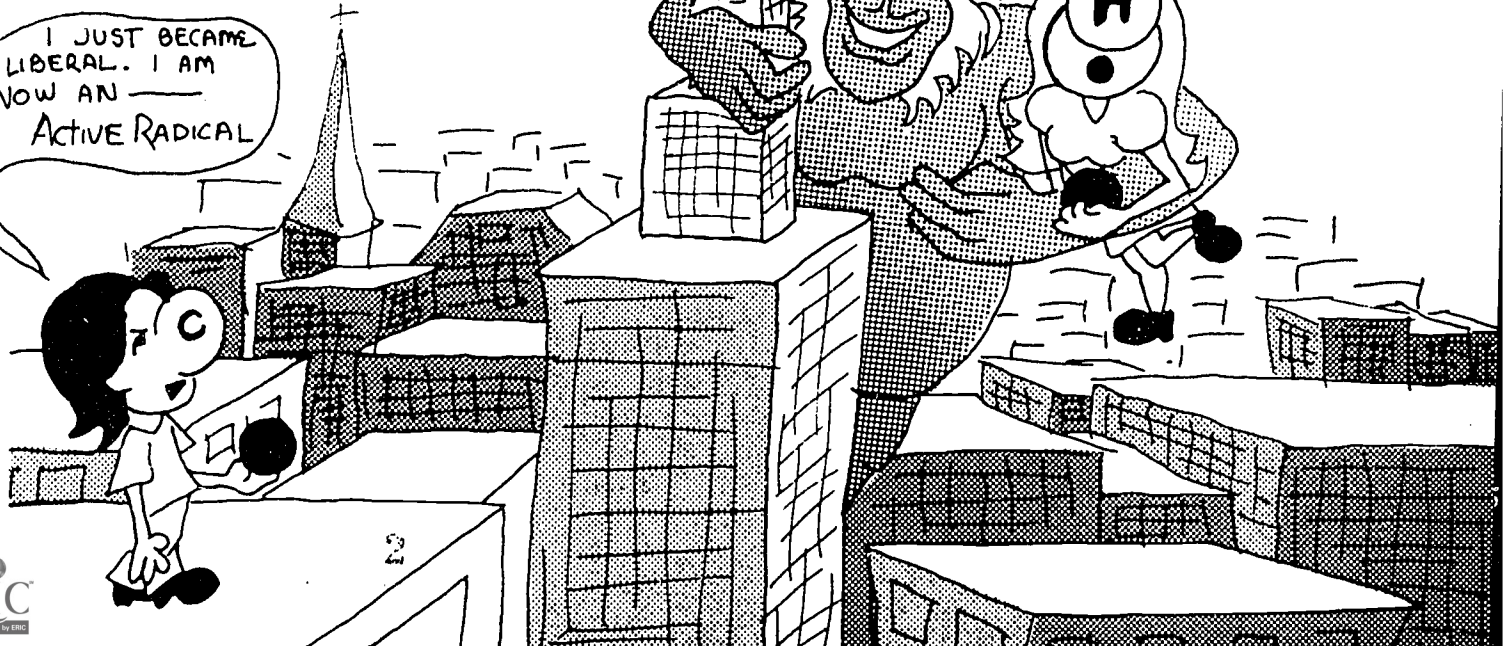
V. Zdravkovich

## ALKANES

## PREPARATIONS AND

## REACTIONS

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021 576

Self Instructional Sequence in

ORGANIC CHEMISTRY

"Copr.," V. Zdravkovich 1976

ALKANES - PREPARATIONS

For 1912, the Nobel Prize was awarded to Victor Grignard (1871-1935) "For the discovery of the so-called Grignard reagent, which has greatly helped in the development of organic chemistry during these last years."

DESCRIPTION OF THE PRIZE-WINNING WORK\*

"The preparation of the organo-magnesium ethers is, in general, extremely simple. The apparatus is just a round-bottomed flask connected with a good ascending condenser and with a dropping funnel with stopcock, but it is indispensable that everything be absolutely dry.

"One atomic weight of magnesium, in the form of fine filings, is placed into the flask. On the other hand, one molecular weight of the halogenated hydrocarbon to be used--for example, methyl iodide--is dissolved in an almost equal volume of perfectly dry ether which was kept over sodium. Of this mixture, 25-30 c.c. are added to the magnesium. A lively reaction begins after a very short time. Then, 250-300 c.c. of ether are added, and the reaction is kept going by addition of the rest of the reaction mixture drop by drop. The reaction is completed by short heating, if necessary. Under these conditions the magnesium disappears completely. In general, a clear or slightly colored solution is obtained, in which, however, very fine particles of iron, an impurity in the magnesium, produce a momentary haze of slate color.

"The compound, prepared as just indicated, shows all the characteristics of organo-metallic compounds; it changes rapidly in air, absorbs oxygen and carbon dioxide, is decomposed violently by water, and reacts strongly with almost all functional groups. These operations can usually be carried out without any change in the apparatus. It suffices to add, through the dropping funnel, the antagonistic compound dissolved in a convenient quantity of water-free ether. Thus, either a solution or an oily or crystalline separation is obtained, and the reaction is completed, if necessary, by a more or less prolonged heating. After that, all that remains to be done is to hydrolyze the compound."

\*Translated from "Le magnesium en chimie organique," Bulletin de la Societe Chimique de France, Vol. XIII (1913), p. 1.

DEFINITIONS -

The student will be able to define and illustrate with appropriate examples where applicable the following terms: GRIGNARD compound, GRIGNARD synthesis, WURTZ synthesis, ORIENTATION, REACTIVITY, SELECTIVITY, CRACKING, PYROLYSIS, HYDROCRACKING, STEAM CRACKING, KNOCKING, COMBUSTION, HEAT OF COMBUSTION.

PREPARATIONS -

The student will be able to write the chemical reactions for the following preparations: Grignard synthesis, Wurtz synthesis, Lithium-Copper synthesis and synthesis using Zinc and Acid.

The student will be able to determine the reagents required for the synthesis of a given alkane from a given reactant. From the given reagents and the product desired, the student will be able to identify the reactant required for the synthesis.

The student will be able to explain why the Grignard synthesis is a two-step synthesis and why it requires dry apparatus.

REACTIONS -

The student will be able to write the balanced reactions for combustion and halogenation of different alkanes.

The student will be able to write the step by step mechanisms for the halogenation of alkane reactions.

The student will be able to predict the orientation in the halogenation of alkane reaction and consequently identify the intermediates and the major product.

The student will be able to compare different alkanes and different halogens with respect to their reactivity.

The student will be able to compare different halogens with respect to their selectivity.

The student will be able to calculate the percentage composition of the mixture of the products obtained in the chlorination or the bromination of simpler alkanes (not more than 5 C atoms).

MULTI-STEP SYNTHETIC SCHEMES -

The student will be able to devise multi-step synthesis schemes for the synthesis of different alkanes from a given reactant.

The student will be able to identify all the reagents in a given multi-step synthetic scheme.

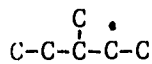
The student will be able to identify the intermediate compounds formed in a multi-step synthetic scheme.

ALKANES - PREPARATIONS AND REACTIONS

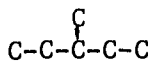
- The reagents which can be used to prepare BUTANE from 2-BROMO BUTANE are:
  - SODIUM
  - ZINC, ACID
  - Li, CuBr, METHYL CHLORIDE
  - MAGNESIUM, ETHER, WATER
- The following statements about the Grignard Synthesis are true:
  - Grignard compound will react with water or alcohol.
  - Grignard synthesis is a two step synthesis.
  - The apparatus used in the Grignard synthesis must be dry.
  - Water, magnesium and ether are added to the reactant in the first step.
- Identify the correct statements below:
  - Best results in Wurtz synthesis are obtained with primary alkyl halides.
  - Wurtz synthesis is useful only for the synthesis of symmetrical alkanes.
  - Lithium dialkyl copper compounds gives best result in the reaction with tertiary alkyl halides.
  - The function of ether in Grignard synthesis is to slow down the reaction.
- In a series of free radicals listed below, identify the one with maximum stability and the one with minimum stability.



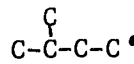
I



II



III



IV

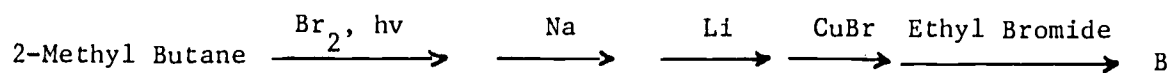
SIP #5  
Form B - Self Evaluation Exercise

Maximum Stability

Minimum Stability

- |        |        |
|--------|--------|
| a) I   | a) IV  |
| b) II  | b) III |
| c) III | c) IV  |
| d) IV  | d) III |

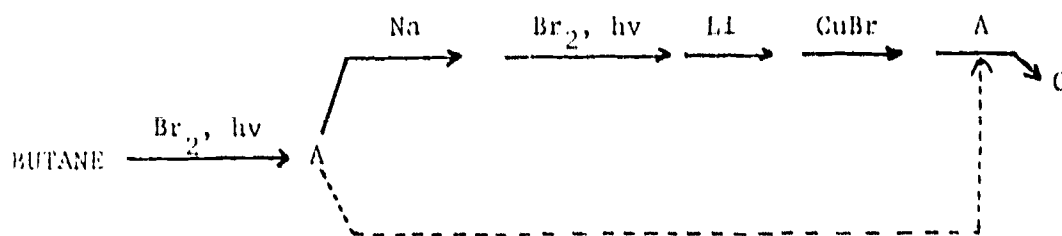
5. Identify the correct statements about the halogenation of alkane reaction:
- a) Bromine is more reactive than chlorine.
  - b) Bromine is more selective than chlorine.
  - c) Bromination of isobutane will produce larger percentage of the major product than chlorination.
  - d) Bromine reacts faster than chlorine.
6. The major product obtained in the bromination of 3-methyl pentane is:
- a) 1-Bromo-3-Methyl Pentane
  - b) 2-Bromo-3-Methyl Pentane
  - c) 3-Bromo-3-Methyl Pentane
  - d) 2-Bromo-2-Methyl Pentane
7. Identify compound B produced in the reaction sequence below:



- a) 3,3,4,4,5-Pentamethyl Heptane
- b) 3,6-Dimethyl-3-Ethyl-Octane
- c) 3,3,4,4-Tetramethyl Octane
- d) 3,6-Dimethyl Decane

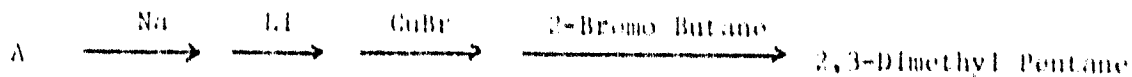


8. Identify compound C formed in the reaction sequence below:



- a) 3,4,7-Trimethyl Nonane
- b) 3,4,5-Trimethyl-4-Ethyl Heptane
- c) 3,4-Dimethyl Decane
- d) 3,4-Dimethyl-4-Ethyl Octane
9. The reagents required for the laboratory synthesis of 3-Methyl Pentane from Ethyl Bromide are:
- a) SODIUM,  $\text{Br}_2$ , Light; Li; CuBr; PROPYL BROMIDE
- b) ZINC,  $\text{Br}_2$ , Light; Li; CuBr; ETHYL BROMIDE
- c) SODIUM
- d) SODIUM,  $\text{Br}_2$ , Light; Li; CuBr; ETHYL BROMIDE
10. The reagents that could be used for the laboratory synthesis of 2,3-Dimethyl Butane from Propane are:
- a) BROMINE, Light; SODIUM
- b) BROMINE, Light; ZINC, ACID
- c) BROMINE, Light; Li; CuBr; ISOPROPYL BROMIDE
- d) BROMINE, Light; Li; CuBr; PROPYL BROMIDE

11. The reactant A which should be used in the synthesis below is:

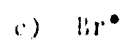
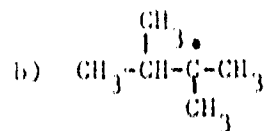
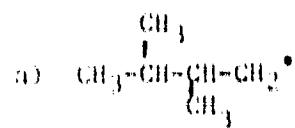


- Ethyl Bromide
  - Propyl Bromide
  - Propane
  - Isopropyl Bromide
12. Reaction of an alkane with heat and excess oxygen will yield:
- Alkenes
  - carbon dioxide, water
  - smaller alkanes
  - carbon dioxide, water, heat
13. Cracking of alkanes can be defined as:
- pyrolysis of alkanes
  - decomposition of larger alkanes by the action of heat
  - reaction of alkanes with excess oxygen
  - reaction of alkanes with steam
14. Circle the correct statements below:
- Hydrocracking is the cracking of alkanes in the presence of oxygen.
  - Octane number indicates the relative anti-knock tendency of the fuel.
  - "Iso-octane" has a low octane number.
  - Tetraethyllead is added to the gasoline to increase the amount of "iso-octane".

STP #5

Form B - Self-Evaluation Exercise

15. The intermediate species in the chlorination of 2,3-dimethyl butane are:



d) Heat

Self Instructional Package No. 5  
Form G - Reference Guide

ALKANES - PREPARATIONS AND REACTIONS

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 1,2,3,9,10,11	Chapter 3, Section 15,16,17	Morrison & Boyd Organic Chemistry
Question 4	Chapter 3, Section 24	
Questions 5,6	Chapter 3, Sections 21,22,27,28	
Question 15	Chapter 3, Section 20,21	
Question 12	Chapter 3, Section 30	
Questions 13,14	Chapter 3, Sections 30,31	

In addition to the above-mentioned sections of Chapter 3 in your textbook, additional explanations and examples to be used for Questions 1,2,3,7,8,9, 10,11, can be found in TAPE 1 - with the accompanying worksheet and answer sheet titled, Alkanes-Preparations.

For Questions 4,5,6,7,8,9,15, additional explanation and examples are provided in TAPE 2 - with the accompanying worksheet and answer sheet titled, Alkanes-Reactions.



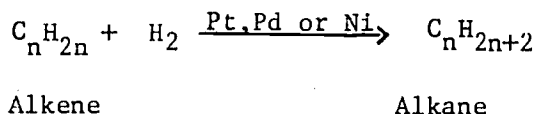
When a king asked Euclid, whether he could not explain his art to him in a more compendious manner, he was answered, that there was no royal way to geometry. Other things may be seized by might, or purchased with money; but knowledge is to be gained only by study, and study to be prosecuted only in retirement.

---Johnson

Self Instructional Package No. 5  
Tape 1 - Worksheet

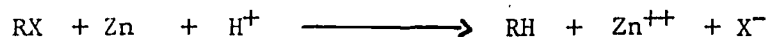
ALKANES - PREPARATION

I. Hydrogenation of Alkenes

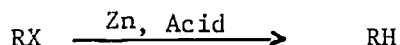


II. Direct Reduction of Alkyl Halides

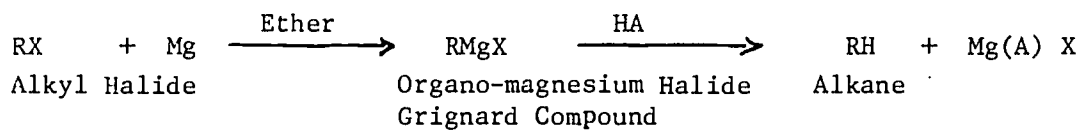
Alkyl Halide      RX      (R = Alkyl group      X = Halogen Atom)



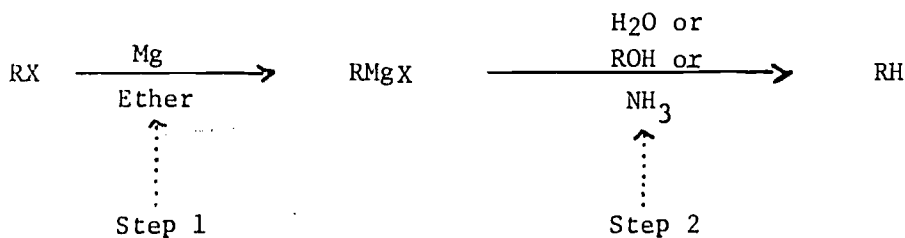
Or



III. Grignard Reaction - Indirect Reduction of Alkyl Halides



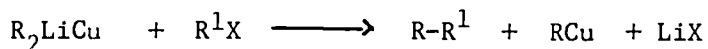
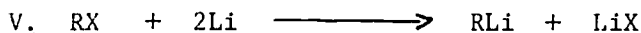
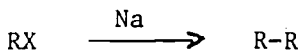
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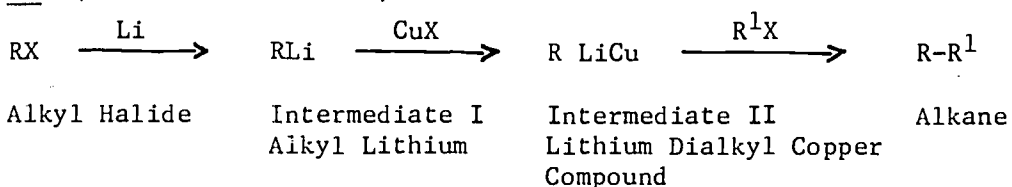
IV. Wurtz Reaction



Or

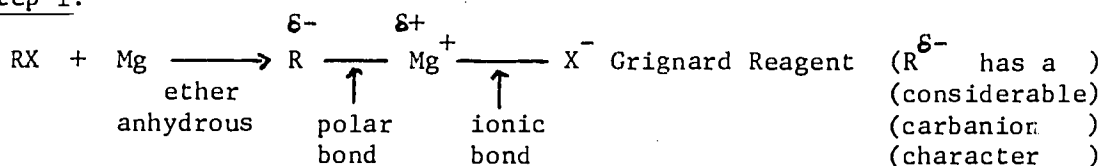


Or (abbreviated version)

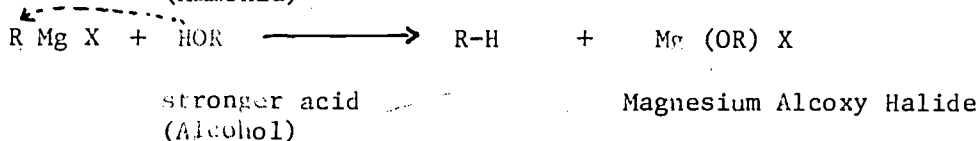
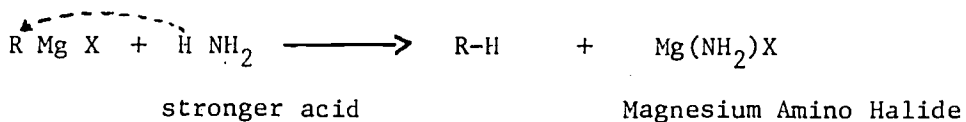
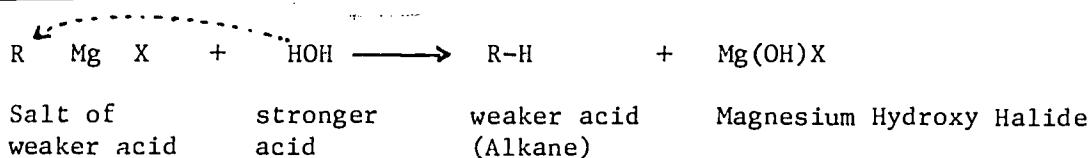


Example 1. Grignard Reaction

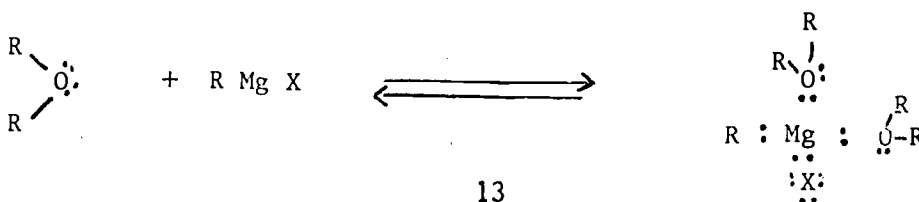
Step 1.



Step 2.



Solvation of Grignard Reagent by Diethyl Ether



Assignment No. 1

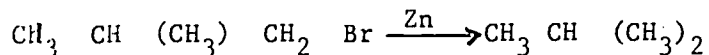
Write the reactions for the preparation of 3-methyl pentane from 1-chloro-3-methyl pentane

Assignment No. 2

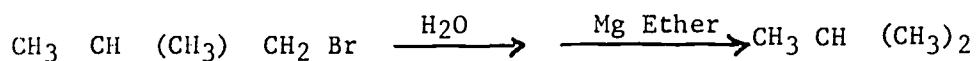
Inert Irma was asked to describe the preparation of isobutane from isobutylbromide. Her answer is given below.

Identify all the mistakes and correct her answer.

I. Reduction with zinc and acid

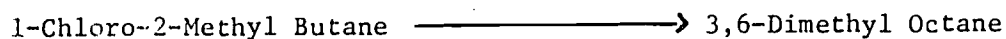
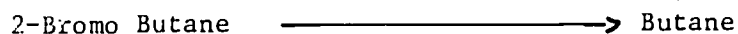
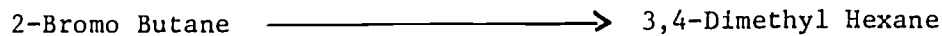


II. Grignard Reaction



Assignment No. 3

Identify the reagents in each one of the preparations listed below.



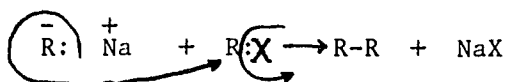
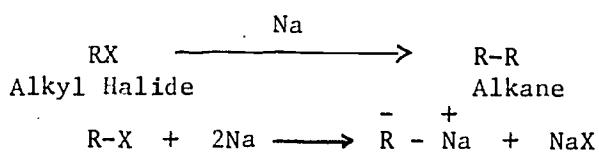


Assignment No. 4

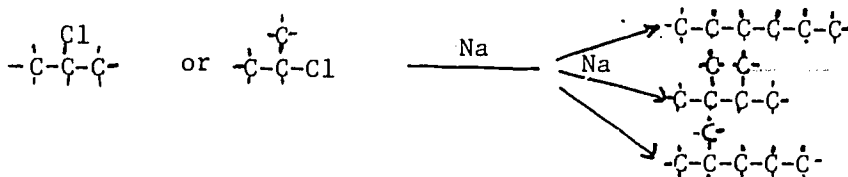
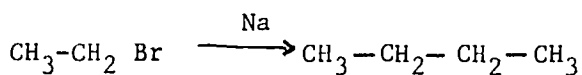
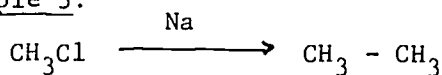
Confused Clyde was asked to identify the reactants in the preparation of a number of alkanes. His answer is given below. Make all the necessary corrections.

- a. Isopropyl Bromide  $\xrightarrow[\text{Na}]{\text{Zn, Acid}}$  2,3-Dimethyl Butane
- b. 2-Bromo Butane  $\xrightarrow{\text{Na}}$  2,3-Dimethyl Butane
- c. 2-Bromo Butane  $\xrightarrow[\text{Ether}]{\text{Mg}}$   $\xrightarrow{\text{H}_2\text{O}}$  Butane

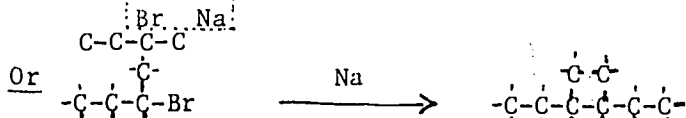
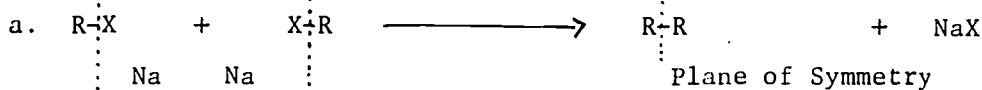
Example 2. Wurtz Synthesis



Example 3.



Example 4.

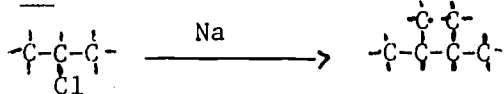


Plane of Symmetry

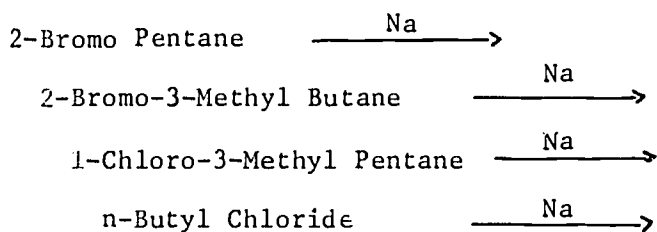


Example 4. (continued)

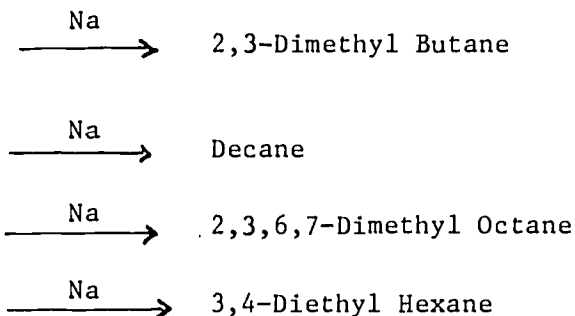
Or

Assignment No. 5

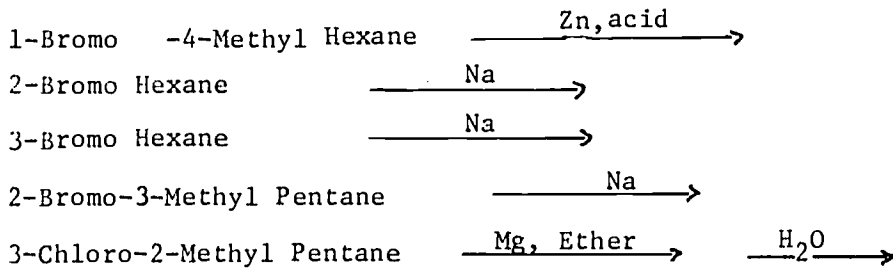
Identify i.e. draw the structures and name the products in the following reactions:

Assignment No. 6

Identify i.e. draw the structure and name the reactants in the reactions below.

Assignment No. 7

From the list of products supplied below, identify the ones which correspond to the given reactions.



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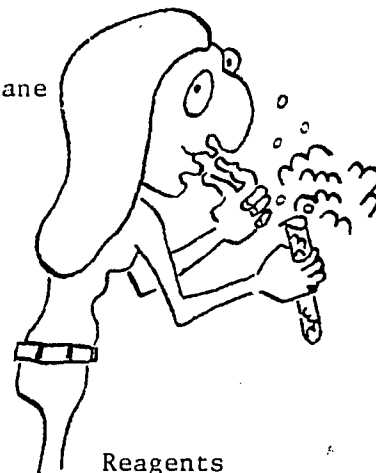
Assignment No. 7 (continued)

Products:

- |                                |                         |
|--------------------------------|-------------------------|
| (1) 3,4,5,6-Tetramethyl Octane | (4) 3-Methyl Hexane     |
| (2) 4,5-Diethyl Octane         | (5) 5,6-Dimethyl Decane |
| (3) 2-Methyl Pentane           |                         |

Assignment No. 8

Forgetful Frieda was asked to identify the reactants and the reagents in a number of synthesis. She has done so but forgot to identify them with the correct product. Match the reactants and the reagents with the correct products.



<u>Reactants</u>	<u>Products</u>	<u>Reagents</u>
(1) 2-Bromo-4-Methyl Hexane	(1) 3,4,-Diethyl Hexane	
(2) 2-Chloro-3Ethyl Pentane	(2) 2,5-Dimethyl Hexane	Na
(3) 3-Bromo Pentane	(3) 2,5-Dimethyl Heptane	<u>or</u>
(4) 3-Bromo-4-Ethyl Hexane	(4) 4,5-Dimethyl-3,6-Diethyl Octane	Mg, Ether H <sub>2</sub> O
(5) Isobutyl Chloride	(5) 3-Methyl Hexane	<u>or</u>
(6) 1-Bromo-2,5-Dimethyl Heptane	(6) 3-Ethyl Hexane	Zn, Acid

Assignment No. 9

Identify (draw the structures and name) all the products obtained in a reaction of a mixture of alkylhalides: isopropyl chloride and n-butyl chloride with sodium.

Assignment No. 10

When a mixture of two alkyl halides reacted with sodium, the following products were obtained. Identify the original reactants.

products: 2,4-dimethyl hexane ; 3,4 dimethyl hexane  
2,5-dimethyl hexane

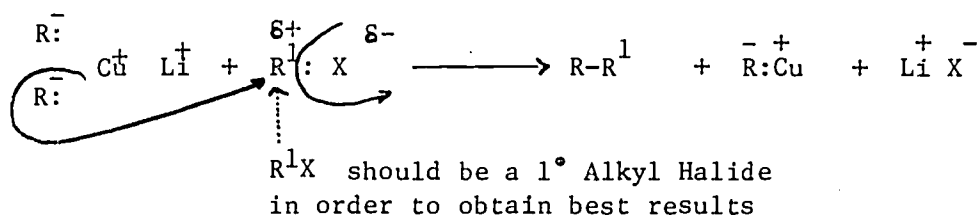
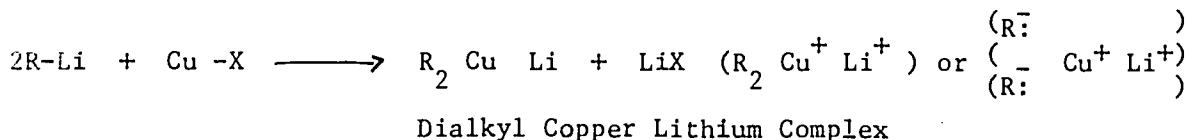
## Assignment No. 10 (continued)

## Example 5. - Copper Lithium Reaction

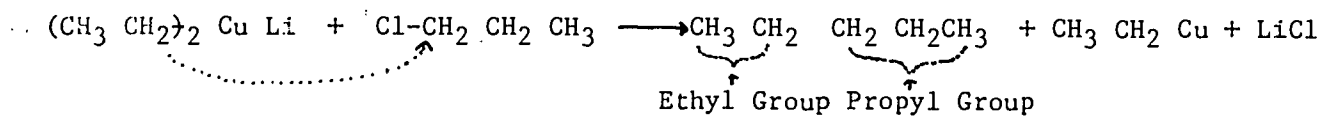
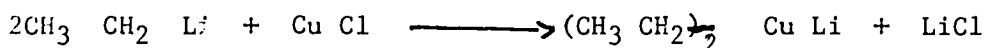
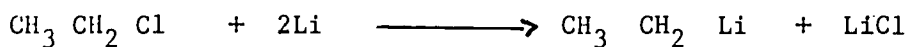


Alkyl Halide

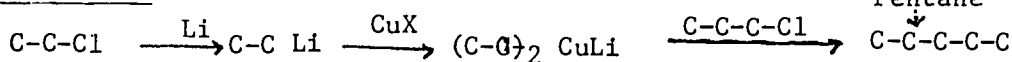
Organo Lithium Compound



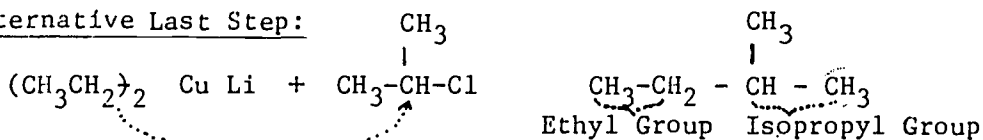
## Example 6.



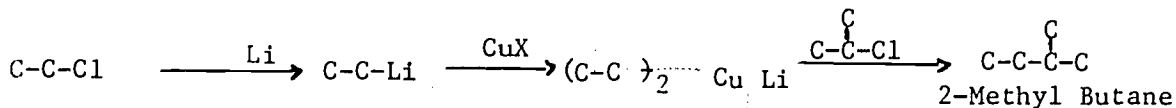
Abbreviated:



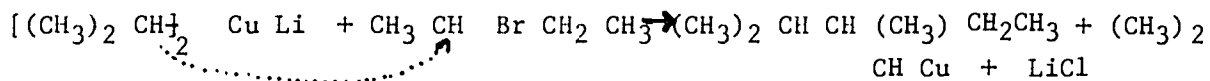
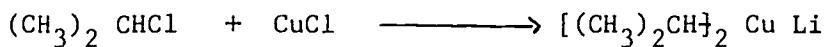
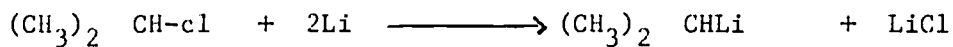
Alternative Last Step:



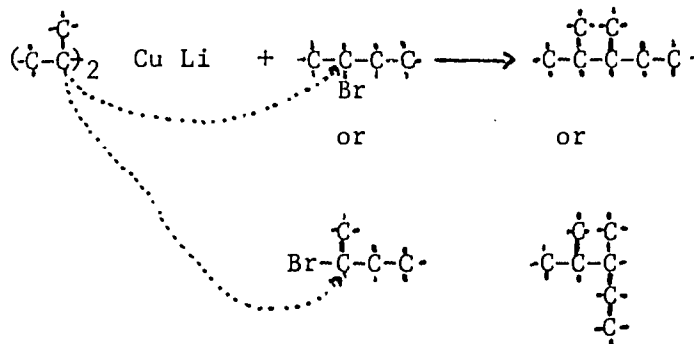
Abbreviated:



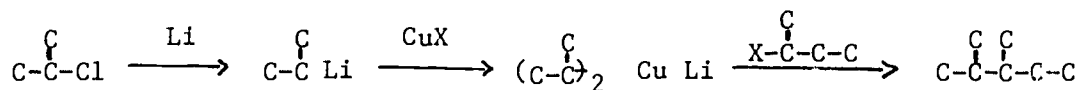
Example 7.



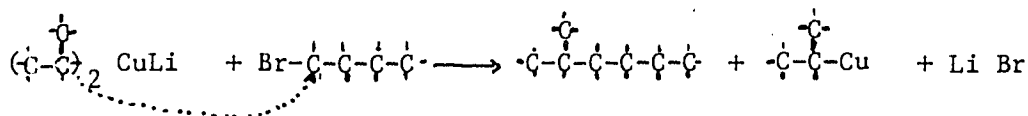
Or



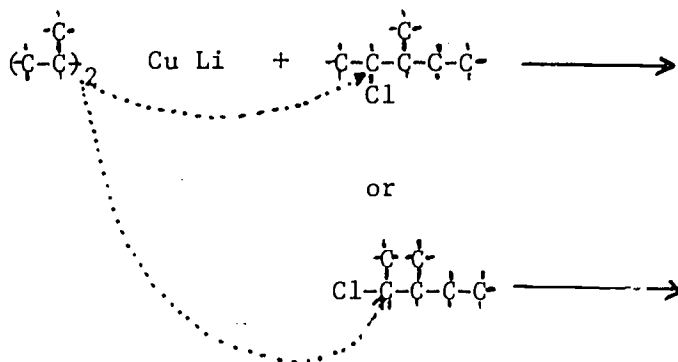
Abbreviated:



Alternate Last Step.

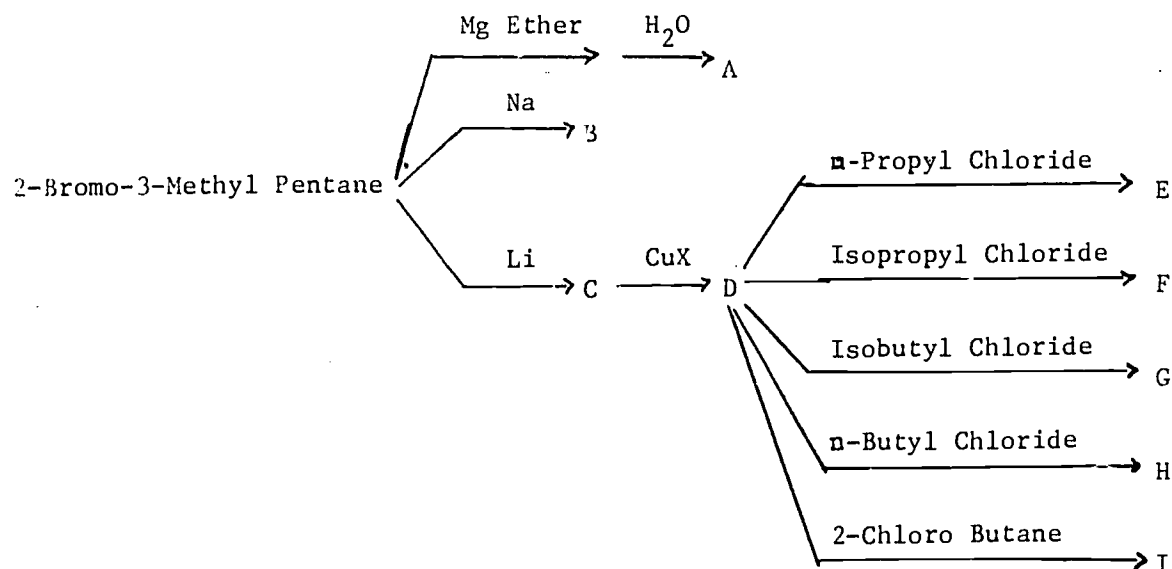


Alternate Last Step.

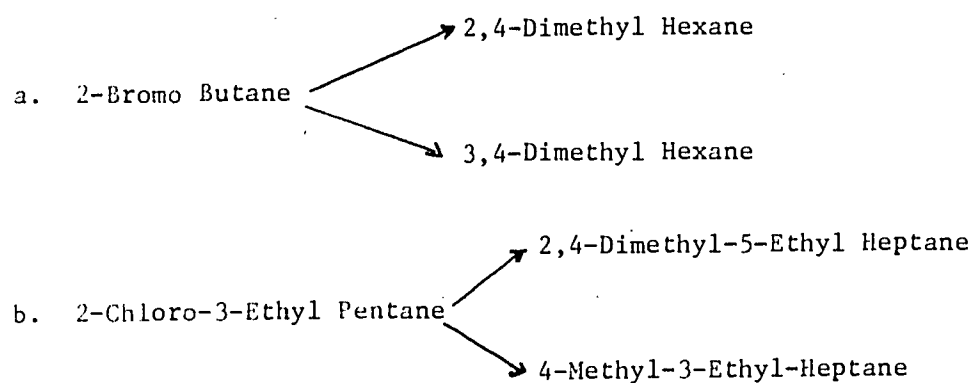


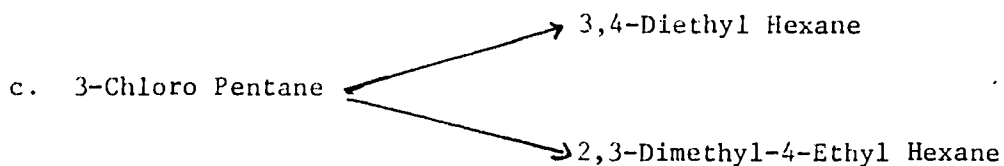
Assignment No. 11

Draw the structures and name compounds A through I in the reactions below. The reactions are given in the abbreviated form. (This should in no way prevent you from writing the balanced equations involved.)

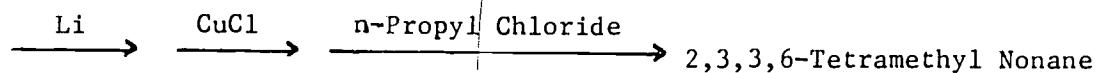
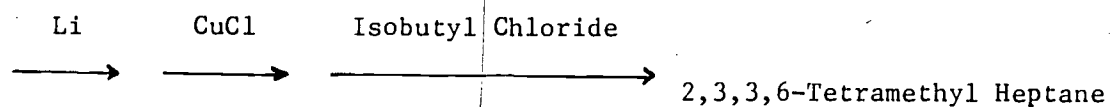
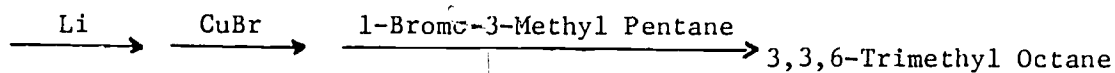
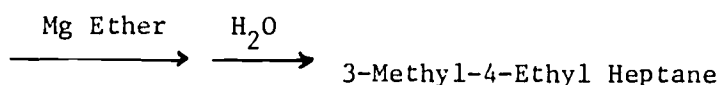
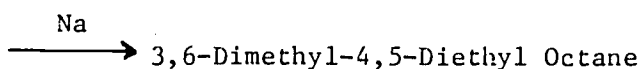
Assignment No. 12

Identify the reagents in the following laboratory synthesis:



Assignment No. 13

Confused Clyde was asked to identify the reactants in a number of laboratory synthesis. He listed all the reactants below but failed to identify them with the synthesis above. It is your task to select the correct reactant for each synthesis.



- Reactants:
- A. 1-Chloro-2,2,3-Trimethyl Butane
  - B. 2-Bromo-3-Methyl-4-Ethyl Heptane
  - C. 3-Chloro-4-Methyl Hexane
  - D. 2-Chloro-5,5,6-Trimethyl Heptane
  - E. 2-Bromo-2-Methyl Butane

Assignment No. 14

Write all the steps in the laboratory synthesis of the following compounds.

- a. 2-Methyl Pentane from Propane
- b. 3-Methyl 4-Ethyl Hexane from Butane
- c. 2,2,4-Trimethyl Pentane from Isobutane
- d. 3,4-Dimethyl Hexane from Butane

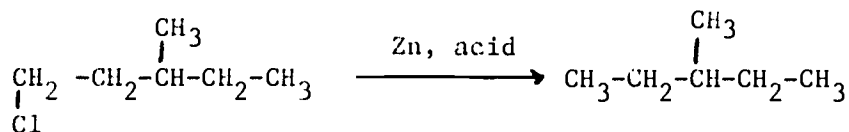


ALKANES - PREPARATION

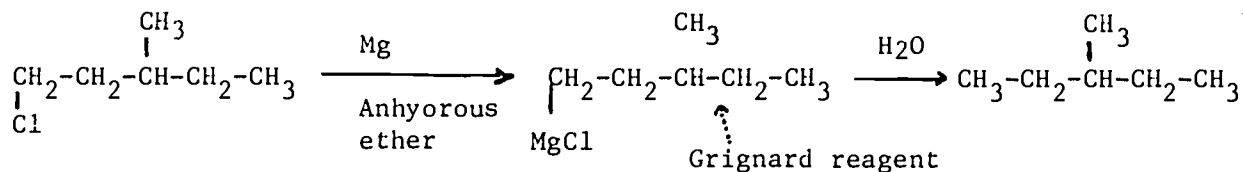
Assignment No. 1

There are two ways to prepare an alkane from an alkyl halide with the SAME (identical) carbon skeleton.

I. Reduction with Zn and acid

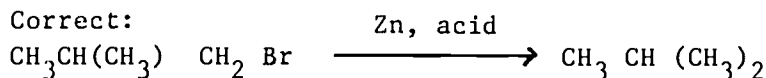
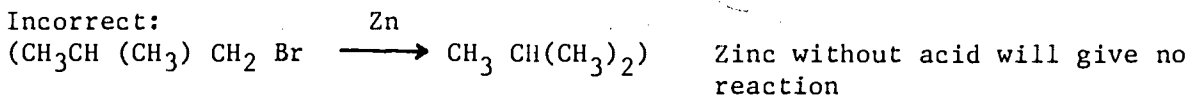


II. Grignard Preparation

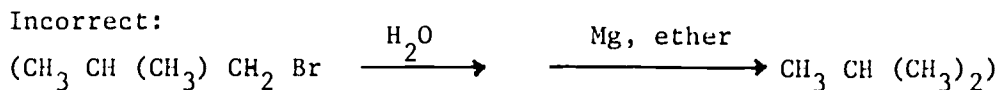


Assignment No. 2

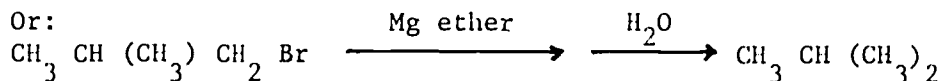
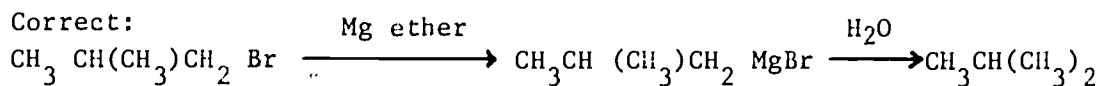
I. Reduction with Zn and acid



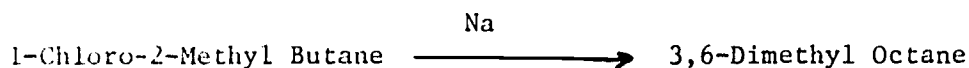
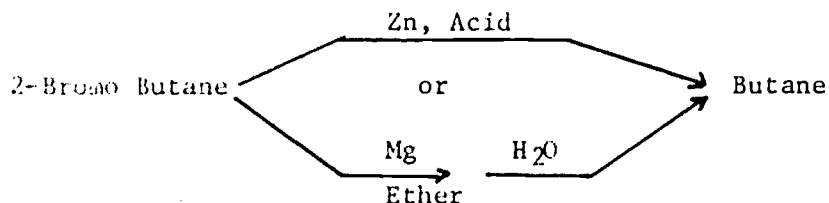
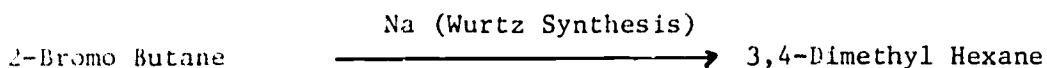
II. Grignard Reaction



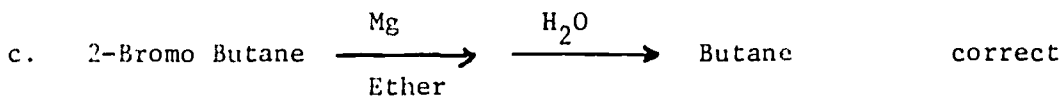
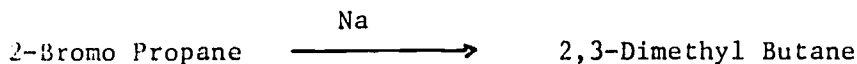
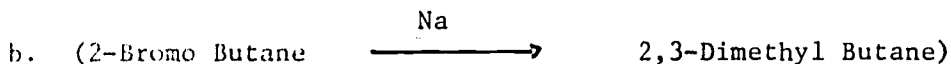
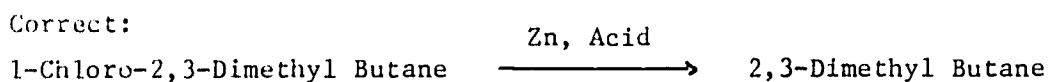
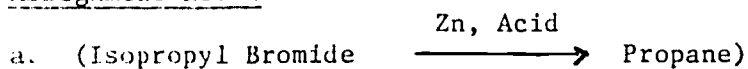
An alkyl halide must react with Mg in ether FIRST and then in the second step the GRIGNARD compound reacts with water to yield the alkane.



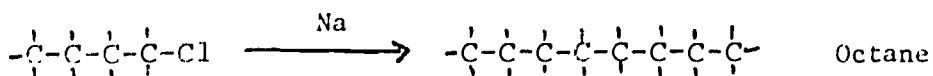
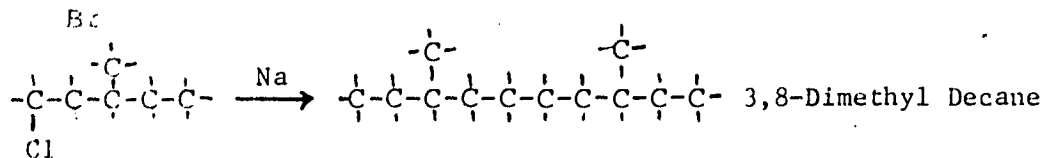
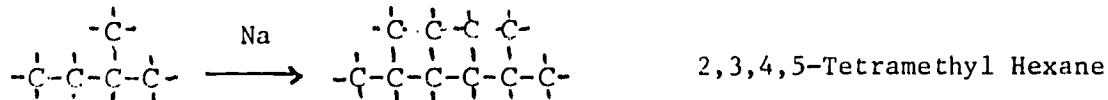
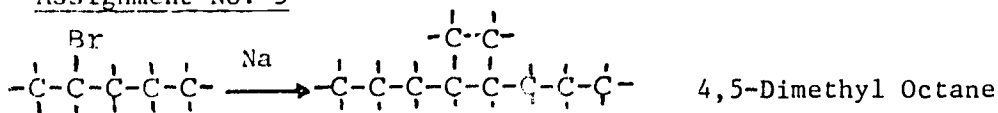
Assignment No. 3



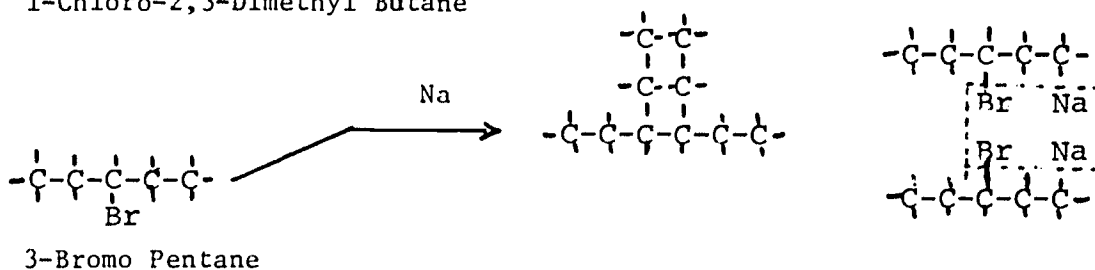
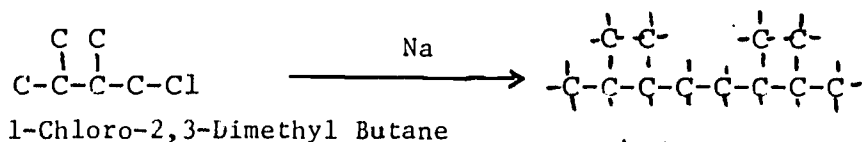
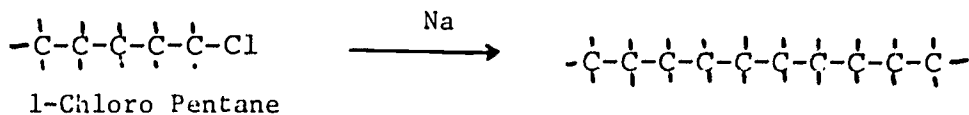
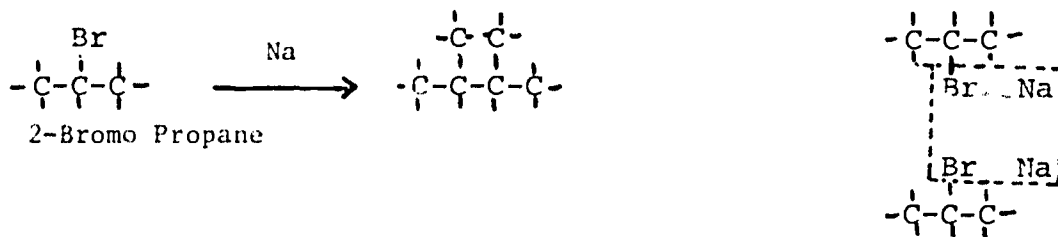
Assignment No. 4



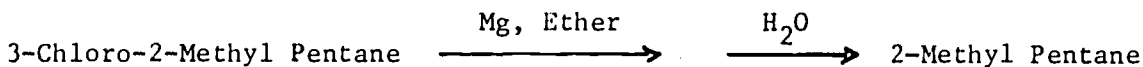
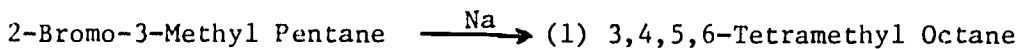
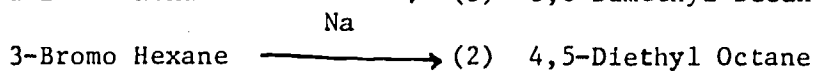
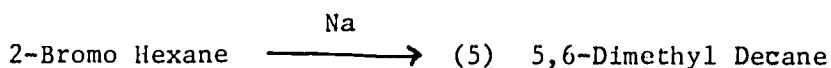
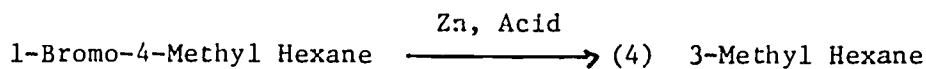
Assignment No. 5



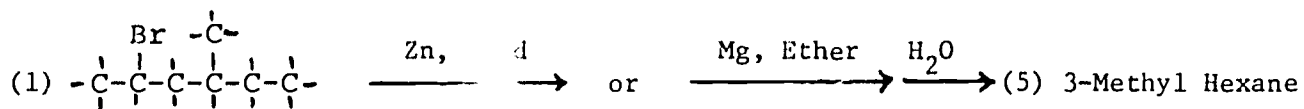
Assignment No. 6



Assignment No. 7

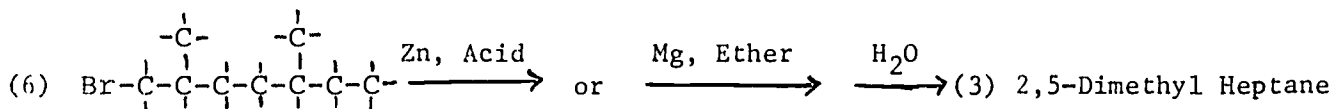
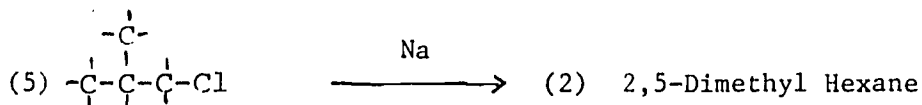
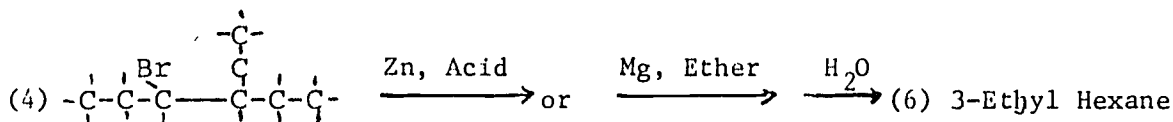
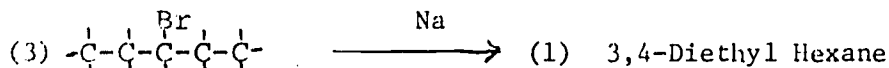
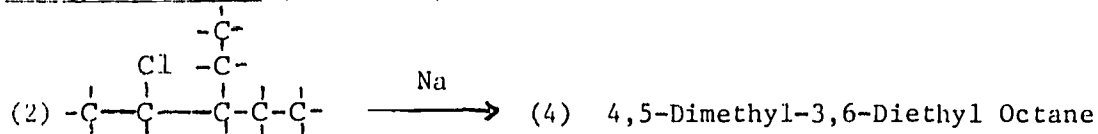


Assignment No. 8

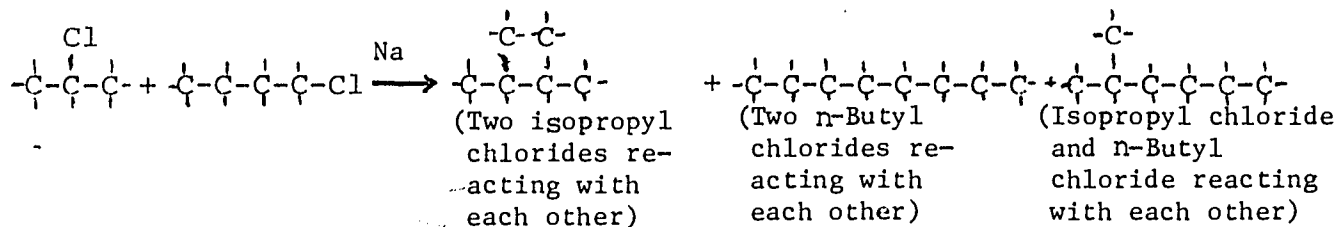




Assignment No. 8 (Continued)



Assignment No. 9

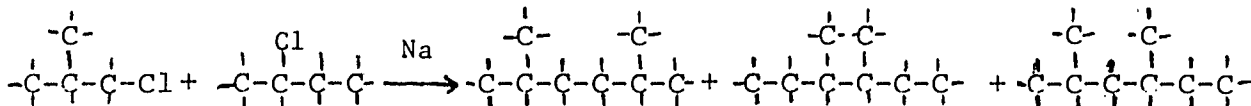


Assignment No. 10

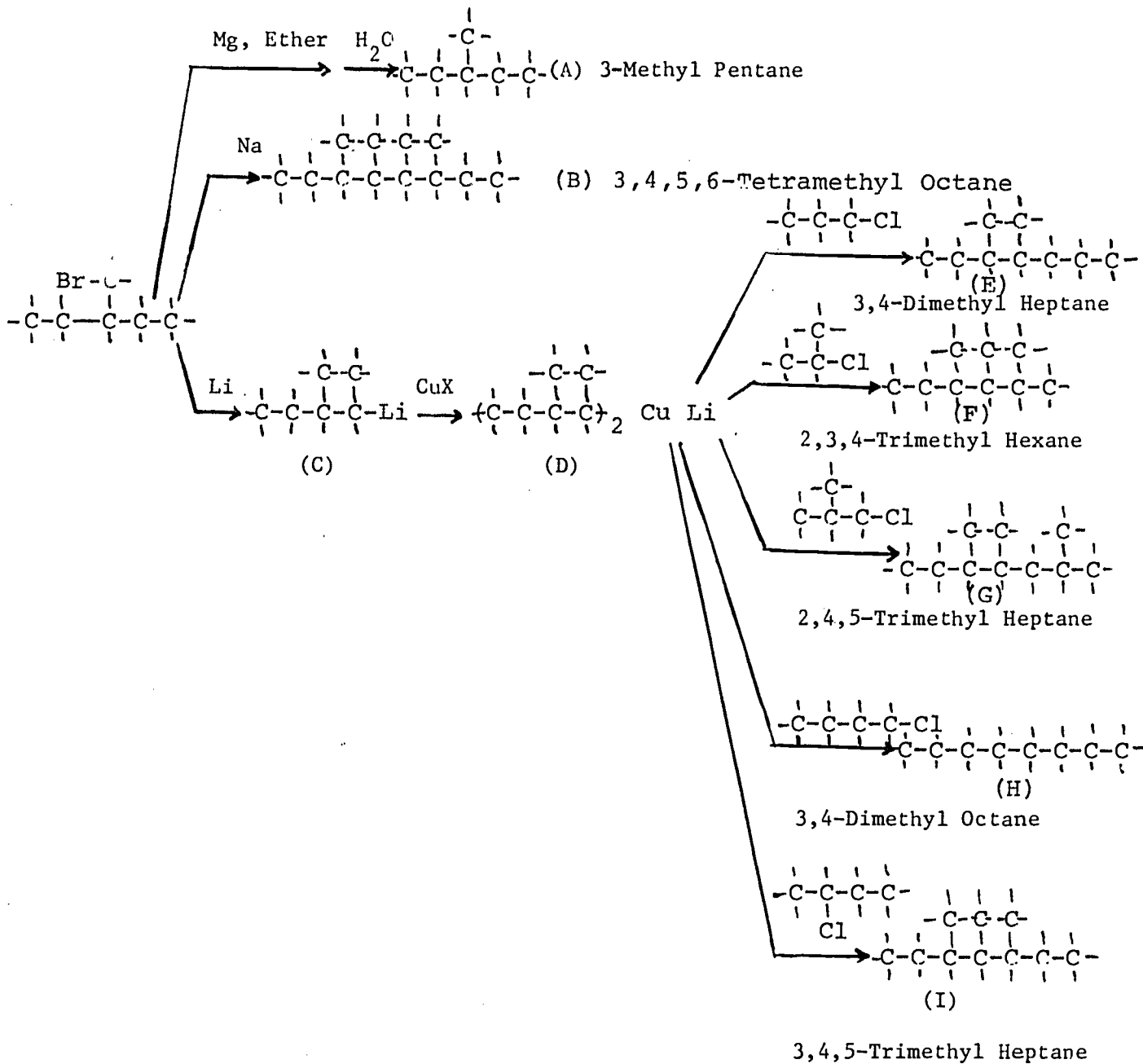
3,4-Dimethyl Hexane is symmetrical and results from the reaction of 2-Chloro Butane with sodium.

2,5-Dimethyl Hexane is symmetrical and results from the reaction of Isobutyl Chloride with sodium.

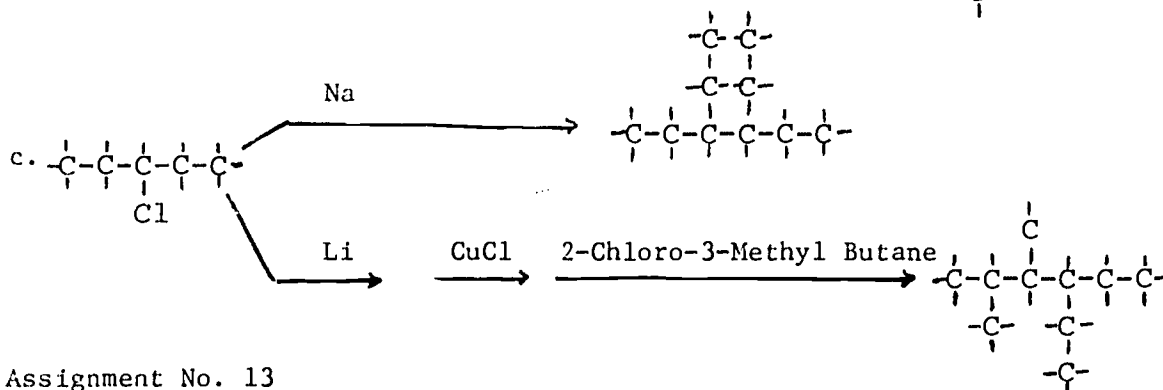
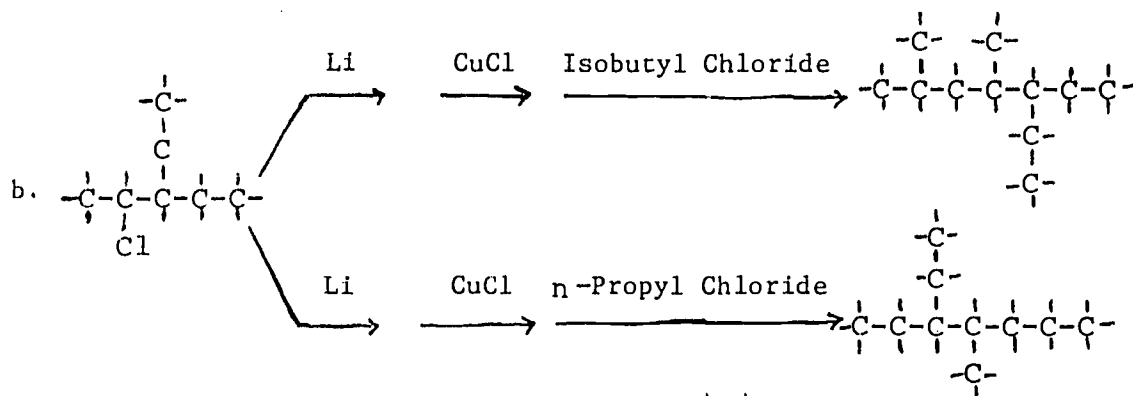
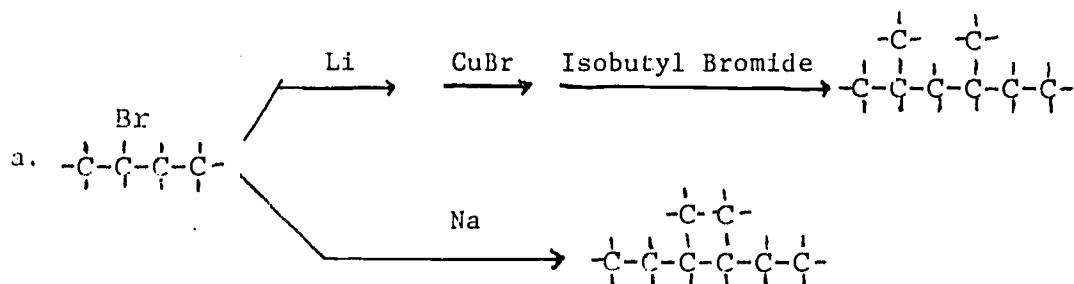
2,4-Dimethyl Hexane is NOT symmetrical and results from the reaction of:  
 2-Chloro Butane and Isobutyl Chloride with sodium.



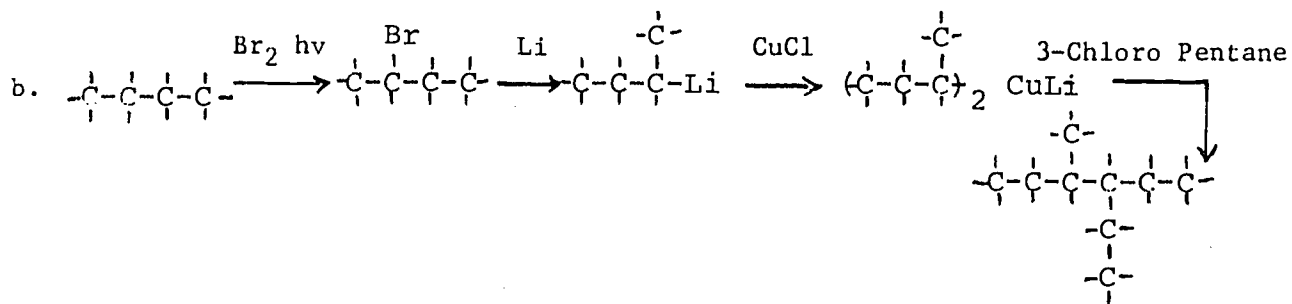
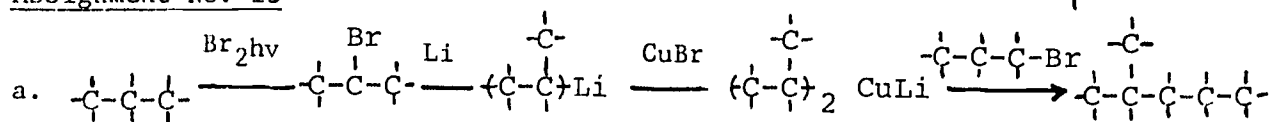
Assignment No. 11



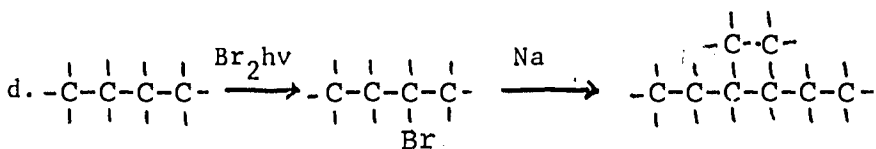
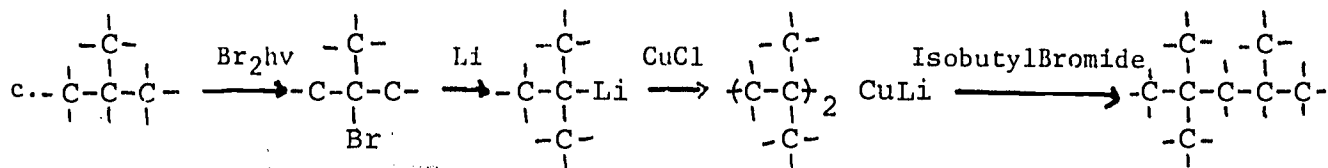
Assignment No. 12



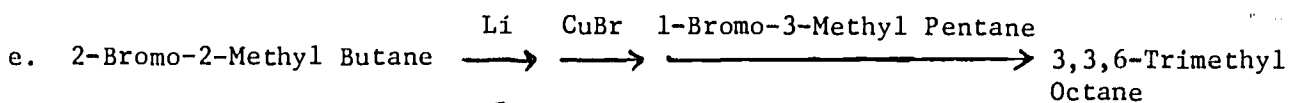
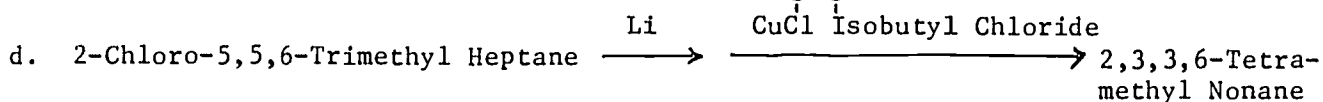
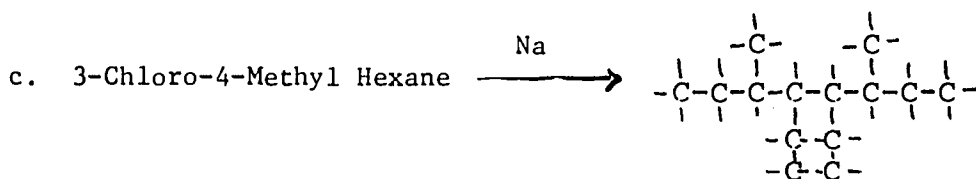
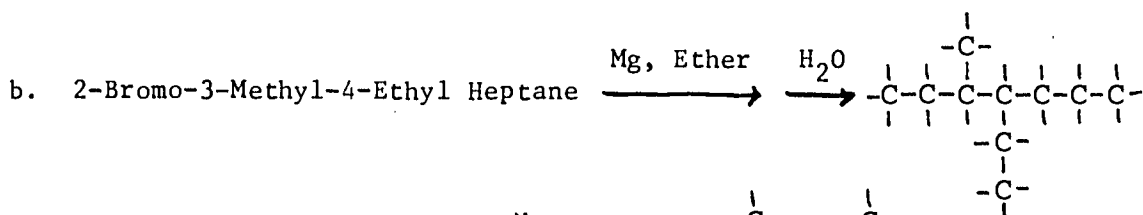
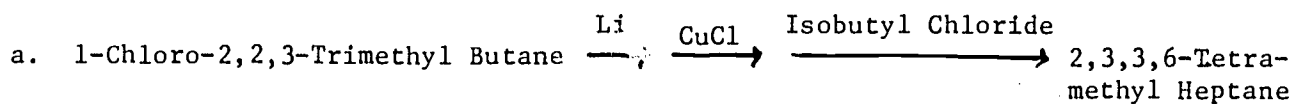
Assignment No. 13



Assignment No. 13 (continued)



Assignment No. 14





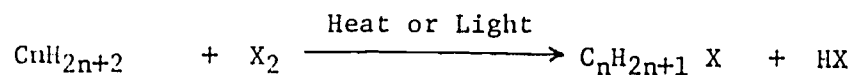
What is not fully understood is not possessed.--Goethe

Self Instructional Package No. 5  
Tape 2 - Worksheet

ALKANES - REACTIONS

Parum Affinis - Without Affinity

I. Halogenation Reaction



II. Combustion Reaction

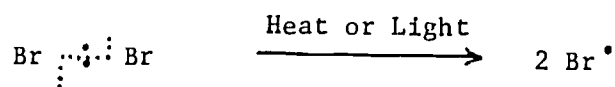


Assignment No. 1

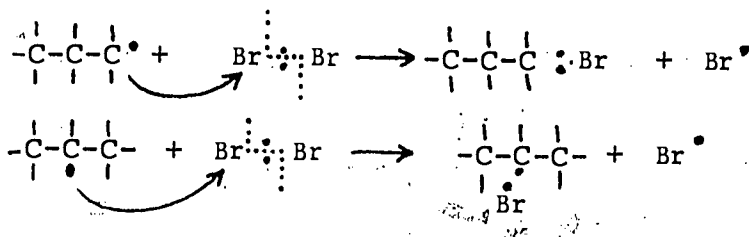
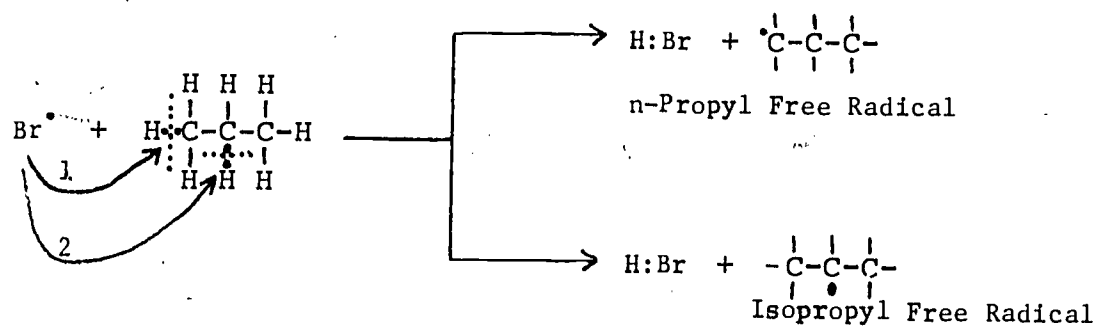
Write the step by step mechanism for the bromination of Ethane.

Example No. 1

Chain Initiating Step:



Chain Propagating Steps:

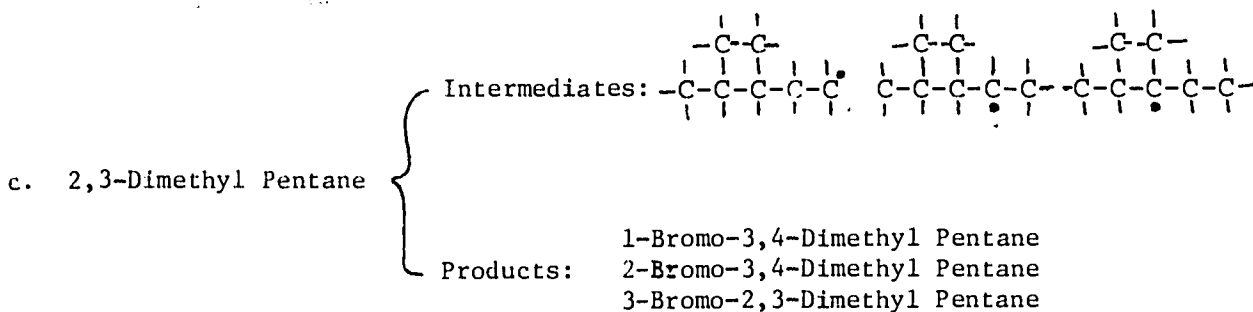
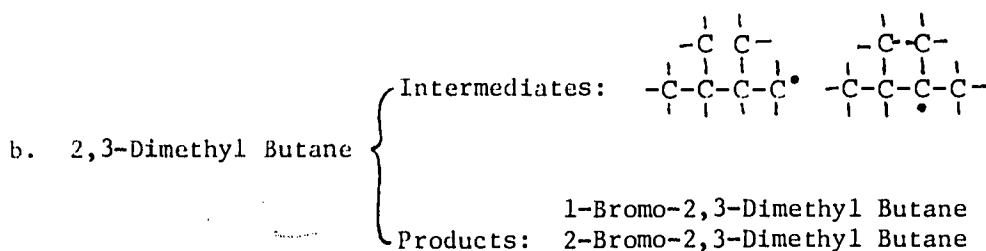
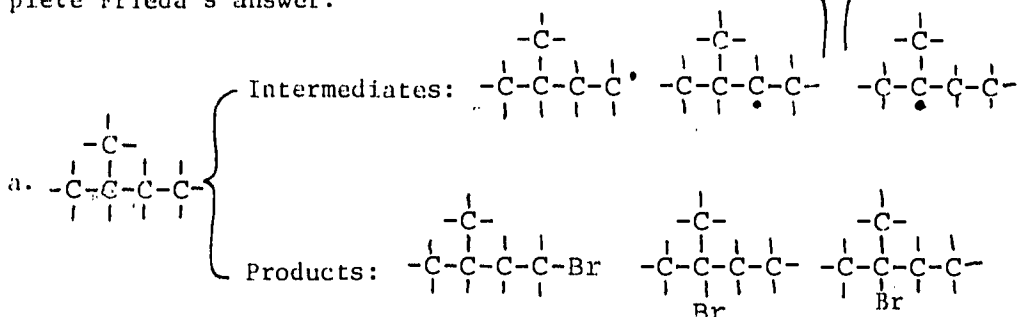


Assignment No. 2

Write the step by step mechanism for the bromination of: Isobutane and 2-Methyl Pentane. Identify (draw the structure and name) all the possible intermediate free radicals and all the products.

Assignment No. 3

Forgetful Frieda was asked to identify all the intermediates and all the products in a number of reactions. Her answer is given below. In many answers she has forgotten something. Complete Frieda's answer.



Assignment No. 4

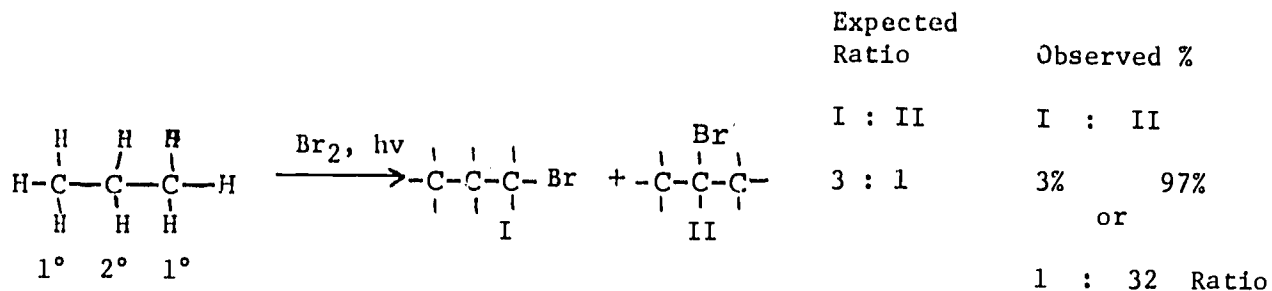
A number of monohalogenated products are listed below. Identify (Draw the structure and name) the reactant for each group of products.

a. 1-Bromo-3-Methyl Pentane    2-Bromo-3-Methyl Pentane    3-Bromo-3-Methyl Pentane

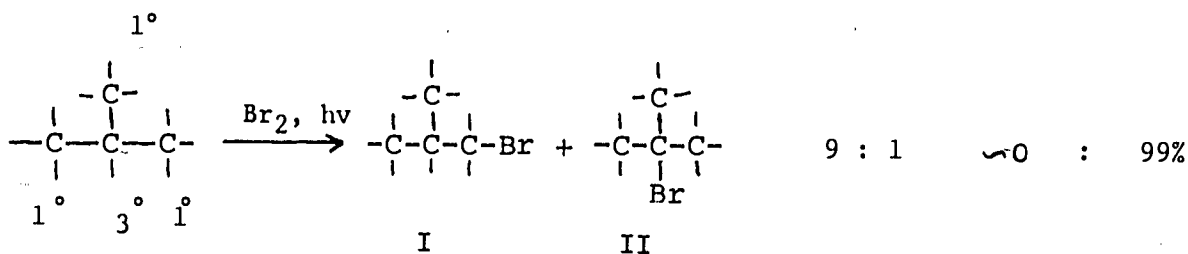
b. 1-Bromo-3,4-Dimethyl Hexane    2-Bromo-3,4-Dimethyl Hexane    3-Bromo-3,4-dimethyl hexane

c. 1-Bromo-3-Ethyl Pentane    2-Bromo-3-Ethyl Pentane    3-Bromo-3-Ethyl Pentane

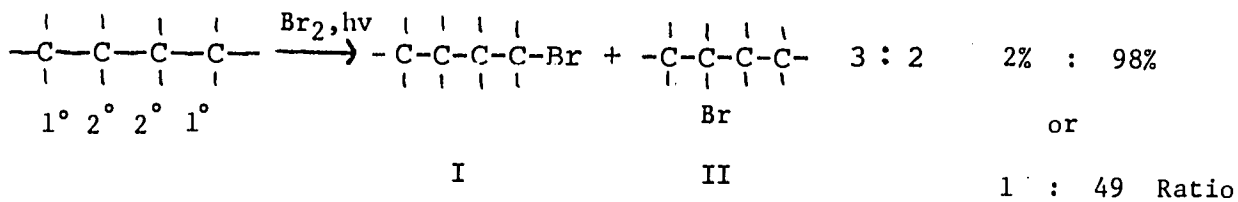
Example No. 2



Ratio:  $1^\circ/2^\circ = 6/2 = \underline{\underline{3/1}}$



Ratio:  $1^\circ/2^\circ = 9/1$



Ratio:  $1^\circ/2^\circ = 6/4 = 3/2$

Example No. 3

Rate of Reaction = Total No. of Collisions per cc per sec. X Fraction of Collisions that have sufficient energy X Fraction of Collisions that have proper orientation

Rate = Collision Frequency X Probability Factor X Energy Factor

Example No. 3 (continued)

E act for the abstraction of 2°H  $\neq$  E act for the abstraction of 1°H

E act 2°  $\begin{matrix} > \\ \neq \\ < \end{matrix}$  E act 1°

E act 3°  $<$  E act 2°  $>$  E act 1°

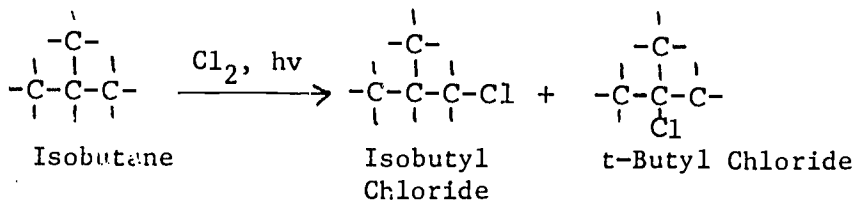
RATE OF ABSTRACTION OF H ATOMS: 3° > 2° > 1°

EASE OF ABSTRACTION OF H ATOMS: 3° > 2° > 1°

Example No. 4

Chlorination Reaction

Relative rates of reaction per hydrogen atom: 5.0 : 3.8 : 1.0  
(3° : 2° : 1°)

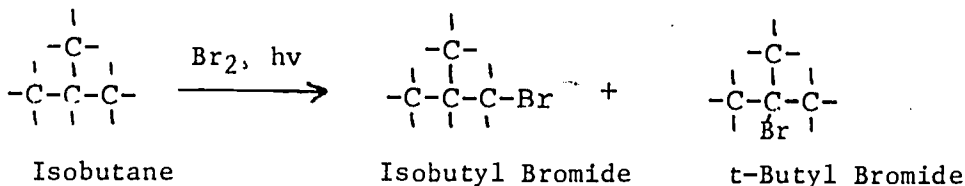


$$\frac{\text{Isobutyl Chloride}}{\text{tert Butyl Chloride}} = \frac{\text{No. of } 1^\circ\text{H}}{\text{No. of } 3^\circ\text{H}} \times \frac{\text{Reactivity of } 1^\circ\text{H}}{\text{Reactivity of } 3^\circ\text{H}} = \frac{9 \times 1.0}{3 \times 5.0} = \frac{9}{15}$$

$$\frac{9}{15} = \frac{35.7\%}{64.3\%} \quad \left( \frac{9}{26} \times 100 \right)$$

Bromination Reaction       $\left( \frac{15}{26} \times 100 \right)$

Relative rates of reaction per hydrogen atom: 1600 : 82 : 1  
(3° : 2° : 1°)



Example No. 4 (continued)

<u>Isobutyl Bromide</u>	<u>No. of 1°H</u>	<u>Reactivity of 1°H</u>	$\frac{9 \times 1}{1 \times 1600}$	$\frac{9}{1600}$	$\frac{1}{178}$
t-Butyl Bromide	No. of 3°H	Reactivity of 3°H			

Exclusively t-Butyl Bromide

Assignment No. 5

Calculate the percentage composition of the products obtained from:  
a.) Chlorination and b.) Bromination of Propane and Butane. Compare these results to those obtained experimentally. (You can find them in Example No. 7)

Assignment No. 6

Identify - draw structure and name the MAJOR product in the reactions written below.

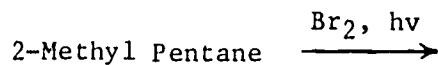
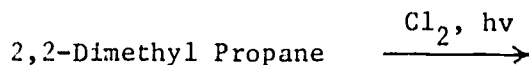
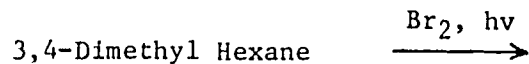


Table I

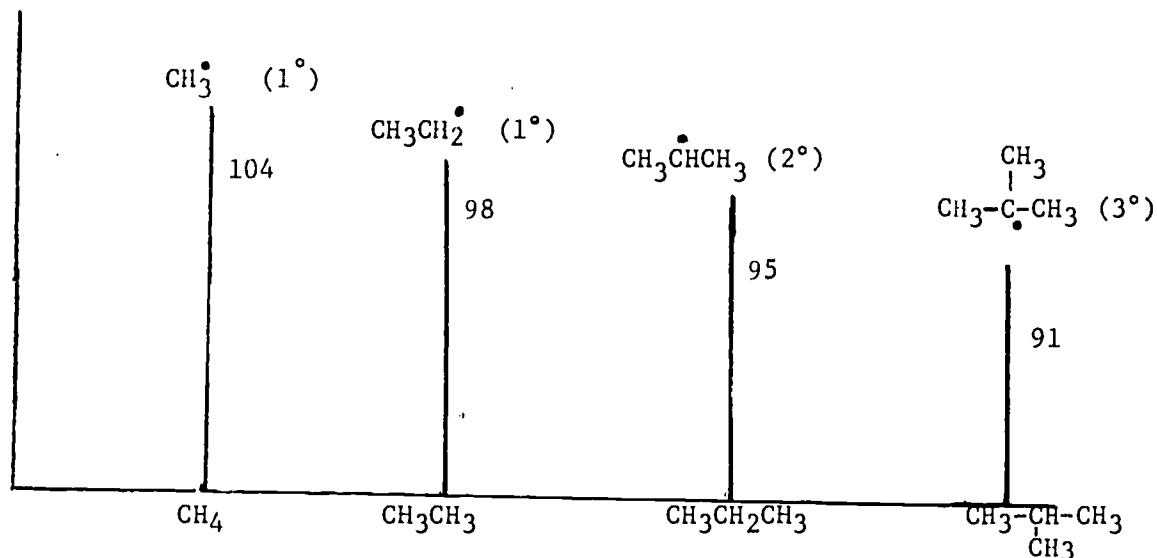
Energies of Reactivation [  $\frac{\text{Kcal}}{\text{Mole}}$  ], for the Reaction:  $\text{R}\cdot\cdot\text{H} + \text{X}\cdot \longrightarrow \text{R}\cdot + \text{H}\cdot\cdot\text{X}$

R	X = Cl	X = Br
$\text{CH}_3$	4	18
$1^\circ$	1	13
$2^\circ$	0.5	10
$3^\circ$	0.1	7.5

Example No. 5

EASE OF FORMATION OF FREE RADICALS:  $3^\circ > 2^\circ > 1^\circ > \text{CH}_3\cdot$

Example No. 6

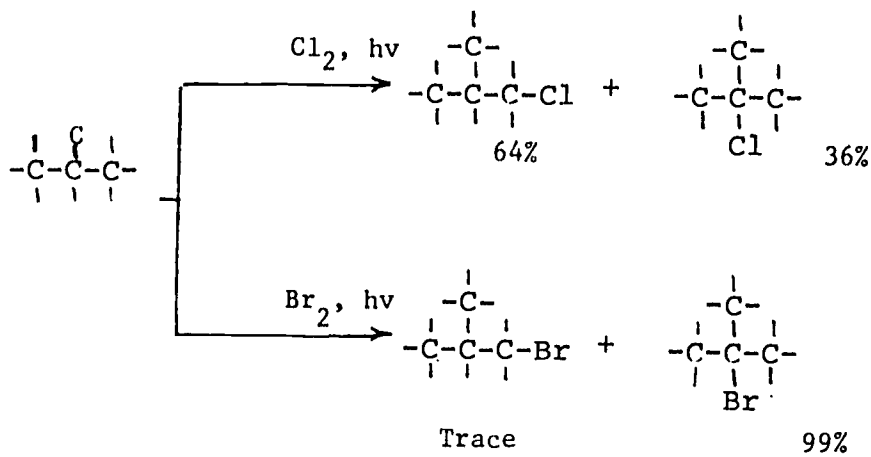
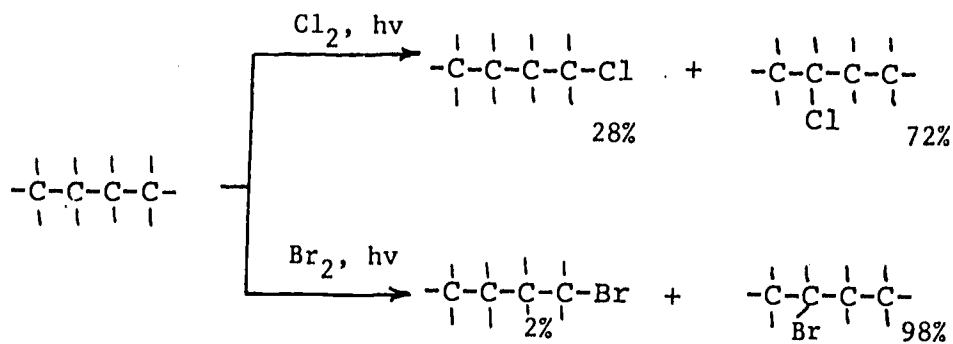
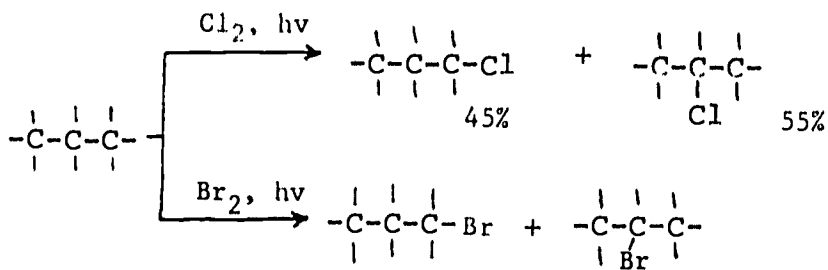


STABILITY OF FREE RADICALS:  $3^\circ > 2^\circ > 1^\circ > \text{CH}_3\cdot$

ORIENTATION - where in the given molecule the reaction will take place predominately - comparison of different sites of the SAME MOLECULE.

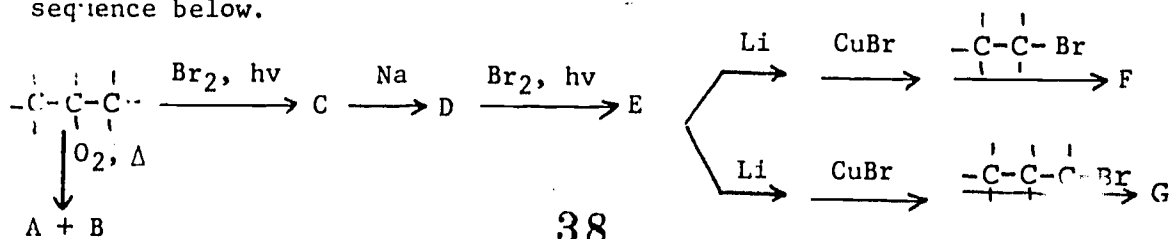
REACTIVITY - Comparison of Different Compounds in a reaction with the same reagent.

Example No. 7



Assignment No. 7

Identify (draw structures and name) compounds A → G in the reaction sequence below.



38

37



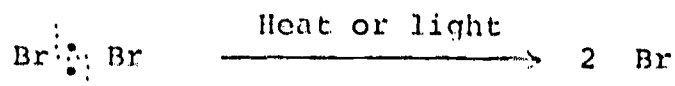
Assignment No. 8

Write all the steps in the laboratory synthesis of 3-Methyl Pentane from n-propyl chloride.

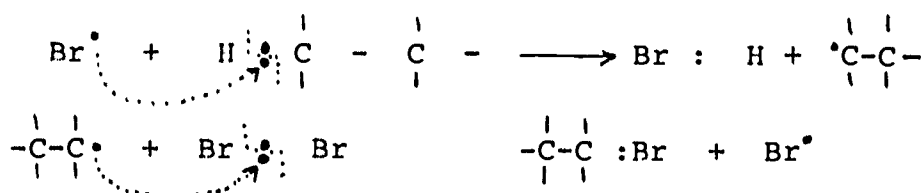
ALKANES - REACTIONS

Assignment No. 1

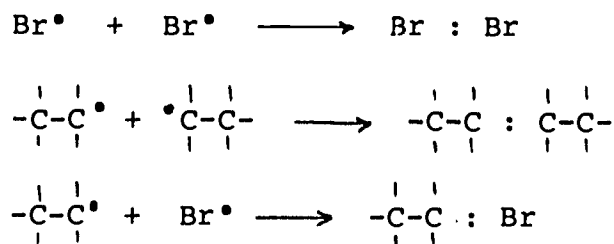
Chain Initiating Step



Chain Propagating Steps

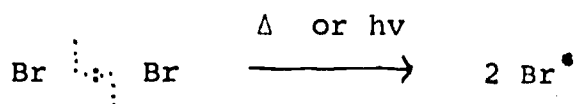


Chain Terminating Steps



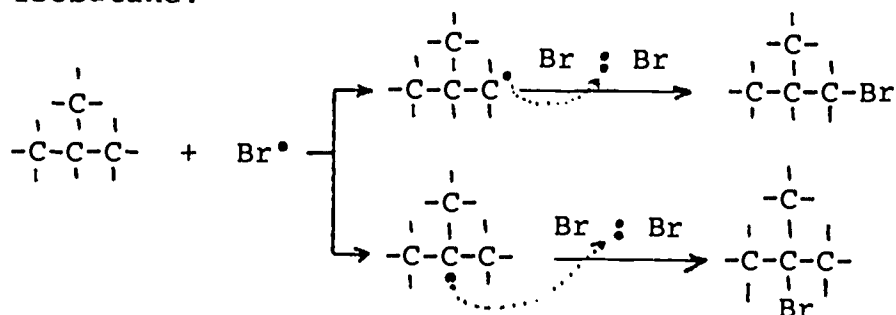
Assignment No. 2

Chain Initiating Step



Chain Propagating Steps

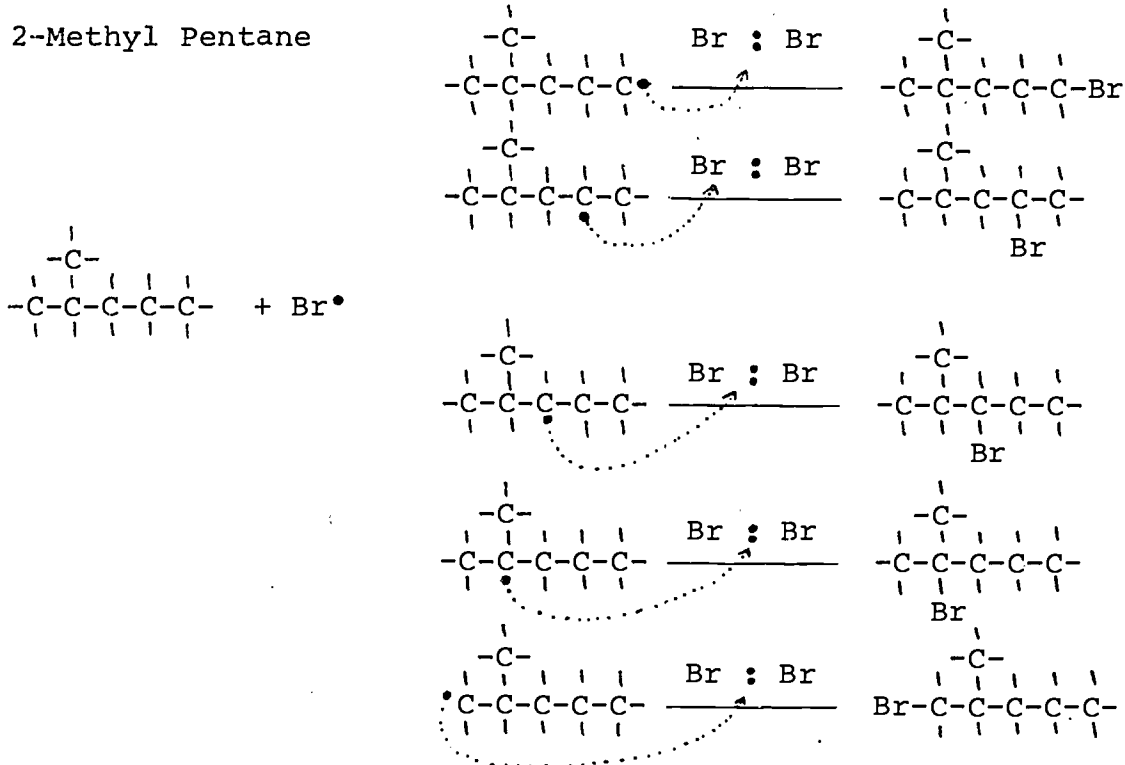
Isobutane:



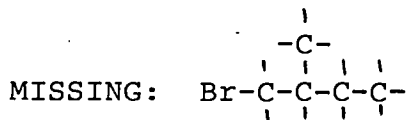
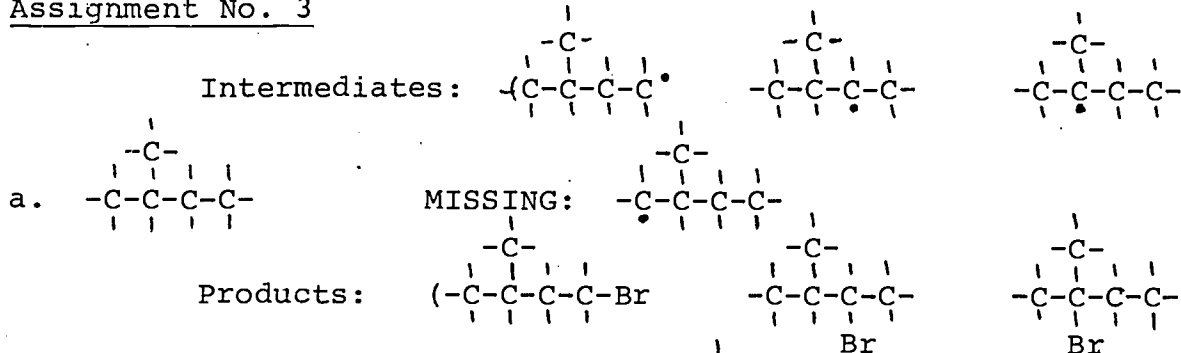


Assignment No. 2 (continued)

2-Methyl Pentane

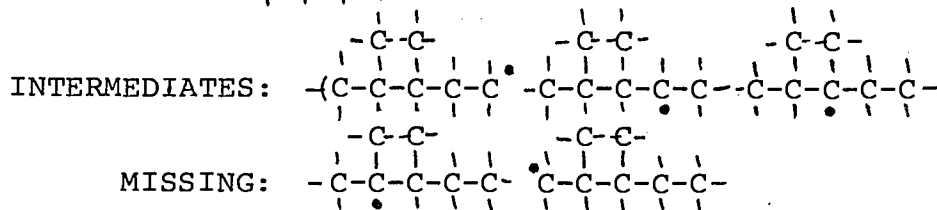


Assignment No. 3



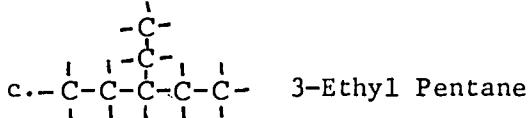
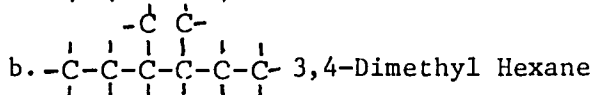
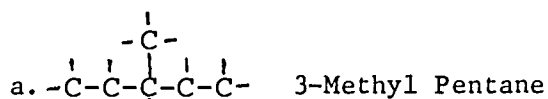
b. Complete

2,3-Dimethyl Pentane

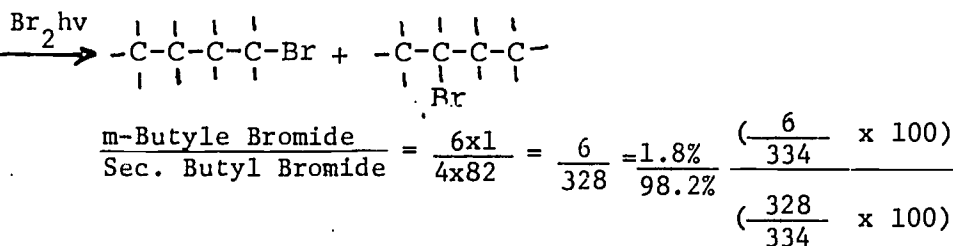
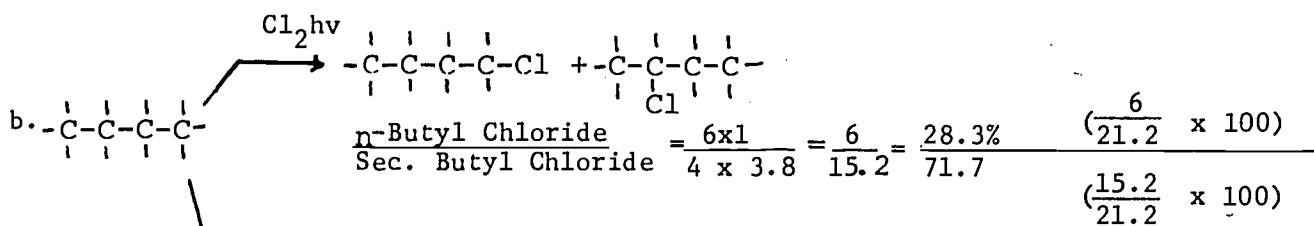
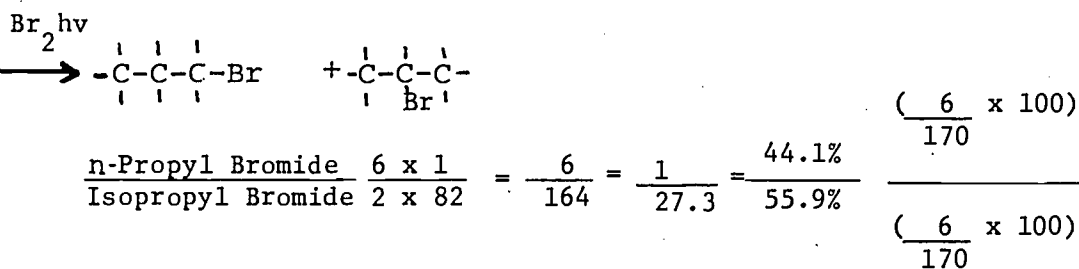
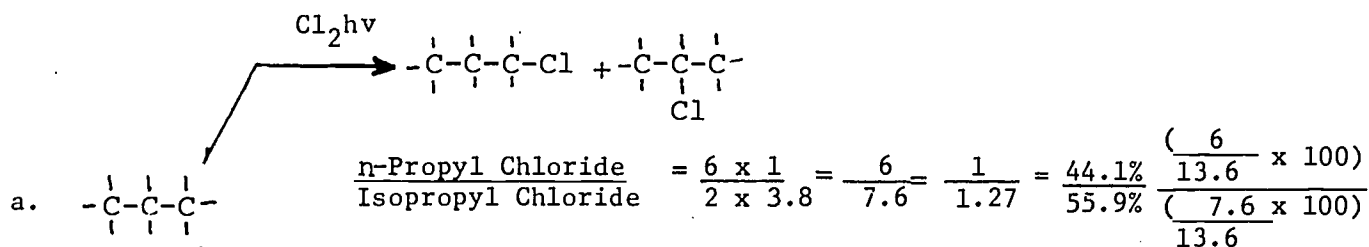


PRODUCTS: 1-Bromo-3,4-Dimethyl Pentane  
 2-Bromo-3,4-Dimethyl Pentane  
 3-Bromo-2,3-Dimethyl Pentane  
 2-Bromo-2,3-Dimethyl Pentane  
 1-Bromo-2,3-Dimethyl Pentane

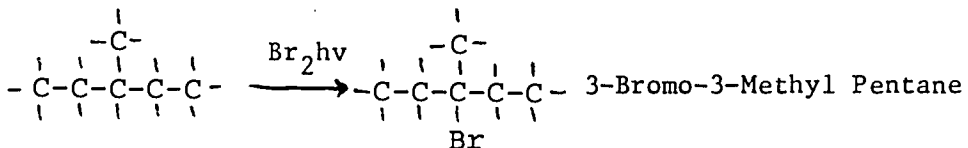
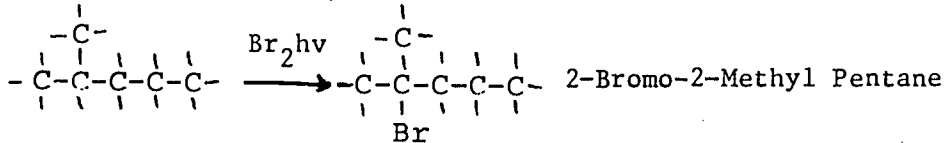
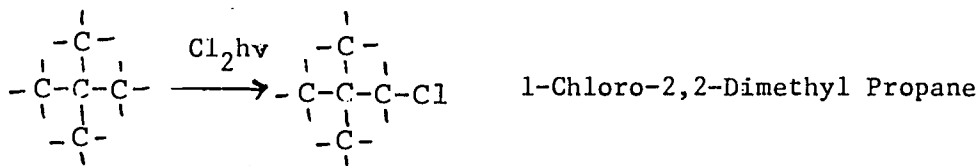
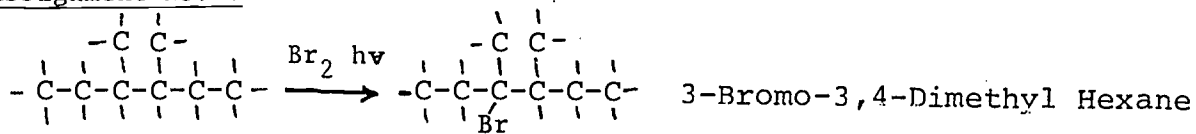
Assignment No. 4



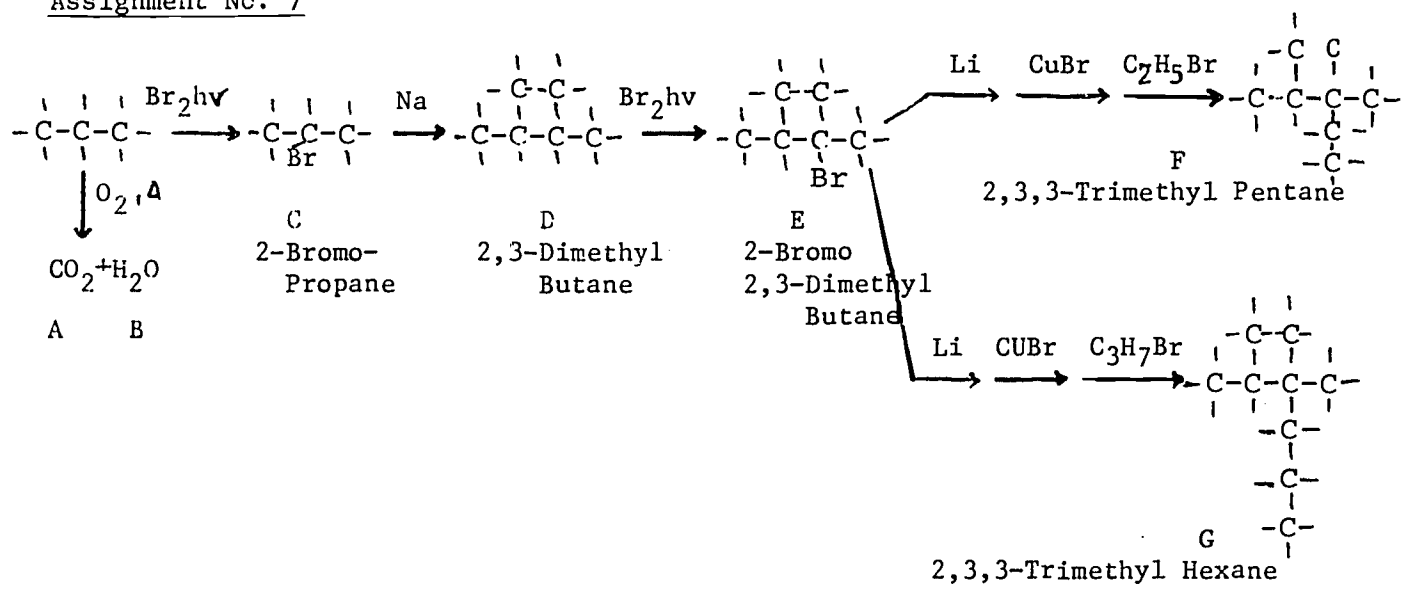
Assignment No. 5



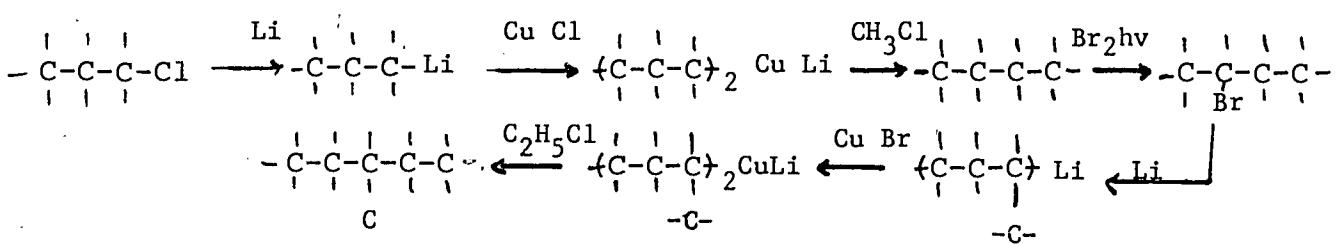
Assignment No. 6



Assignment No. 7

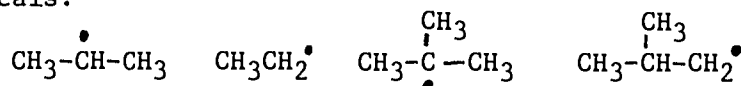


Assignment No. 8



ALKANES - PREPARATION AND REACTIONS

1. When butane reacts with excess oxygen in the presence of heat the products will be:
  - a) carbon dioxide
  - b) carbon dioxide and water
  - c) heat and carbon monoxide
  - d) carbon dioxide, water and heat.
2. Hydrocracking of alkanes can be defined as:
  - a) the reaction of an alkane with excess oxygen.
  - b) the reaction of alkanes in which smaller alkanes are produced.
  - c) the decomposition of alkanes with heat in presence of hydrogen.
  - d) the decomposition of alkanes with heat in presence of steam.
3. The following statements about the pyrolysis are true:
  - a) the pyrolysis of alkanes is known as cracking.
  - b) the pyrolysis is the decomposition of a compound.
  - c) the pyrolysis is the decomposition of a compound by the action of heat.
  - d) the pyrolysis is the decomposition of a compound in the presence of steam.
4. The most and the least stable free radical in the series of free radicals:



are:

SIP #5  
Form D - Progress Check Evaluation

The most stable free radical

- a) Ethyl
- b) T-Butyl
- c) Isobutyl
- d) Ethyl

The least stable free radical

- a) Isobutyl
- b) Ethyl
- c) Isopropyl
- d) T-Butyl

5. In each pair of alkanes, identify the one which is more reactive toward halogenation reaction:

More Reactive

- a) Methane(A), Ethane (B)
- b) Propane(A), Isobutane (B)
- c) Isobutane(A), Butane (B)
- d) Ethane (A), Propane (B)

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

6. The laboratory preparation of 3,4-dimethyl hexane from butane can be achieved by the use of the following reagents:

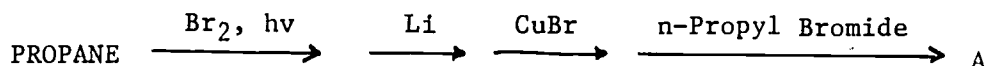
- a) BROMINE, light, SODIUM
- b) BROMINE, Light, MAGNESIUM IN ETHER, WATER
- c) SODIUM
- d) BROMINE, Light, LITHIUM, COPPER BROMIDE, 2-BROMO BUTANE

7. The reactant required for the Grignard synthesis is:

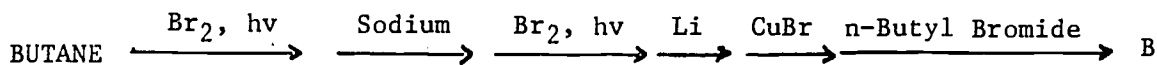
- a) an alkane
- b) an alkyl bromide
- c) an alkyl chloride
- d) an alcohol.



8. Identify the correct statements below:
- a) Tertiary alkyl halides give best results in Wurtz synthesis.
  - b) Primary alkyl halides give best results in the reaction with Lithium Dialkyl Copper Intermediate.
  - c) Grignard synthesis is a one-step preparation.
  - d) A Grignard compound can react with water or ammonia or alcohols to produce an alkane.
9. The reagents required to convert 2-Chloro Butane into 3-Methyl Pentane are:
- a) SODIUM
  - b) MAGNESIUM IN ETHER, WATER
  - c) LITHIUM, COPPER CHLORIDE, ETHYL CHLORIDE
  - d) LITHIUM, COPPER, CHLORIDE, PROPYL CHLORIDE
10. The product A obtained in the reaction sequence below is:



- a) Hexane
  - b) 3-Methyl Pentane
  - c) 2-Methyl Pentane
  - d) 2-Methyl Hexane
11. The compound B produced in the reaction below is:



- a) 4-n-Butyl Octane
- b) 3,4-Dimethyl-4-Ethyl Octane
- c) 3,4,4-Trimethyl Nonane
- d) Dodecane

SIP #5

Form D - Progress Check Evaluation

12. The major product in the Bromination of 2-Methyl Butane is:
- a) 1-Bromo-2-Methyl Butane
  - b) 2-Bromo-2-Methyl Butane
  - c) 2-Bromo-3-Methyl Butane
  - d) 1-Bromo-3-Methyl Butane
13. The major product in the reaction of 2-Bromo Butane with Zinc in presence of Acid is:
- a) 3,4-Dimethyl Hexane
  - b) Octane
  - c) Butane
  - d) Organozinc Compound

Self Instructional Package No. 5

Form B1 - Answer Sheet

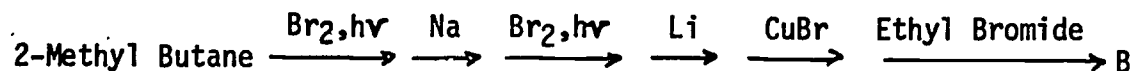
ALKANES - PREPARATIONS AND REACTIONS

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

Self Instructional Package No. 5  
Form D<sup>1</sup> - Answer Sheet

ALKANES - PREPARATIONS AND REACTIONS

1. d
2. c
3. a, c
4. b
5. B, B, A, A
6. a, d
7. b, c
8. b, d
9. c
10. c
11. b
12. b
13. c

S.I.P. #5 - ERRATAFORM B - Question #7 - Reaction:

Question #11 - Reaction:



Question #14 - Part a.

- a) Hydrocracking is the cracking of alkanes in the presence of hydrogen

FORM D<sup>1</sup> - Answer Sheet

5 - B. B. A. B

TAPE 1 - Answer Sheet

The answers for assignments 13 and 14 are reversed. (The answer listed for assignment 13 is actually the answer for assignment 14.)

TAPE 2 - Worksheet - Example No. 4

$$\frac{\text{Isobutyl Chloride}}{\text{Tert. Butyl Chloride}} = \frac{\text{No. of } 1^\circ\text{H}}{\text{No. of } 3^\circ\text{H}} \times \frac{\text{Reactivity of } 1^\circ\text{H}}{\text{Reactivity of } 3^\circ\text{H}} = \frac{9 \times 1.0}{1 \times 5.0} =$$

$$= \frac{9}{5} = \frac{64.3\%}{35.7\%} \left( \frac{9}{14} \times 100 \right)$$

$$\left( \frac{5}{14} \times 100 \right)$$

