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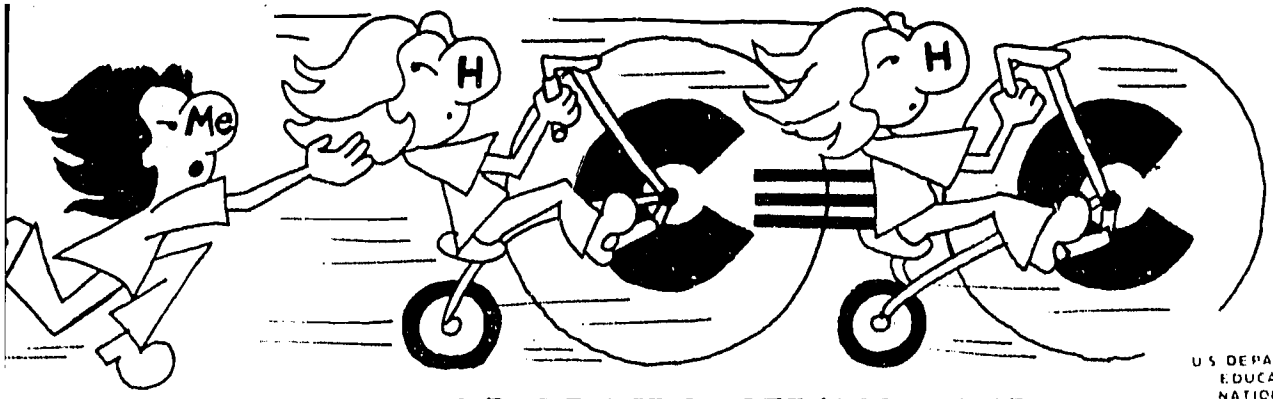
ABSTRACT

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 alkynes. (SL)



ORGANIC CHEMISTRY

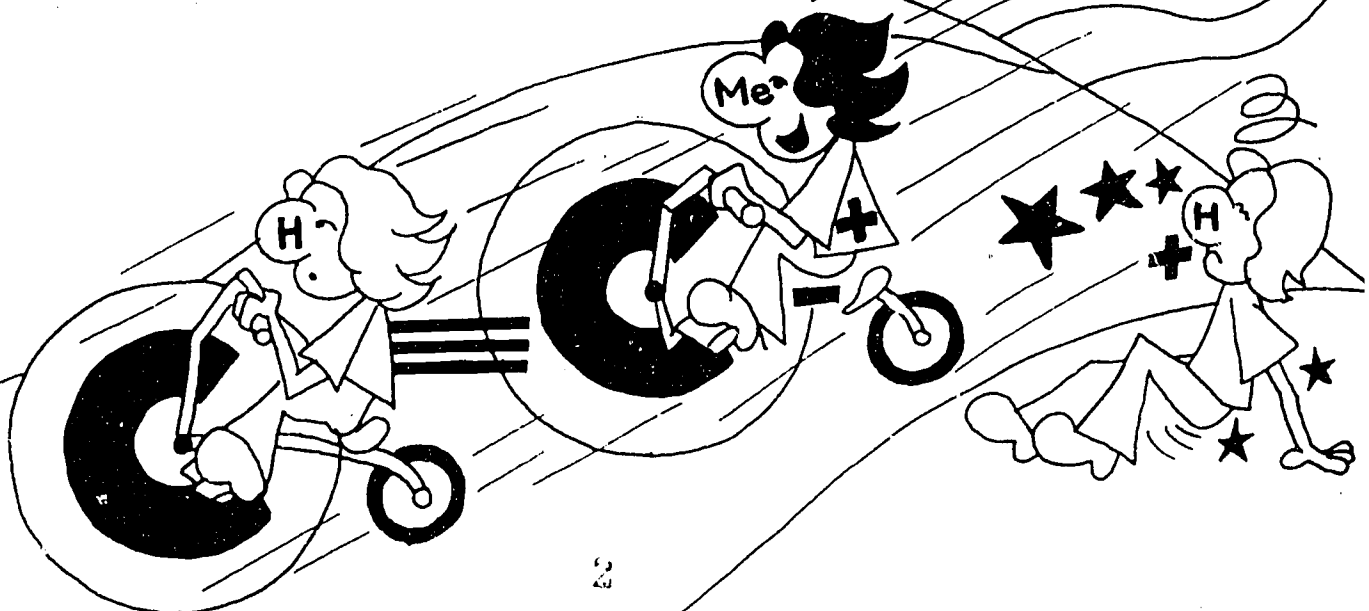
V. Zdravkovich

12

Self
Instructional
Package

V. Zdravkovich

ALKYNES



Self Instructional Sequence in

ORGANIC CHEMISTRY

ALKYNES

Introduction

In this module you will learn about the preparation and behavior of a colorless gas that boils at 84°. It used to be used as an illuminant. It is used in torches since it burns with an intense white flame when mixed with the proper amount of air. About half of this gas consumed in the United States is used for the welding, cutting and cleaning of iron and steel by means of a flame which has a temperature in the neighborhood of 2800°. Its great importance is for the preparation of acetaldehyde CH_3CHO, acrylonitrile $H_2C = CHCN$, tetrachloro ethane and many other organic compounds.

Do you know what this gas is?

Do you know how to prepare acetaldehyde, tetrachloro alkane or acrylonitrile from it?

The answers to these questions can be found in this self instructional package.

ALKYNES

Definitions

The student will be able to define, explain and illustrate with appropriate examples the following terms: STRONGER ACID, WEAKER ACID, KETO-ENOL TAUTOMERISM, KETONE, ENOL, TAUTOMERS, Sp HYBRIDIZATION, TRIPLE BOND.

Preparations

The student will be able to identify the necessary reagents and to write the reactions for the preparation of alkynes from dihalo and tetrahalo derivatives of alkanes.

The student will be able to write the preparation of larger alkynes from acetylene.

The student will be able to write all the steps in the commercial preparation of acetylene from coal and limestone.

Reactions

The student will be able to write the balanced reactions for the addition of hydrogen, halogen, hydrogen halide and water in acidic medium to an alkyne.

The student will be able to write the final products obtained in the ozonolysis of an alkyne.

The student will be able to identify the original alkyne from the products obtained in the ozonolysis reaction.

The student will be able to write the balanced reactions for the reaction of terminal alkynes with Na, Li, K, Na^+, Li^+, $Cu^+(NH_3)_2\ NO_3$ and $Ag + (NH_3)_3Cl$.

The student will be able to identify the stronger and the weaker acid from a given reaction.

The student will be able to write a correct reaction showing the relative acidity of the species.

The student will know the relative acidity of acetylene as compared to that of water, ammonia, alcohol.

The student will be able to show and explain the difference in the reaction of sodium acetylide with a primary and a tertiary halide.

Reaction mechanism

The student will be able to write the mechanism and draw the resonance structures involved in the reaction of an alkyne with water in acidic medium.

The student will be able to write a tentative mechanism showing the difference in the reaction of sodium acetylide with a primary and a tertiary alkylhalide.

Multi-step synthetic schemes

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

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 given multi-step synthetic scheme.

Self Instructional Package No. 12
Form B - Self Evaluation Exercise

ALKYNES

Identify the statements below as true or false by placing a capital T or F in the space provided.

1. _____ Methyl ethyl acetylene has a higher boiling point than diethyl acetylene.

2. _____ Acetylene is commercially obtained from calcium carbide.

3. _____ Aluminum carbide can be used as a source for the commercial preparation of acetylene.

4. _____ A reaction of sodium acetylide with tertiary alkyl halide results in elimination and formation of an alkene.

5. _____ The triple bonded carbon in an alkyne is Sp hybridized.

6. _____ Hydrogen attached to the triple bond is more acidic than the hydrogen in water molecule.

7. _____ Carbon-carbon triple bond is shorter than the carbon-carbon double bond.

8. _____ Carbon-carbon triple bond is stronger than the carbon-carbon double bond.

9. _____ Greater s character of an atomic orbitol means that electrons are closer to the nucleus.

10. _____ Keto form or keto tautomer is more acidic than the enol form or the enol tantomer.

11. _____ Tautomers are compounds whose structures differ markedly in arrangement of atoms, but which exist in equilibrium.

Circle the correct answer or answers in each question.

12. The major product in the reaction of 1-propyne with water in presence of acid is:

    a) acetaldehyde $CH_3-CH_2-\overset{\overset{O}{\|}}{CH}$

    b) acetone $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

12. c) 2-propenol $CH_2=\underset{\underset{OH}{|}}{C}-CH_3$

d) 1-propenol $\underset{\underset{OH}{|}}{CH}=CH-CH_3$

13. The major product or products in the reaction of sodiumacetylide with 2-chloro-2-methyl propane is:

a) 3,3-dimethyl-1-butyne

b) acetylene

c) isobutene

d) 4-methyl-1-pentyne

14. The correct statements made on the basis of the reaction below are:

$$HC\equiv C^- Na^+ + C_6H_5OH \longrightarrow HC\equiv CH + C_6H_5O^-Na^+$$

a) Phenol (C_6H_5OH) is stronger acid than acetylene

b) Phenol is weaker acid than acetylene

c) Phenol acts as hydrogen donor

d) Acetylene displaces phenol from the salt

15. Identify the reactions that will take place.

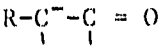
a) $NH_3 + HC\equiv C^-Na^+ \longrightarrow Na^+NH_2 + HC\equiv CH$

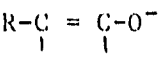
b) $NaOH + HC\equiv CH \longrightarrow Na^+ \bar{C}\equiv CH + H_2O$

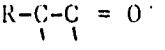
c) $C_2H_5OH + HC\equiv C^-Na^+ \longrightarrow HC\equiv CH + \overset{+}{Na}\overset{-}{O}C_2H_5$

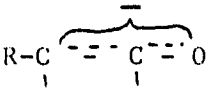
d) $HC\equiv C^-Na^+ + H_2O \longrightarrow HC\equiv CH + Na\ OH$

16. The correct resonance structures for the intermediate species in the keto-enol tautomerism are:

a) 

b) 

c) 

d) 

17. The major product in the reaction of 1-propyne with excess hydrogen bromide is:

a) 1,2-dibromopropane

b) 1,1-dibromopropane

c) 2,2-dibromopropane

d) 2-bromopropene

18. The major product in the reaction of 2-butyne with bromine in CCl_4 solution is:

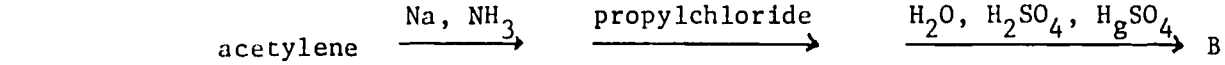
a) 2,3-dibromo-2-butene

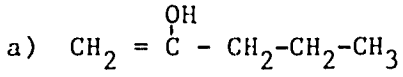
b) 2,2,3,3-tetrabromobutane

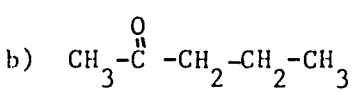
c) 1,1,1,3-tetrachloro-2-methyl-2-butene

d) 1,1,1,3-tetrachloro-2-methyl butane

19. Identify compound B thati s produced in the multi-step synthesis below:



a) 

b) 

19. c) $CH(OH) = CH - CH_2-CH_3$

d) $CH(=O)-CH_2-CH_2-CH_3$

20. Identify the alkyne that will yield the following products upon ozonolysis:

$CH_3-CH(CH_3)-COOH$ $\qquad$ $CH_3-CH(CH_3)-CH_2-COOH$

a) 2-methyl-3-heptyne

b) 2,5-dimethyl-3-heptyne

c) 2,6-dimethyl-3-heptyne

d) 2,4-dimethyl-2-pentyne

21. Identify reactant A in the multi-step synthetic scheme below:

$$A \xrightarrow{KOH} \xrightarrow{NaNH_2} \xrightarrow{Na,NH_3} \xrightarrow{\text{propylchloride}} \xrightarrow{\text{excess HBr}} CH_3-C(Br)(Br)-CH_2-CH_2-CH_3$$

a) ethane

b) 1,1-dichloropropane

c) 1,2-dichloroethane

d) pentyne

22. The reagents that can be used for the synthesis of 1-propyne from 1,2-dibromopropane are:

a) potassium hydroxide KOH

b) potassium tertiary butoxide $(CH_3)_3\ CO^-\ K^+$

c) sodamide $NaNH_2$

d) potassium hydroxide and sodamide

23. The major products in the reaction of 1-pentyne with n-butylmagnesium-bromide (Grignard compound) are:

a) $CH_3\ CH_2\ CH_2\ CH_3$

b) $CH_3CH_2CH_2CH_2\ C{\equiv}C\ CH_2\ CH_2\ CH_3$

c) $CH_3CH_2CH_2CH_2\ C{\equiv}C\ CH_2CH_2CH_2MgBr$

d) $CH_3CH_2CH_2C{\equiv}C\ MgBr$

Self Instructional Package No. 12
Form C - Reference Guide

ALKYNES

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.

Question 1	Chapter 8, Section 4	Morrison & Boyd
Questions 2, 3	Chapter 8, Section 5	Organic Chemistry
Questions 4, 13	Chapter 8, Section 12	
Questions 5, 7, 8, 9	Chapter 8, Section 2	
Questions 6, 14, 15, 19, 21, 23	Chapter 8, Section 10	
Questions 10, 11, 12, 16, 19	Chapter 8, Section 13	
Questions 17, 18, 21	Chapter 8, Sections 7, 8	
Question 22	Chapter 8, Section 6	

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

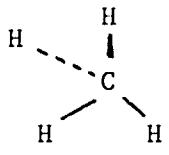
ALKYNES

Example No. 1

$HC \equiv CH$	CH_2H_2	acetylene or ethyne
$HC \equiv C-CH_3$	C_3H_4	methylacetylene or propyne
$HC \equiv C-CH_2\ CH_3$	C_4H_6	ethylacetylene or 1-butyne
$H_3C-C \equiv C-CH_3$	C_4H_6	dimethylacetylene or 2-butyne
$HC \equiv C-CH_2-CH_2-CH_3$	C_5H_8	propylacetylene or 1-pentyne
$H_3C-C \equiv C-CH_2-CH_3$	C_5H_8	methylethylacetylene or 2-pentyne

C_nH_{2n-2}		general formula for alkynes
C_nH_{2n+2}	Alkanes	functional group: C-C
C_nH_{2n}	Alkenes	functional group: C=C
C_nH_{2n-2}	Alkynes	functional group: C≡C

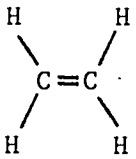
Example No. 2



sp^3 hybridization

$\alpha = 109.5°$

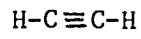
C atom possesses four equivalent SP^3 hybrid AO.'s



sp^2 hybridization

$\alpha = 120°$

each C atom possesses three equivalent SP^2 hybrid AO.'s and one P orbital



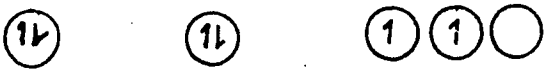
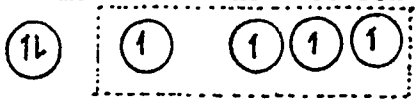
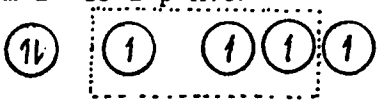
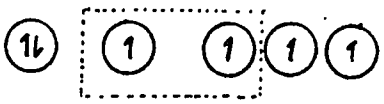
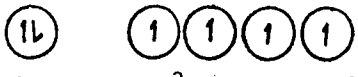
sp hybridization

α = _____

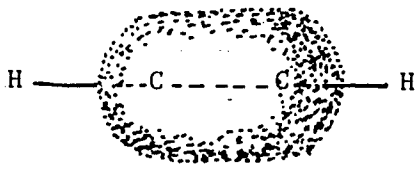
each C atom possesses two equivalent SP hybrid AO.'s and two P orbitals

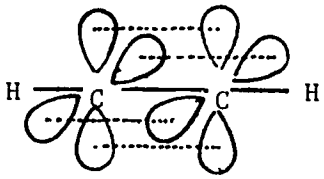
SIP No. 12
Tape 1 - Work Sheet

Example No. 3 - Hybridization in CH_4, C_2H_6 and C_2H_2

Methane CH_4	Ethylene C_2H_6	Acetylene C_2H_2
Ground state configuration of the carbon atom		
		
1s 2s 2p		
Promotion of one electron from 2s to 2 p A.O.		
		
1s 2s 2p	1s 2s 2p	1s 2s 2p
Mixing - hybridization of atomic orbitals		
		
1s Sp^3 hybrid AO's	1s Sp^2 hybrid AO's p AO	1s Sp hybrid AO's Py P_2 AO's

Example No. 4 - Structure and shape of acetylene





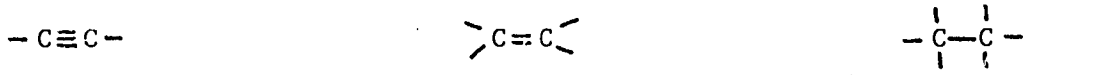
H-C σ bond in acetylene results from the overlap of s A.O. from H and sp hybrid AO from carbon

C-C σ bond in acetylene results from the overlap of sp hybrid AO. from one carbon and sp hybrid AO. from the other carbon

The two C-C π bonds in acetylene results from the overlap of the two p A.O.'s from one carbon and the two p A.O.'s from the other carbon

SIP No. 12
Tape 1 - Work Sheet

Example No. 5



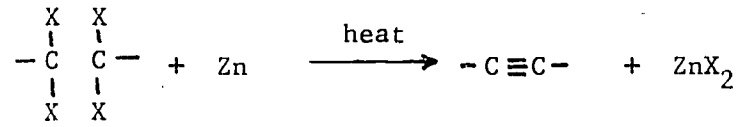
198 kcal/mole 163 kcal/mole 88 kcal/mole

Strength: C≡C > C=C > C—C

Length: C≡C < C=C < C—C

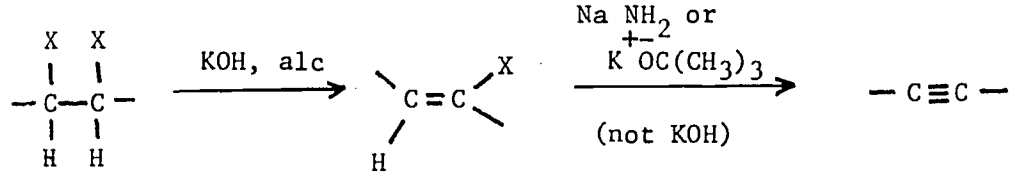
Example No. 6 - Preparations of alkynes

1. Dehalogenation



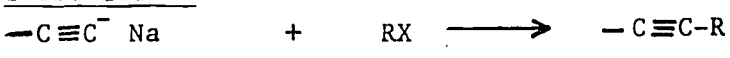
vicinal tetrahalide

2. Dehydrahalogenation



vicinal dihalide vinyl halide

3. Substitution



1° alkylhalide
or
2° alkylhalide
not
3° alkyhalide

SIP No. 12
Tape 1 - Work Sheet

Example No. 7 - Commercial preparations of acetylene

I. coal $\longrightarrow$ coke (c)

$$\text{limestone } (CaCO_3) \xrightarrow{\text{heat}} CaO$$

$$CaO + 3\,C \xrightarrow{2000°C} CaC_2 + CO$$

$$CaC_2 + 2H_2O \longrightarrow HC{\equiv}CH + Ca(OH)_2$$

calcium carbide

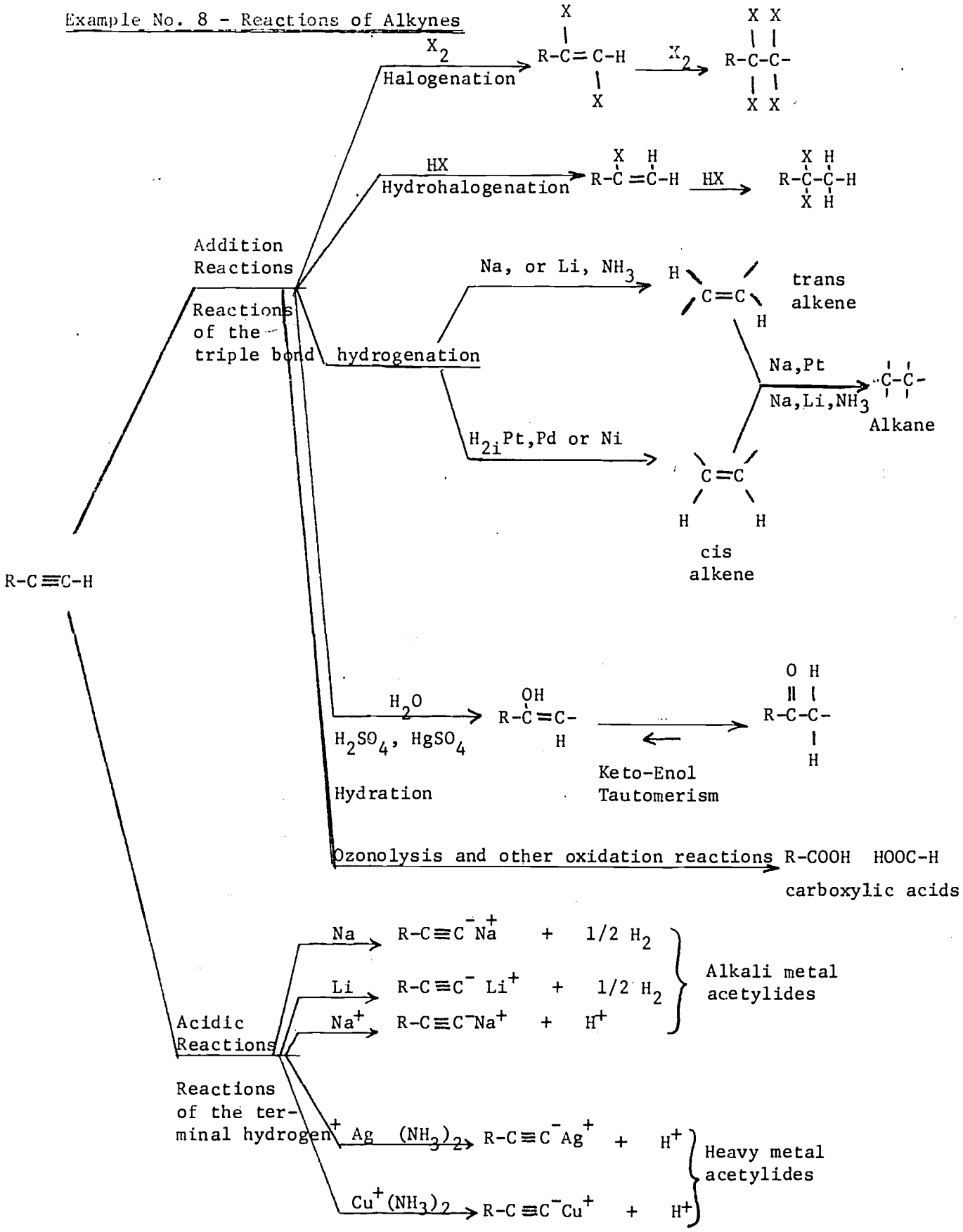
II. $$2CH_4 \underset{\text{very high temperature}}{\rightleftharpoons} C_2H_2 + 3H_2 - 95.5 \text{ kcal/mole}$$

$$Al_4C_3 + 12H_2O \longrightarrow 3\,CH_4 + 4\,Al(OH)_3)$$

Aluminum carbide

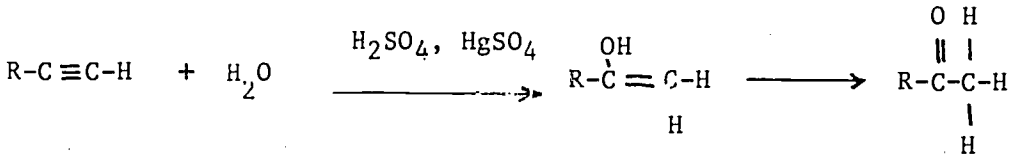
SIP No. 12
Tape 1 - Work Sheet

Example No. 8 - Reactions of Alkynes



SIP No. 12
Tape 1 - Work Sheet

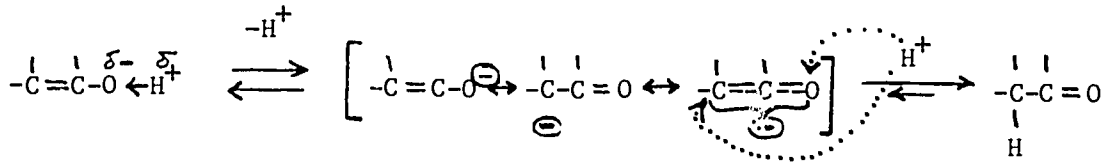
Example No. 9 - Hydration and Keto-Enol Tautomerism



Vinyl alcohol
or
Enol Form
(en=double bond)
(ol=OH group)

Keto-Form
(>C=O = carbonyl group)

Tautomers

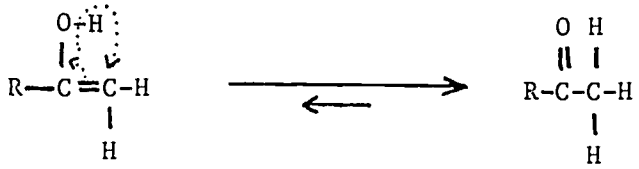


Enol form

Keto form

stronger acid (O-H bond in enol is weaker than the C-H bond in ketone) weaker acid

abbreviated:



Assignment No. 1

Assign the IUPAC names and the derived names to all the isomeric alkynes of formula C_6H_{10}. Draw their structure and the structures of the ozonolysis products expected from each alkyne.

SIP No. 12
Tape 1 - Work Sheet

Assignment No. 2

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

a) 2-pentyne $\xrightarrow{H_2, Ni}$

b) 2-pentyne $\xrightarrow{Na, NH_3}$

c) 3-methyl-1-butyne $\xrightarrow{H_2O,\ H_2SO_4,\ HgSO_4}$

d) 1-butyne $\xrightarrow{\text{excess HCl}}$

e) 2-pentyne $\xrightarrow{\text{excess } Br_2,\ CCl_4}$

f) 3-methyl-1-butyne $\xrightarrow{H_2, Pt}$

Assignment No. 3

This assignment requires careful thinking but it is by no means beyond your abilities. Outline all steps in the conversion of a mixture of trans-2-hexene and cis-2-hexene into essentially pure cis-2-hexene.

SIP No. 12
Tape 1 - Work Sheet

Assignment No. 4

Write all the steps and all the resonance structures involved in a reaction of propyne with water in presence of sulfuric acid and mercuric sulfate.

Example No. 10 - Reactions of terminal alkynes as acids

General Reactions of acids:

$$\text{HA} + \text{Me} \longrightarrow \underset{\text{Salt}}{\text{Me}^+ \text{A}^-} + 1/2\ \text{H}_2$$

or

$$\underset{\text{Acid}}{\text{HA}} + \text{Me}^+ \longrightarrow \text{Me}^+\text{A}^- + \text{H}^+$$

I. $\text{R-C}\equiv\text{C-H} + \underset{\text{Alkali metal}}{\text{Me}} \longrightarrow \underset{\text{Salt-metal acetylide}}{\text{R-C}\equiv\text{C}^- \text{Me}^+} + 1/2\ \text{H}_2$

Examples:

1) $\text{R-C}\equiv\text{C-H} + \text{Na} \longrightarrow \underset{\text{sodium acetylide}}{\text{R-C}\equiv\text{C}^- \text{Na}^+} + 1/2\ \text{H}_2$

2) $\text{R-C}\equiv\text{C-H} + \text{Li} \longrightarrow \text{R-C}\equiv\text{C}^- \text{Li}^+ + 1/2\ \text{H}_2$

3) $\text{R-C}\equiv\text{C-H} + \text{K} \longrightarrow \text{R-C}\equiv\text{C}^- \text{K}^+ + 1/2\ \text{H}_2$

II. $\text{R-C}\equiv\text{C-H} + \underset{\substack{\text{Alkali metal ions} \\ \text{or} \\ \text{heavy metal ions}}}{\text{Me}^+} \longrightarrow \text{R-C}\equiv\text{C}^- \text{Me}^+ + \text{H}^+$

4) $R\text{-}C{\equiv}C\text{-}H + Na^+ NH_2^- \xrightarrow{\text{ether}} R\text{-}C{\equiv}C^- Na^+ + H^+ (NH_3)$

(sodamide)

5) $R\text{-}C{\equiv}C\text{-}H + Cu(NH_3)_2^+ \longrightarrow R\text{-}C{\equiv}C\ Cu^+ + H^+$

6) $R\text{-}C{\equiv}C\text{-}H + Ag^+ \longrightarrow R\text{-}C{\equiv}C^- Ag^+ + H^+$

Example No. 11 - Relative acidities of different compounds

$H\text{-}A + Me^+ B^- \longrightarrow Me^+ A^- + HB$

stronger acid — weaker acid

A stronger acid has the ability to displace a weaker acid from salts.

Comparison of the relative acidity of $HC{\equiv}CH$, H_2O, C_2H_5OH and NH_3

IF acetylene is a stronger acid than H_2O, C_2H_5OH, and NH_3 the following reactions will take place.

1) $HC{\equiv}CH + NaOH \longrightarrow HC{\equiv}C^- Na^+ + HOH$

stronger acid — salt — salt — weaker acid

2) $HC{\equiv}CH + Na^+ \bar{O} C_2H_5 \longrightarrow HC{\equiv}C^- Na^+ + C_2H_5OH$

stronger acid — sodium ethoxide — sodiumacetylide — weaker acid

3) $HC{\equiv}CH + Na^+ NH_2 \longrightarrow HC{\equiv}C^- Na^+ + NH_3$

acetylene — sodamide — sodium acetylide — weaker acid

Example No. 11 (continued)

Reactions 1 and 2 do NOT take place indicating that acetylene is a weaker, stronger (circle one) acid than H_2O and C_2H_5OH.

Acidity:

$$H_2O \quad ? \quad C_2H_5OH \quad > \quad HC\equiv CH \quad > \quad NH_3$$

Example No. 12

$$H_2O + Na^+ \bar{O}C_2H_5 \longrightarrow NaOH + C_2H_5OH$$

Water is weaker, stronger (circle one) acid than alcohol.

Assignment No. 5

In the reactions below identify the stronger and the weaker acid.

a) $Ca^{++} C\equiv C^{--} + H_2O \longrightarrow Ca(OH)_2 + HC\equiv CH$

b) $C_6H_5OH + NaOH \longrightarrow C_6H_5O^- Na^+ + H_2O$

c) $Na^+\bar{C}\equiv CH + C_6H_5OH \longrightarrow HC\equiv CH + C_6H_5O^-Na^+$

Assignment No. 6

From the reactions below select the ones that will actually take place. Use the table in which compounds are written in the order of decreasing acidity.

CH_3COOH	acetic acid	max acidity ↑
ClC_6H_4OH	p-chloro phenol	
C_6H_5OH	phenol	
R-OH	alcohol	

Assignment No. 6 (continued)

H_2O	water	
$HC\equiv CH$	acetylene	
NH_3	ammonia	
RH	hydrocarbon	min. acidity

a) $CH_3COO^- K^+ + H_2O \longrightarrow CH_3COOH + KOH$

b) $C_2H_6 + CH_3CH_2C\equiv C\,Mg\,Br \longrightarrow C_2H_5\,Mg\,Br + CH_3CH_2C\equiv CH$

c) $H_2O + Na\,NH_2 \longrightarrow Na\,OH + NH_3$

d) $C_6H_5O^-Na^+ + CH_3COOH \longrightarrow C_6H_5OH + CH_3COO^-Na^+$

e) $HC\equiv CH + CH_3CH_2CH_2MgBr \longrightarrow HC\equiv C\,MgBr + CH_3CH_2CH_3$

f) $HC\equiv CH + Na^+\,\bar{O}CH_3 \longrightarrow CH_3\,OH + HC\equiv C^-Na^+$

Assignment No. 7

Complete the reactions below. Identify the major products and the byproducts.

1-pentyne $\xrightarrow{Cu(NH_3)_2\,Cl}$

2-hexyne $\xrightarrow{Ag(NH_3)_2NO_3}$

3-butyne $\xrightarrow{Li,\ NH_3}$

acetylene $\xrightarrow{Na^+\bar{N}H_2}$

Assignment No. 7 (continued)

1-propyne $\xrightarrow{Ag^{+}(NH_3)_2\ NO_3}$

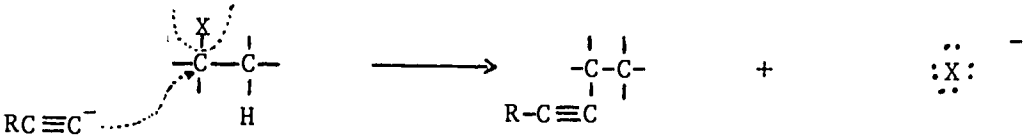
2-propyne $\xrightarrow{Na,\ NH_3}$

Example No. 13

$$RC{\equiv}CH \xrightarrow{Na} RC{\equiv}C^{-}Na^{+}$$

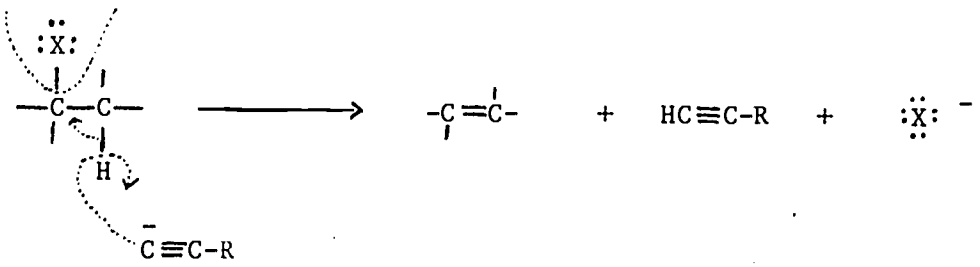
$$RC{\equiv}C^{-}Na^{+} + R^{1}X \longrightarrow RC{\equiv}CR^{1} + NaX$$

Nucleophilic substitution - Sn reaction - primary halide



acetylide anion substitutes the halide anion in the 1° RX. Attack is on C atom.

Elimination - tertiary halide



acetylide anion abstracts the hydrogen from a 3° RX. Attack is on H atom.

SIP No. 12
Tape 1 - Work Sheet

Assignment No. 8

Compare the reaction of sodium propyde with n-butyl bromide and tertiary butyl bromide. Name all the products and draw their structure.

Assignment No. 9

Identify all steps in a multi-step laboratory synthesis of the following compounds from acetylene.

a) 1-butyne

b) 2-methyl-3-hexyne

c) 2-pentyne

d) diisopropyl acetylene

e) trans-2-butene

Assignment No. 9 (continued)

f) 2,2-dichloro propane

g) acetone $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

Assignment No. 10

Identify the reagents in the following reactions:

a) acetylene ⟶ sodium acetylide ⟶ 5-methyl-1-hexyne

b) 2,3-dichloro pentane ⟶ 2-pentyne

c) 2,2,3,3-tetrachloro butane ⟶ 2-butyne

Assignment No. 11

Write all the steps in the multi-step laboratory synthesis of:

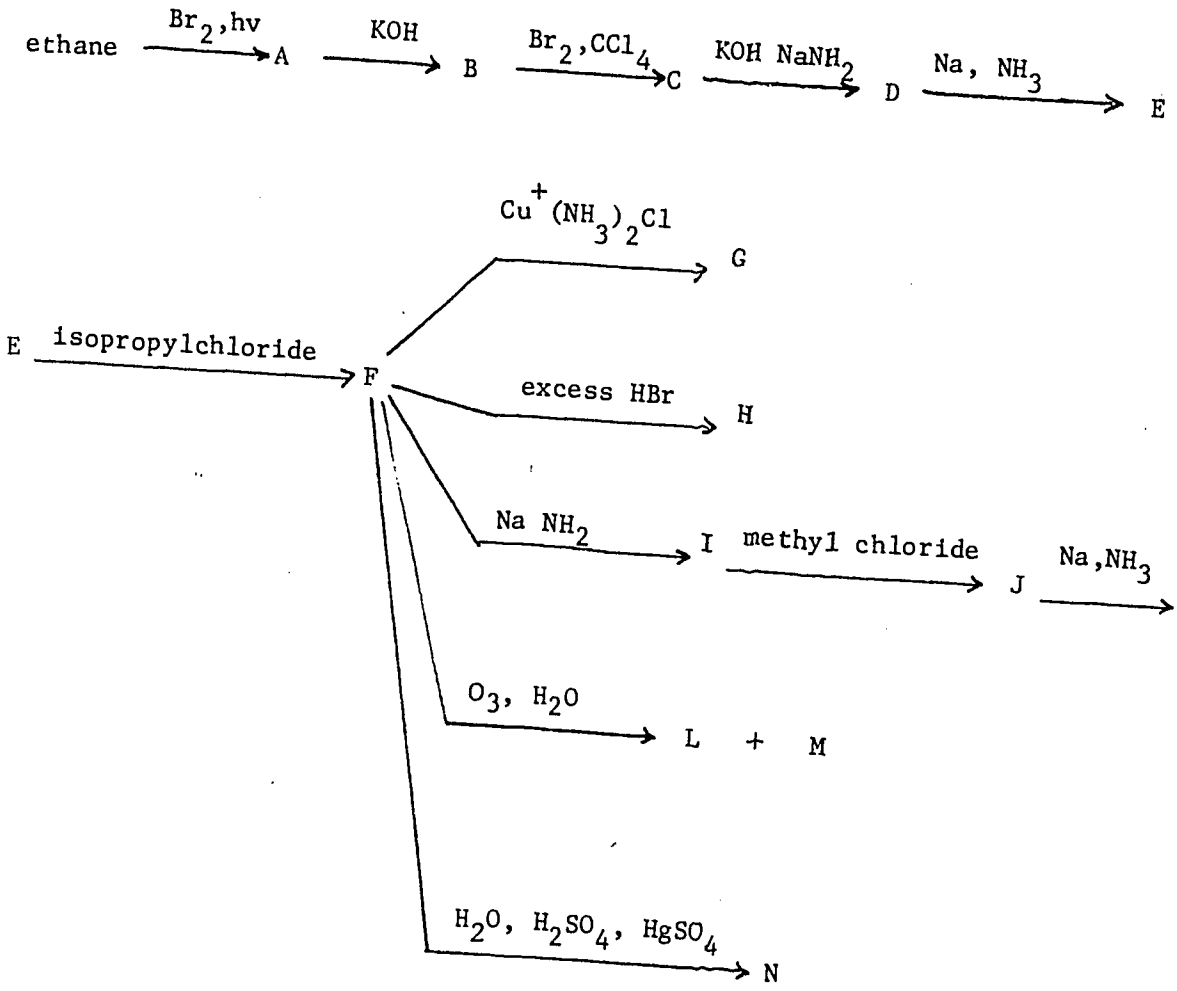
a) cis-2-pentene from ethane

b) $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$ (2-butanone) from propane

SIP No. 12
Tape 1 - Work Sheet

Assignment No. 12

Identify - draw the structures and name compounds A through N formed in the multi-step synthetic scheme below.



Self Instructional Package No. 12
Tape 1 - Answer Sheet

ALKYNES

Assignment No. 1

1. $CH{\equiv}C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 \xrightarrow{O_3,H_2O} HCOOH + CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}COOH$

   1-hexyne

2. $CH_3\text{-}C{\equiv}C\text{-}CH_2\text{-}CH_2\text{-}CH_3 \xrightarrow{O_3,H_2O} CH_3COOH + CH_3\text{-}CH_2\text{-}CH_2\text{-}COOH$

   2-hexyne

3. $CH_3\text{-}CH_2\text{-}C{\equiv}C\text{-}CH_2\text{-}CH_3 \xrightarrow{O_3,H_2O} 2\ CH_3\text{-}CH_2\text{-}COOH$

   3-hexyne

4. $CH_3\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}C{\equiv}C\text{-}CH_3 \xrightarrow{O_3,H_2O} CH_3\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}COOH + CH_3COOH$

   4-methyl-2-pentyne

5. $CH_3\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{--}CH_2\text{-}C{\equiv}CH \xrightarrow{O_3,H_2O} CH_3\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_2\text{-}COOH + HCOOH$

   4-methyl-1-pentyne

6. $CH{\equiv}C\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_2\text{-}CH_3 \xrightarrow{O_3,H_2O} HCOOH + CH_3\ CH_2\ CH(CH_3)COOH$

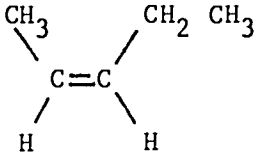
   3-methyl-1-pentyne

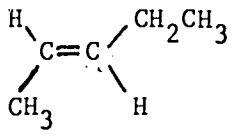
7. $CH_3\text{-}\underset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}\text{-}C{\equiv}CH \xrightarrow{O_3,H_2O} CH_3\ C(CH_3)_2COOH + HCOOH$

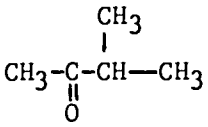
   3,3-dimethyl-1-butyne

SIP No. 12
Tape 1 - Answer Sheet

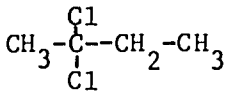
Assignment No. 2

a) 2-pentyne $\xrightarrow{H_2,\ Ni}$  cis-2-pentene

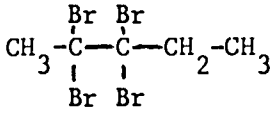
b) 2-pentyne $\xrightarrow{Na,NH_3}$  trans-2-pentene

c) 3-methyl-1-butyne $\xrightarrow{H_2O,\ H_2SO_4,\ HgSO_4}$ 

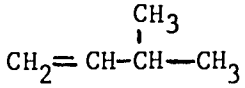
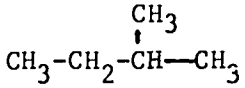
3-methyl-2-butanone

d) 1-butyne $\xrightarrow{\text{excess HCl}}$ 

2,2-dibromobutane

e) 2-pentyne $\xrightarrow{\text{excess Br , CCl}}$ 

2,2,3,3-tetrabromopentane

f) 3-methyl-1-butyne $\xrightarrow{H_2,\ Pt}$  $\xrightarrow{H_2,Pt}$ 

3-methyl-1-butene 3-methyl butane

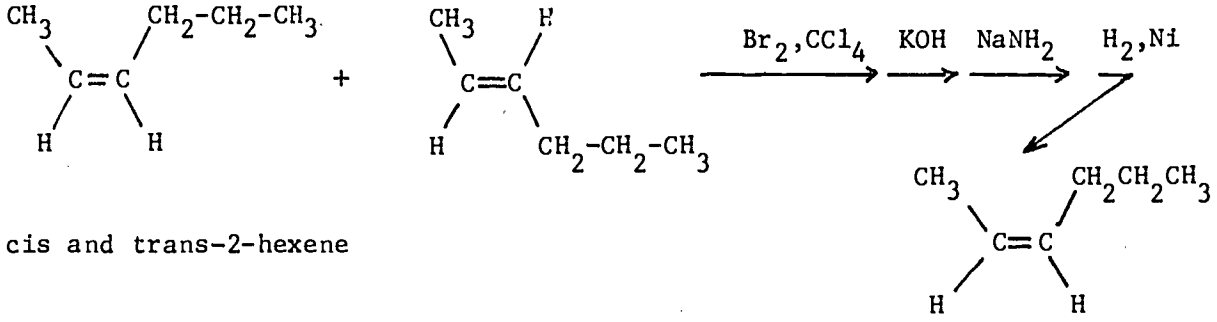
SIP No. 12
Tape 1 - Answer Sheet

Assignment No. 3

Step 1 - A mixture is brominated. An optically inactive mixture of 2,3-dibromo hexane is obtained.

Step 2 - Elimination with KOH and $NaNH_2$, 2-hexyne is produced.

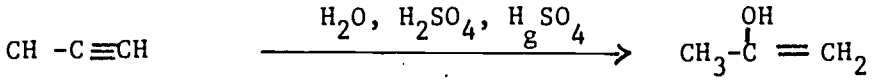
Step 3 - Reaction of 2-hexyne with hydrogen in presence of nickel (cis addition) yields cis-2-hexene.

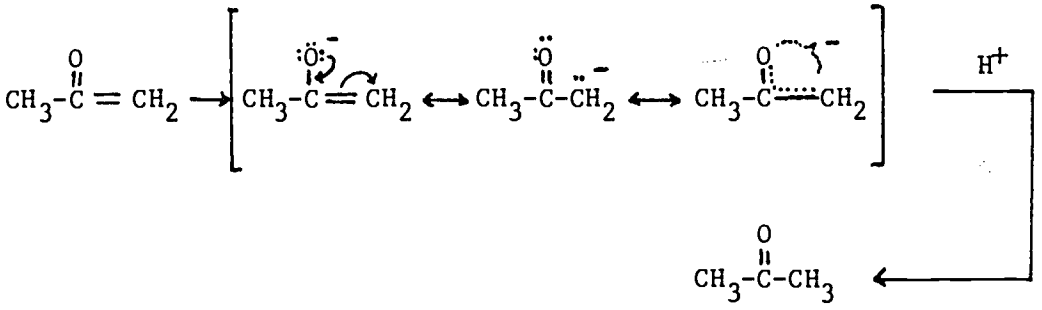


cis and trans-2-hexene

cis-2-hexene

Assignment No. 4





acetone

SIP No. 12
Tape 1 - Answer Sheet

Assignment No. 5

	stronger acid	weaker acid
a)	water	acetylene
b)	phenol, C_6H_5OH	water
c)	phenol, C_6H_5OH	acetylene

Assignment No. 6

Reactions that will actually take place are:

c, d, e. In these reactions a stronger acid displaces a weaker acid.

Assignment No. 7

1-pentyne $\xrightarrow{Cu(NH_3)_2Cl}$ $CH_3CH_2CH_2\ C{\equiv}C^-Cu^+ + NH_4^+ + Cl^-$
cuprous pentyde

2-hexyne $\xrightarrow{Ag(NH_3)_2NO_3}$ No Reaction

1-butyne $\xrightarrow{Li,\ NH_3}$ $Li^+\bar{C}{\equiv}C\ CH_2CH_3 + 1/2\ H_2\uparrow$
lithium butyde

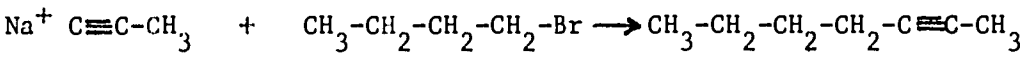
acetylene $\xrightarrow{Na^+\ \bar{N}H_2}$ $Na^+\ C{\equiv}CH + NH_3$
sodium acetylide

1-propyne $\xrightarrow{Ag^+(NH_3)_2\ NO_3}$ $Ag^+\ C{\equiv}CH\text{-}CH_3 + NH_4^+ + NO_3^-$
silver propyde

2-propyne $\xrightarrow{Na,NH_3}$ N. R.

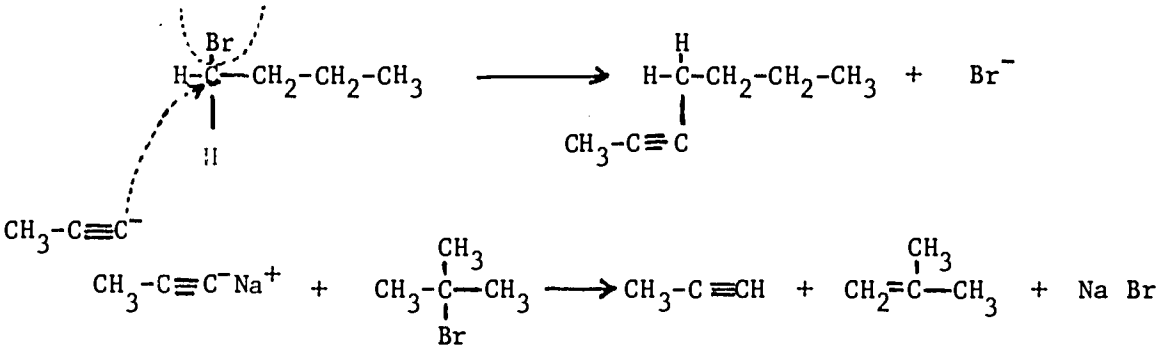
SIP No. 12
Tape 1 - Answer Sheet

Assignment No. 8

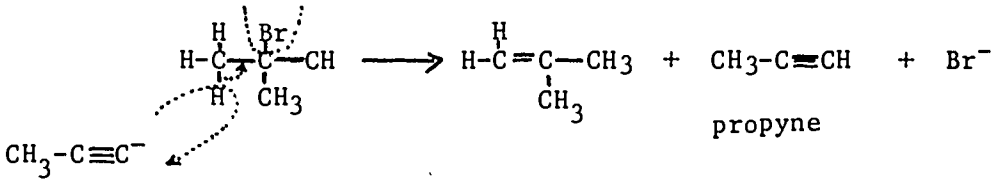


2-heptyne

Mechanism:



Possible Mechanism:



propyne

Assignment No. 9

a) $HC\equiv CH \xrightarrow{Na,\ NH_3} Na^+C\equiv C \xrightarrow{\text{ethylchloride}} CH_3-CH_2-C\equiv CH$

b) $HC\equiv CH \xrightarrow{Na,NH_3} Na^+C\equiv CH \xrightarrow{\text{isopropylchloride}} CH_3-\underset{CH_3}{CH}-C\equiv CH \xrightarrow{Na,NH_3} CH_3-\underset{CH_3}{CH}-C\equiv C^-Na^+$

$\xrightarrow{\text{ethylchloride}} CH_3-\underset{CH_3}{CH}-C\equiv C-CH_2-CH_3$

Assignment No. 9 (continued)

c) $HC\equiv CH \xrightarrow{Na,NH_3} Na^+\bar{C}\equiv CH \xrightarrow{CH_3Br} CH_3C\equiv CH \xrightarrow{Na,NH_3} CH_3C\equiv C^-Na^+$

$CH_3C\equiv C^-Na^+ \xrightarrow{C_2H_5Br} CH_3-C\equiv C-CH_2-CH_3$

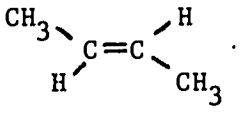
d) $HC\equiv CH \xrightarrow{Na,NH_3} \xrightarrow{\text{isopropylbromide}} \xrightarrow[Na,NH]{Na,NH_3} \xrightarrow{\text{isopropylbromide}}$

$CH_3-CH(CH_3)-C\equiv C-CH(CH_3)-CH_3$

OR:

$HC\equiv CH \xrightarrow{\text{excess } Na,NH_3} Na^+C\equiv C^-Na^+ \xrightarrow{\text{excess isopropylbromide}}$ (same product)

e) $HC\equiv CH \xrightarrow{Na,NH_3} \xrightarrow{CH_3\ Br} \xrightarrow{Na,NH_3} \xrightarrow{CH_3\ Br} CH_3-C\equiv C-CH_3$

$CH_3-C\equiv C-CH_3 \xrightarrow{Na,NH_3}$ 

f) $HC\equiv CH \xrightarrow{Na,NH_3} \xrightarrow{CH_3\ Cl} CH_3-C\equiv CH \xrightarrow{\text{excess HCl}} CH_3-\underset{Cl}{\overset{Cl}{C}}-CH_3$

g) $HC\equiv CH \xrightarrow{Na,NH_3} \xrightarrow{CH_3\ Br} CH_3-C\equiv CH \xrightarrow{H_2O,H_2SO_4,HgSO_4} CH_3-\underset{OH}{C}=CH_2$

$CH_3-\underset{OH}{C}=CH_2 \rightleftharpoons CH_3-\underset{O}{\overset{\|}{C}}-CH_3$

SIP No. 12
Tape 1 - Answer Sheet

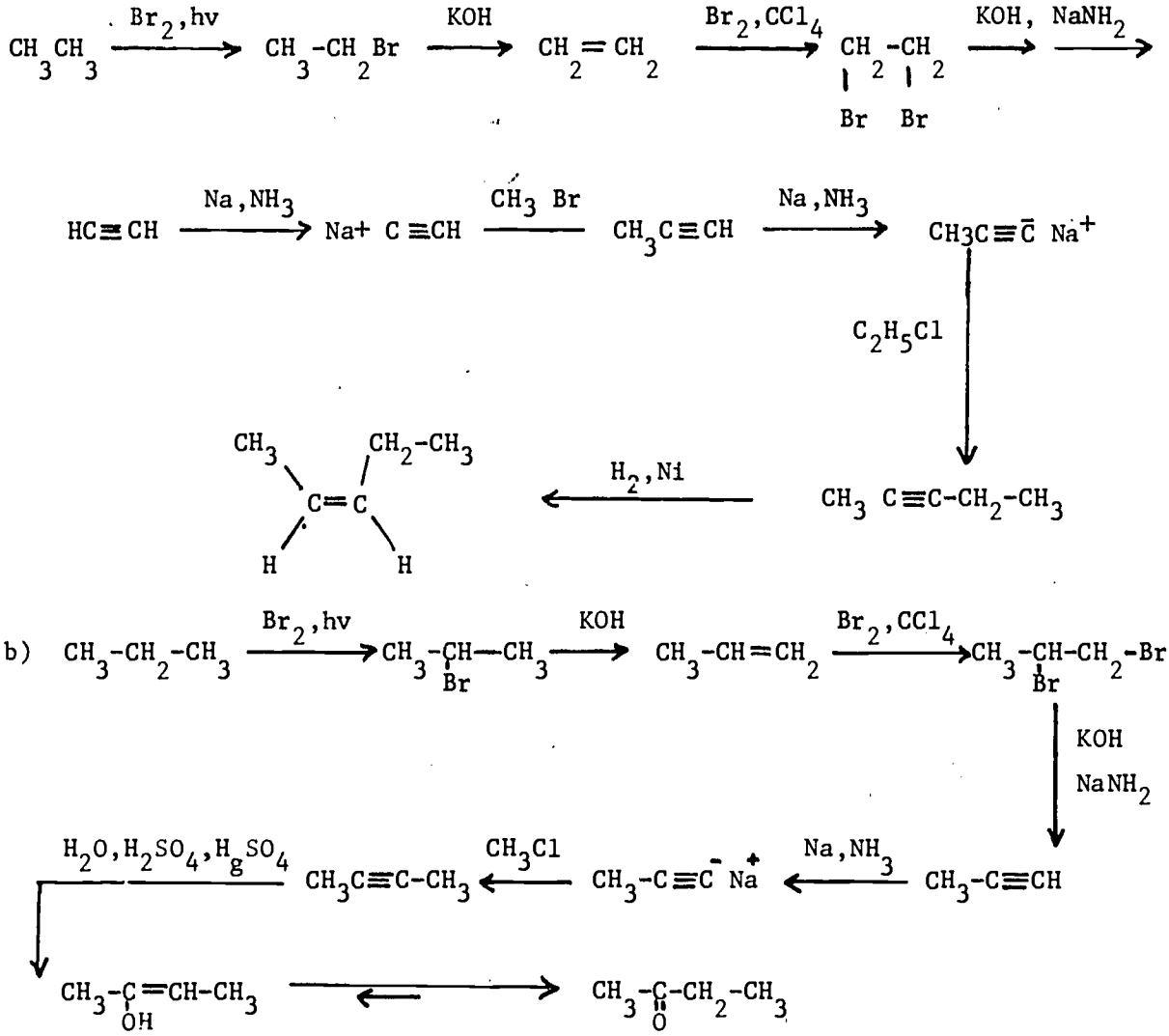
Assignment No. 10

a) acetylene $\xrightarrow{Na,NH_3}$ sodium acetylide $\xrightarrow{\text{1-chloro-3-methylbutane}}$ 5-methyl-1-hexyne

b) 2,3-dichloropentane $\xrightarrow{KOH,NaNH_2}$ 2-pentyne

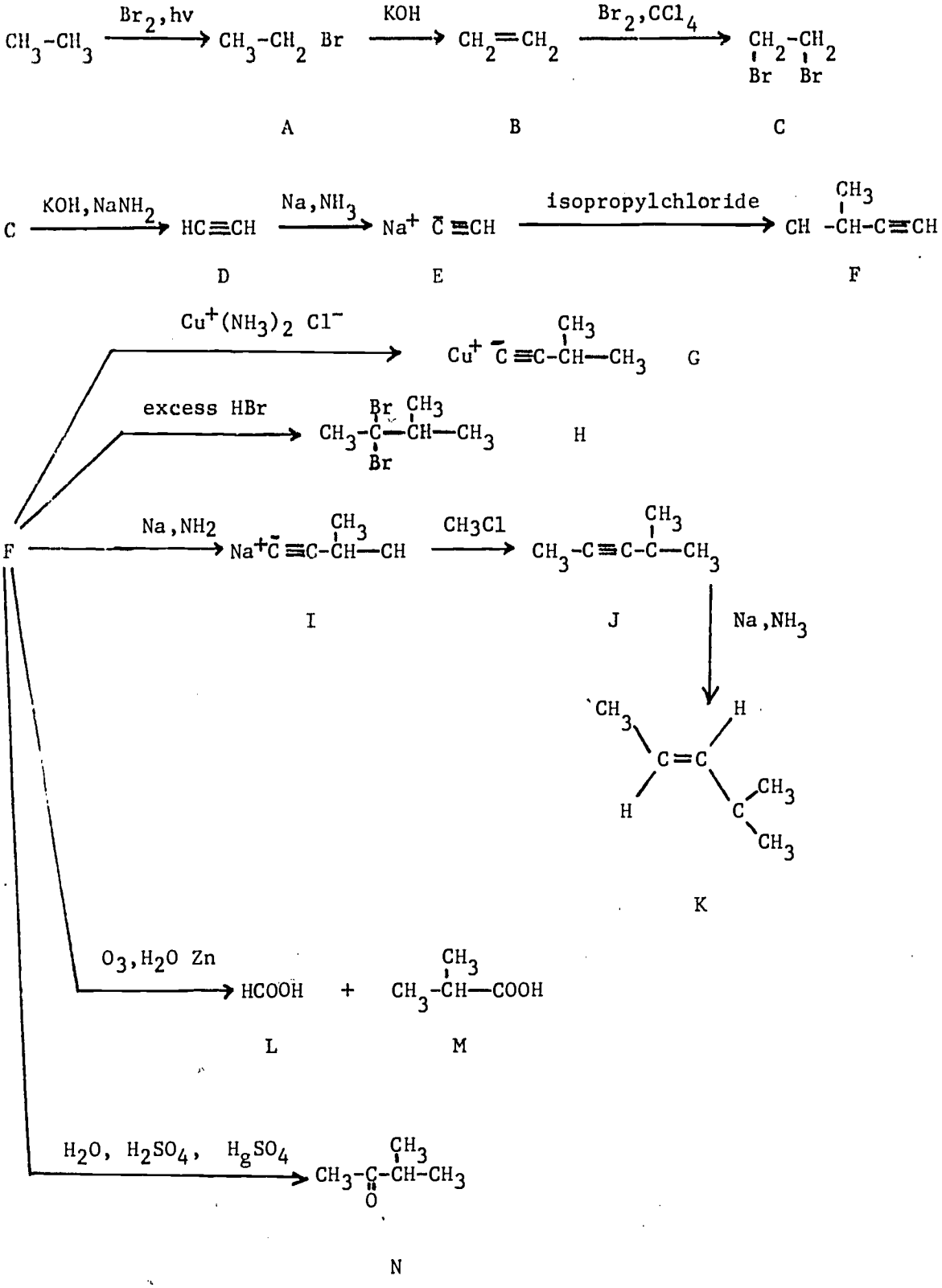
c) 2,2,3,3-tetrachlorobutane $\xrightarrow{Zn}$ 2-butyne

Assignment No. 11



SIP No. 12
Tape 1 - Answer Sheet

Assignment No. 12



SIP No. 12
Tape 1 - Answer Sheet

A - bromoethane

B - ethylene

C - 1,2-dibromoethane

D - acetylene

E - sodium acetylide

F - 3-methyl-1-butyne

G - cuproup salt of 3-methyl-1-butyne (cuprous alkyde)

H - 2,2-dibromo-3-methyl-butane

I - sodium alkyde

J - 4-methyl-2-pentyne

K - trans-4-methyl-2-pentyne

(L - formic acid)

(M - isobutanoic acid or α-methyl-propanoic acid)

(N - 3-methyl-2-butanone)

Self Instructional Package No. 12
Form D - Progress Check Evaluation

ALKYNES

Identify the statements below as true or false by placing a capital T or F in the space provided.

1. _____ Dissociation of the OH bond and the hydrogen shift is the essential part of the keto-enol tantomerism.

2. _____ Electrons of the C-H bond in acetylene are held more closely by the carbon nucleus than the electrons of the C-H bond in an alkane.

3. _____ Addition of water to an alkyne follows the Markovnikov rule.

4. _____ Addition of hydrogen is presence of paladium is a trans addition.

5. _____ Hydrogen in acetylene is more acidic than the hydrogen in ammonia.

6. _____ 2-pentyne has higher boiling point than 1-hexyne.

7. _____ Carbon-carbon bond in ethylene is stronger than the carbon-carbon bond in acetylene.

8. _____ The shape of the acetylene molecule is flat with angles of 120°.

9. _____ Reaction of a tertiary alkylhalide with sodium acetylide results in the elimination reaction.

10. _____ Calcium carbide is the major source for the commercial preparation of acetylene.

Circle the correct answer or answers in the questions below.

11. Identify the major product obtained in the following reaction:

$$\text{acetylene} \xrightarrow{Na,\ NH_3} \xrightarrow{\text{1-chloro-3-methyl butane}} \xrightarrow{Cu^+\ (NH_3)_2NO_3^-}$$

a) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-C\equiv C-NO_3$

11. b) $CH_3-CH_2-\underset{\displaystyle CH_3}{CH}-CH_2-C\equiv C\ Cu$

c) $CH_3-CH_2-\underset{\displaystyle CH_3}{CH}-CH_2-C\equiv C\ NO_3$

d) $CH_3-\underset{\displaystyle CH_3}{CH}-CH_2-CH_2-C\equiv C\ Cu$

12. The reagents that can be used to convert acetylene into 2-methylhexane are:

a) Na, NH_3; methylchloride; Na, NH_3; isopropyl bromide; H_2, Pt

b) Na, NH_3; 1-bromo-3-methyl butane; H_2, Ni

c) Na, NH_3; 1-bromo-2-methyl butane; H_2, Pd

d) Na, NH_3; methylbromide; Na, NH_3; isobutylbromide; Na, NH_3

13. Reagents required to produce cis 2-pentene from 2-pentyne are:

a) H_2, Pt

b) H_2, Ni

c) Na, NH_3

d) Li, NH_3

14. Reagents required to produce 1-propyne from 1,1,2,2-tetrachloropropane are:

a) KOH, $NaNH_2$

b) KOH, $(CH_3)_3\ CO^-K^+$

c) $NaNH_2$

d) Zn

15. When 5-methyl-2-hexyne is subjected to ozonolysis the following products are obtained:

a) $CH_3\ COOH$ $\quad CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2-COOH$

b) $CH_3-CH=O$ $\quad CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2-CH=O$

c) CH_3-COOH $\quad CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}H-COOH$

d) CH_3-CHO $\quad CH_3-CH_2-\underset{CH_3}{\underset{|}{C}}H-CHO$

16. Identify product B in the following reaction synthesis:

$$\text{acetylene} \xrightarrow{Na,\ NH_3} \xrightarrow{\text{isobutylbromide}} \xrightarrow{Na,\ NH_3} \xrightarrow{CH_3Br} \xrightarrow{Br_2, CCl_4} B$$

a) 2,2,3,3-tetrabromo-5-methyl hexane

b) 3,3-dibromo-5-methyl hexane

c) 1,1,1,3-tetrachloro-2,3-dibromo-2,5-dimethyl hexane

d) 1,1,1,3-tetrachloro-2,5-dimethyl hexane

17. The compound obtained in the reaction of 1-butyne with water in acidic medium and in presence of H_gSO_4 is:

a) $CH_3-\overset{OH}{\overset{|}{C}}H-CH_2-CH_3$

b) $CH_2 = \overset{OH}{\overset{|}{C}}H-CH_2-CH_3$

c) $\underset{\underset{O}{\|}}{CH}-CH_2-CH_2-CH_3$

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

18. The major products in the reaction of 1-propyne with isopropylmagnesiumbromide (Grignard compound) are:

a) $CH_3-\overset{CH_3}{\overset{|}{C}}H-C\equiv C-CH_2-CH_3$

b) $CH_3CH_2CH_3$

c) $CH_3-C\equiv C^-\overset{+}{M}gBr$

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

19. The major product or products in the reaction of sodium propyde with 2-chlorobutane is:

a) 4-methyl-2-hexyne

b) propyne

c) 1-butene

d) 2-butene

20. The correct statements about the reaction below are:

$$CH_3\bar{O}Na^+ + C_6H_5OH \longrightarrow C_6H_5O^-Na^+ + CH_3OH$$

a) methanol CH_3OH is stronger acid than phenol C_6H_5OH

b) phenol donates hydrogen to sodium methoxide $CH_3O^-Na^+$

c) phenol is stronger acid than methanol

d) methanol displaces phenol from the salt

21. Identify the reactions that will take place:

a) $CH_3OH + NaOH \longrightarrow CH_3O^-Na^+ + H_2O$

b) $CH_3OH + HC\equiv C^-Na^+ \longrightarrow CH_3O^-Na^+ + HC\equiv CH$

21. c) $NaNH_2 + H_2O \longrightarrow NH_3 + NaOH$

d) $NaOH + HC \equiv CH \longrightarrow H_2O + Na^{+}\bar{C} \equiv CH$

Self Instructional Package No. 12
Form B^1 - Answer Sheet

ALKYNES

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

Self Instructional Package No. 12
Form D1 - Answer Sheet

ALKYNES

1.	T	11.	d	21.	b, c
2.	T	12.	b, d		
3.	T	13.	a, b		
4.	F	14.	d		
5.	T	15.	a		
6.	F	16.	a		
7.	F	17.	d		
8.	F	18.	b, c		
9.	T	19.	b, d		
10.	T	20.	b, c		