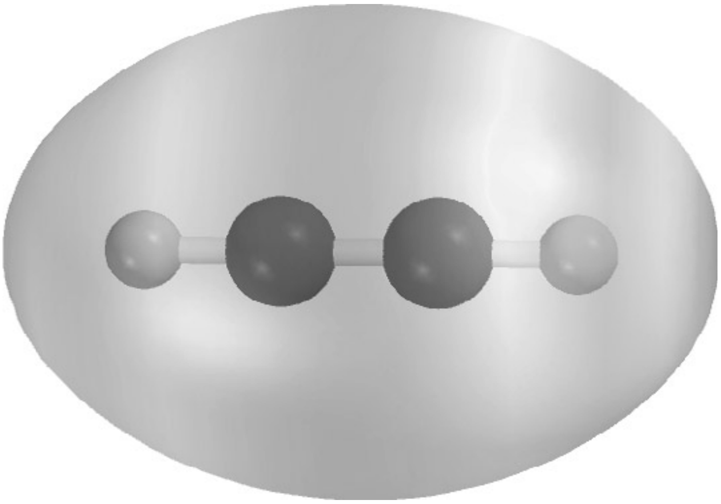
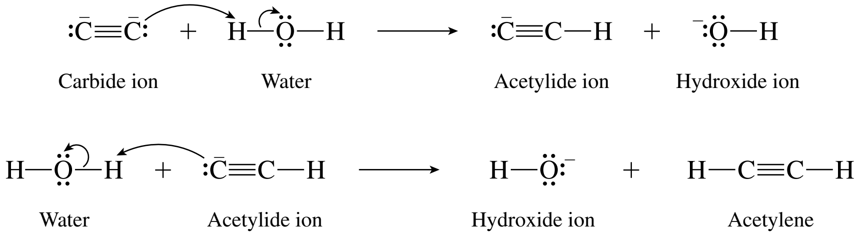


CHAPTER 9

ALKYNES

SOLUTIONS TO TEXT PROBLEMS

9.1 The reaction is an acid–base process; water is the proton donor. Two separate proton-transfer steps are involved.

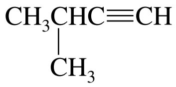


9.2 A triple bond may connect C-1 and C-2 or C-2 and C-3 in an unbranched chain of five carbons.

$CH_3CH_2CH_2C{\equiv}CH$ 1-Pentyne

$CH_3CH_2C{\equiv}CCH_3$ 2-Pentyne

One of the C_5H_8 isomers has a branched carbon chain.



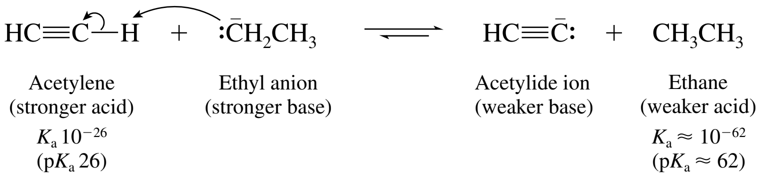
$$\underset{\displaystyle CH_3}{CH_3\underset{|}{C}HC{\equiv}CH}$$

3-Methyl-1-butyne

9.3 The bonds become shorter and stronger in the series as the electronegativity increases.

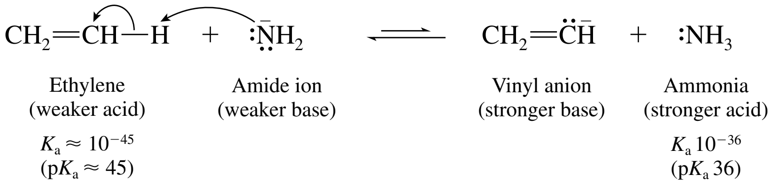
	NH_3	H_2O	HF
Electronegativity:	N (3.0)	O (3.5)	F (4.0)
Bond distance (pm):	N—H (101)	O—H (95)	F—H (92)
Bond dissociation energy (kJ/mol):	N—H (435)	O—H (497)	F—H (568)
Bond dissociation energy (kcal/mol):	N—H (104)	O—H (119)	F—H (136)

9.4 (*b*) A proton is transferred from acetylene to ethyl anion.

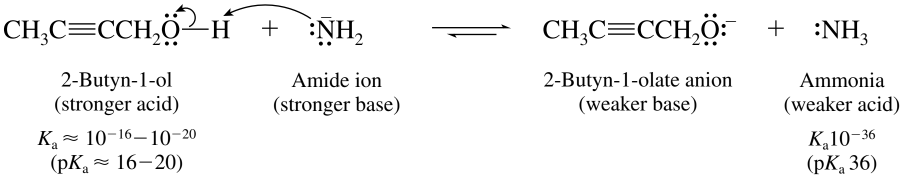


The position of equilibrium lies to the right. Ethyl anion is a very powerful base and deprotonates acetylene quantitatively.

(*c*) Amide ion is not a strong enough base to remove a proton from ethylene. The equilibrium lies to the left.



(*d*) Alcohols are stronger acids than ammonia; the position of equilibrium lies to the right.



9.5 (*b*) The desired alkyne has a methyl group and a butyl group attached to a —C≡C— unit. Two alkylations of acetylene are therefore required: one with a methyl halide, the other with a butyl halide.

$$HC\equiv CH \xrightarrow[2.\ CH_3Br]{1.\ NaNH_2,\ NH_3} CH_3C\equiv CH \xrightarrow[2.\ CH_3CH_2CH_2CH_2Br]{1.\ NaNH_2,\ NH_3} CH_3C\equiv CCH_2CH_2CH_2CH_3$$

Acetylene Propyne 2-Heptyne

It does not matter whether the methyl group or the butyl group is introduced first; the order of steps shown in this synthetic scheme may be inverted.

(*c*) An ethyl group and a propyl group need to be introduced as substituents on a —C≡C— unit. As in part (*b*), it does not matter which of the two is introduced first.

$$HC\equiv CH \xrightarrow[2.\ CH_3CH_2CH_2Br]{1.\ NaNH_2,\ NH_3} CH_3CH_2CH_2C\equiv CH \xrightarrow[2.\ CH_3CH_2Br]{1.\ NaNH_2,\ NH_3} CH_3CH_2CH_2C\equiv CCH_2CH_3$$

Acetylene 1-Pentyne 3-Heptyne

9.6 Both 1-pentyne and 2-pentyne can be prepared by alkylating acetylene. All the alkylation steps involve nucleophilic substitution of a methyl or primary alkyl halide.

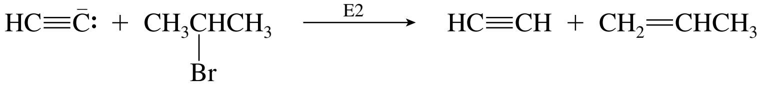
$$HC{\equiv}CH \xrightarrow[\text{2. } CH_3CH_2CH_2Br]{\text{1. } NaNH_2,\ NH_3} CH_3CH_2CH_2C{\equiv}CH$$

Acetylene 1-Pentyne

$$HC{\equiv}CH \xrightarrow[\text{2. } CH_3CH_2Br]{\text{1. } NaNH_2,\ NH_3} CH_3CH_2C{\equiv}CH \xrightarrow[\text{2. } CH_3Br]{\text{1. } NaNH_2,\ NH_3} CH_3CH_2C{\equiv}CCH_3$$

Acetylene 1-Butyne 2-Pentyne

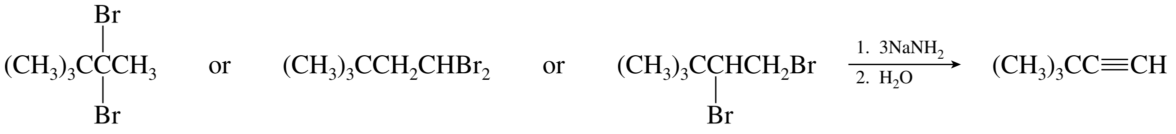
A third isomer, 3-methyl-1-butyne, cannot be prepared by alkylation of acetylene, because it requires a secondary alkyl halide as the alkylating agent. The reaction that takes place is elimination, not substitution.



$$HC{\equiv}\bar{C}{:} + CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \xrightarrow{E2} HC{\equiv}CH + CH_2{=}CHCH_3$$

Acetylide ion Isopropyl bromide Acetylene Propene

9.7 Each of the dibromides shown yields 3,3-dimethyl-1-butyne when subjected to double dehydrohalogenation with strong base.



$$(CH_3)_3C\overset{\displaystyle Br}{\underset{\displaystyle Br}{C}}CH_3 \text{ or } (CH_3)_3CCH_2CHBr_2 \text{ or } (CH_3)_3C\underset{\displaystyle Br}{C}HCH_2Br \xrightarrow[\text{2. } H_2O]{\text{1. } 3NaNH_2} (CH_3)_3CC{\equiv}CH$$

2,2-Dibromo-3,3-dimethylbutane 1,1-Dibromo-3,3-dimethylbutane 1,2-Dibromo-3,3-dimethylbutane 3,3-Dimethyl-1-butyne

9.8 (*b*) The first task is to convert 1-propanol to propene:

$$CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{H_2SO_4} CH_3CH{=}CH_2$$

1-Propanol Propene

After propene is available, it is converted to 1,2-dibromopropane and then to propyne as described in the sample solution for part (*a*).

(*c*) Treat isopropyl bromide with a base to effect dehydrohalogenation.

$$(CH_3)_2CHBr \xrightarrow{NaOCH_2CH_3} CH_3CH{=}CH_2$$

Isopropyl bromide Propene

Next, convert propene to propyne as in parts (*a*) and (*b*).

(*d*) The starting material contains only two carbon atoms, and so an alkylation step is needed at some point. Propyne arises by alkylation of acetylene, and so the last step in the synthesis is

$$HC{\equiv}CH \xrightarrow[\text{2. } CH_3Br]{\text{1. } NaNH_2,\ NH_3} CH_3C{\equiv}CH$$

Acetylene Propyne

The designated starting material, 1,1-dichloroethane, is a geminal dihalide and can be used to prepare acetylene by a double dehydrohalogenation.

$$CH_3CHCl_2 \xrightarrow[\text{2. } H_2O]{\text{1. } NaNH_2,\ NH_3} HC{\equiv}CH$$

1,1-Dichloroethane Acetylene

(*e*) The first task is to convert ethyl alcohol to acetylene. Once acetylene is prepared it can be alkylated with a methyl halide.

$$CH_3CH_2OH \xrightarrow[\text{heat}]{H_2SO_4} H_2C{=}CH_2 \xrightarrow{Br_2} BrCH_2CH_2Br \xrightarrow[2.\ H_2O]{1.\ NaNH_2,\ NH_3} HC{\equiv}CH \xrightarrow[2.\ CH_3Br]{1.\ NaNH_2,\ NH_3} CH_3C{\equiv}CH$$

Ethyl alcohol — Ethylene — 1,2-Dibromoethane — Acetylene — Propyne

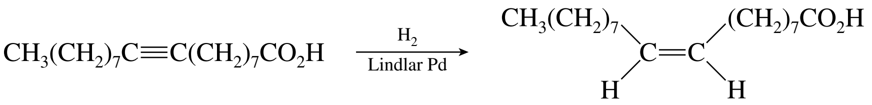
9.9 The first task is to assemble a carbon chain containing eight carbons. Acetylene has two carbon atoms and can be alkylated via its sodium salt to 1-octyne. Hydrogenation over platinum converts 1-octyne to octane.

$$HC{\equiv}CH \xrightarrow[NH_3]{NaNH_2} HC{\equiv}CNa \xrightarrow{BrCH_2(CH_2)_4CH_3} HC{\equiv}CCH_2(CH_2)_4CH_3 \xrightarrow[Pt]{H_2} CH_3CH_2CH_2(CH_2)_4CH_3$$

Acetylene — Sodium acetylide — 1-Octyne — Octane

Alternatively, two successive alkylations of acetylene with $CH_3CH_2CH_2Br$ could be carried out to give 4-octyne ($CH_3CH_2CH_2C{\equiv}CCH_2CH_2CH_3$), which could then be hydrogenated to octane.

9.10 Hydrogenation over Lindlar palladium converts an alkyne to a cis alkene. Oleic acid therefore has the structure indicated in the following equation:



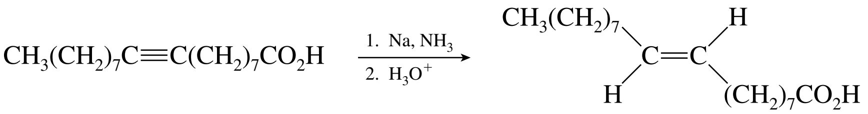
Stearolic acid — Oleic acid

Hydrogenation of alkynes over platinum leads to alkanes.

$$CH_3(CH_2)_7C{\equiv}C(CH_2)_7CO_2H \xrightarrow[Pt]{2H_2} CH_3(CH_2)_{16}CO_2H$$

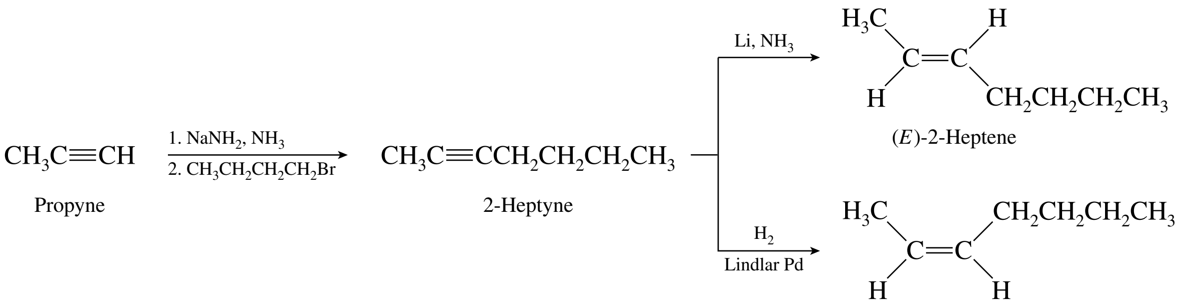
Stearolic acid — Stearic acid

9.11 Alkynes are converted to trans alkenes on reduction with sodium in liquid ammonia.



Stearolic acid — Elaidic acid

9.12 The proper double-bond stereochemistry may be achieved by using 2-heptyne as a reactant in the final step. Lithium–ammonia reduction of 2-heptyne gives the trans alkene; hydrogenation over Lindlar palladium gives the cis isomer. The first task is therefore the alkylation of propyne to 2-heptyne.



Propyne

2-Heptyne

(*E*)-2-Heptene

(*Z*)-2-Heptene

9.13 (*b*) Addition of hydrogen chloride to vinyl chloride gives the geminal dichloride 1,1-dichloroethane.

$$H_2C{=}CHCl \xrightarrow{HCl} CH_3CHCl_2$$

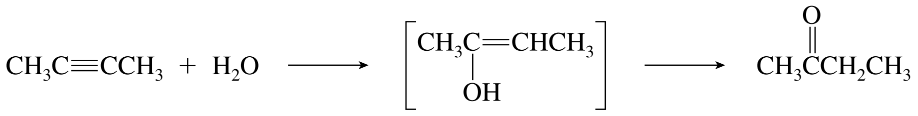
Vinyl chloride 1,1-Dichloroethane

(*c*) Since 1,1-dichloroethane can be prepared by adding 2 mol of hydrogen chloride to acetylene as shown in the sample solution to part (*a*), first convert 1,1-dibromoethane to acetylene by dehydrohalogenation.

$$CH_3CHBr_2 \xrightarrow[2.\ H_2O]{1.\ NaNH_2,\ NH_3} HC{\equiv}CH \xrightarrow{2HCl} CH_3CHCl_2$$

1,1-Dibromoethane Acetylene 1,1-Dichloroethane

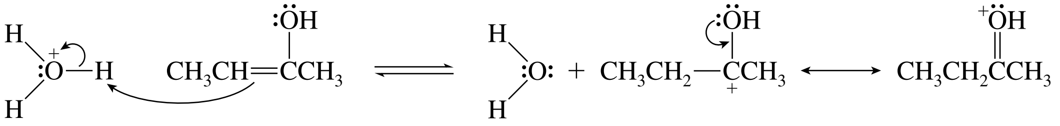
9.14 The enol arises by addition of water to the triple bond.



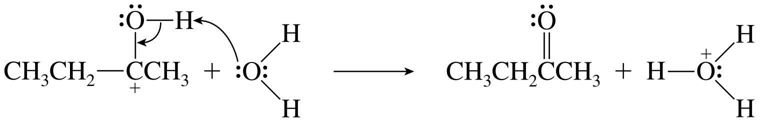
$$CH_3C{\equiv}CCH_3 + H_2O \longrightarrow \left[\begin{array}{c} CH_3\underset{\displaystyle OH}{\underset{|}{C}}{=}CHCH_3 \end{array}\right] \longrightarrow CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_3$$

2-Butyne 2-Buten-2-ol (enol form) 2-Butanone

The mechanism described in the textbook Figure 9.6 is adapted to the case of 2-butyne hydration as shown:



Hydronium ion 2-Buten-2-ol Water Carbocation

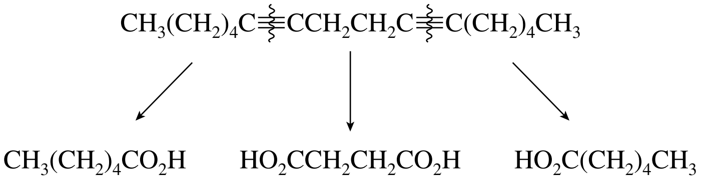


Carbocation Water 2-Butanone Hydronium ion

9.15 Hydration of 1-octyne gives 2-octanone according to the equation that immediately precedes this problem in the text. Prepare 1-octyne as described in the solution to Problem 9.9, and then carry out its hydration in the presence of mercury(II) sulfate and sulfuric acid.

Hydration of 4-octyne gives 4-octanone. Prepare 4-octyne as described in the solution to Problem 9.9.

9.16 Each of the carbons that are part of —CO_2H groups was once part of a —C≡C— unit. The two fragments $CH_3(CH_2)_4CO_2H$ and $HO_2CCH_2CH_2CO_2H$ account for only 10 of the original 16 carbons. The full complement of carbons can be accommodated by assuming that two molecules of $CH_3(CH_2)_4CO_2H$ are formed, along with one molecule of $HO_2CCH_2CH_2CO_2H$. The starting alkyne is therefore deduced from the ozonolysis data to be as shown:



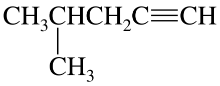
9.17 Three isomers have unbranched carbon chains:

$CH_3CH_2CH_2CH_2C\equiv CH$ 1-Hexyne

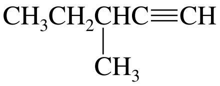
$CH_3CH_2CH_2C\equiv CCH_3$ 2-Hexyne

$CH_3CH_2C\equiv CCH_2CH_3$ 3-Hexyne

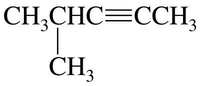
Next consider all the alkynes with a single methyl branch:


$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2C\equiv CH$

4-Methyl-1-pentyne

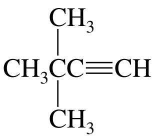

$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HC\equiv CH$

3-Methyl-1-pentyne


$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HC\equiv CCH_3$

4-Methyl-2-pentyne

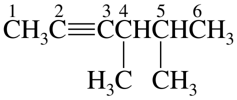
One isomer has two methyl branches. None is possible with an ethyl branch.

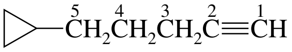

$CH_3\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}C\equiv CH$

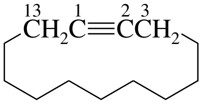
3,3-Dimethyl-1-butyne

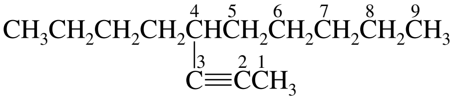
9.18 (*a*) $\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}\equiv\overset{1}{C}H$ is 1-pentyne

(*b*) $\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}\equiv\overset{2}{C}\overset{1}{C}H_3$ is 2-pentyne

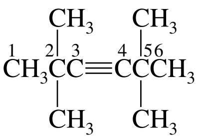
(*c*) 
$\overset{1}{C}H_3\overset{2}{C}\equiv\overset{3}{C}\underset{\displaystyle H_3C}{\underset{|}{\overset{4}{C}}}H\underset{\displaystyle CH_3}{\underset{|}{\overset{5}{C}}}H\overset{6}{C}H_3$ is 4,5-dimethyl-2-hexyne

(*d*)  is 5-cyclopropyl-1-pentyne

(*e*)  is cyclotridecyne

(*f*) 
$CH_3CH_2CH_2CH_2\underset{\displaystyle \overset{3}{C}\equiv\overset{2}{C}\overset{1}{C}H_3}{\underset{|}{\overset{4}{C}}}H\overset{5}{C}H_2\overset{6}{C}H_2\overset{7}{C}H_2\overset{8}{C}H_2\overset{9}{C}H_3$ is 4-butyl-2-nonyne

(Parent chain must contain the triple bond.)

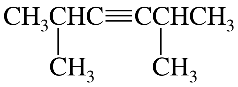
(*g*) 
$\overset{1}{C}H_3\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{\overset{2}{C}}}}}\overset{3}{C}\equiv\overset{4}{C}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{\overset{5}{C}}}}}\overset{6}{C}H_3$ is 2,2,5,5-tetramethyl-3-hexyne

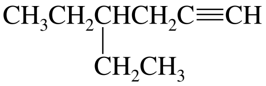
9.19 (*a*) 1-Octyne is $HC\equiv CCH_2CH_2CH_2CH_2CH_2CH_3$

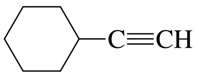
(*b*) 2-Octyne is $CH_3C\equiv CCH_2CH_2CH_2CH_2CH_3$

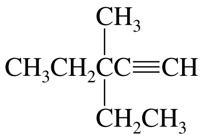
(*c*) 3-Octyne is $CH_3CH_2C\equiv CCH_2CH_2CH_2CH_3$

(*d*) 4-Octyne is $CH_3CH_2CH_2C\equiv CCH_2CH_2CH_3$

(*e*) 2,5-Dimethyl-3-hexyne is 
$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HC\equiv C\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$

(*f*) 4-Ethyl-1-hexyne is 
$CH_3CH_2\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}HCH_2C\equiv CH$

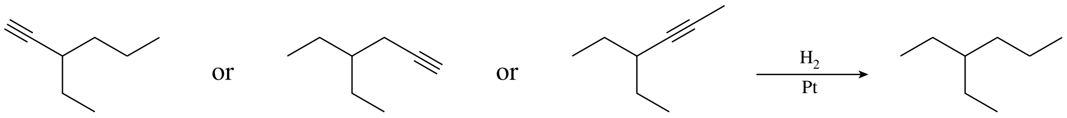
(*g*) Ethynylcyclohexane is 

(*h*) 3-Ethyl-3-methyl-1-pentyne is 

$$CH_3CH_2\overset{CH_3}{\underset{CH_2CH_3}{C}}C\equiv CH$$

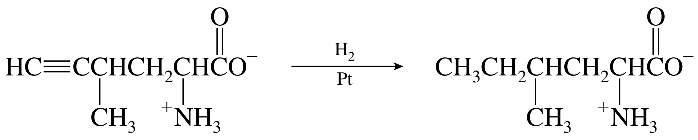
9.20 Ethynylcyclohexane has the molecular formula C_8H_{12}. All the other compounds are C_8H_{14}.

9.21 Only alkynes with the carbon skeletons shown can give 3-ethylhexane on catalytic hydrogenation.



3-Ethyl-1-hexyne 4-Ethyl-1-hexyne 4-Ethyl-2-hexyne 3-Ethylhexane

9.22 The carbon skeleton of the unknown acetylenic amino acid must be the same as that of homoleucine. The structure of homoleucine is such that there is only one possible location for a carbon–carbon triple bond in an acetylenic precursor.



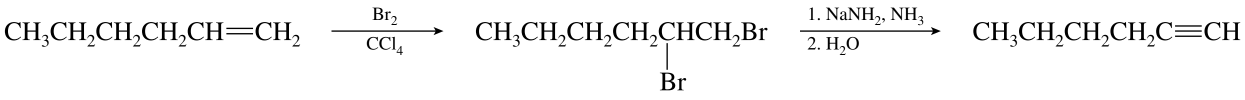
$$HC\equiv C\underset{CH_3}{C}HCH_2\underset{^+NH_3}{C}H\overset{O}{\overset{\|}{C}}O^- \xrightarrow[Pt]{H_2} CH_3CH_2\underset{CH_3}{C}HCH_2\underset{^+NH_3}{C}H\overset{O}{\overset{\|}{C}}O^-$$

$C_7H_{11}NO_2$ Homoleucine

9.23 (*a*) $CH_3CH_2CH_2CH_2CH_2CHCl_2 \xrightarrow[2.\ H_2O]{1.\ NaNH_2,\ NH_3} CH_3CH_2CH_2CH_2C\equiv CH$

1,1-Dichlorohexane 1-Hexyne

(*b*)



$$CH_3CH_2CH_2CH_2CH{=}CH_2 \xrightarrow[CCl_4]{Br_2} CH_3CH_2CH_2CH_2\underset{Br}{C}HCH_2Br \xrightarrow[2.\ H_2O]{1.\ NaNH_2,\ NH_3} CH_3CH_2CH_2CH_2C\equiv CH$$

1-Hexene 1,2-Dibromohexane 1-Hexyne

(*c*) $HC\equiv CH \xrightarrow[NH_3]{NaNH_2} HC\equiv C^-Na^+ \xrightarrow{CH_3CH_2CH_2CH_2Br} CH_3CH_2CH_2CH_2C\equiv CH$

Acetylene 1-Hexyne

(*d*) $CH_3CH_2CH_2CH_2CH_2CH_2I \xrightarrow[DMSO]{KOC(CH_3)_3} CH_3CH_2CH_2CH_2CH{=}CH_2$

1-Iodohexane 1-Hexene

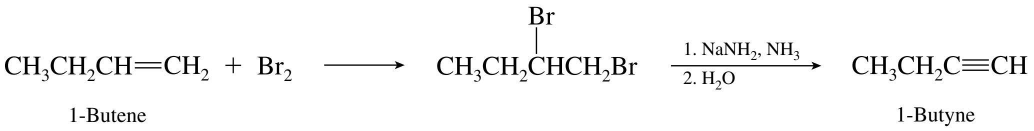
1-Hexene is then converted to 1-hexyne as in part (*b*).

9.24 (*a*) Working backward from the final product, it can be seen that preparation of 1-butyne will allow the desired carbon skeleton to be constructed.

$CH_3CH_2C\equiv CCH_2CH_3$ prepared from $CH_2CH_2C\equiv C{:}^- + BrCH_2CH_3$

3-Hexyne

The desired intermediate, 1-butyne, is available by halogenation followed by dehydrohalogenation of 1-butene.



$$CH_3CH_2CH{=}CH_2 + Br_2 \longrightarrow CH_3CH_2\overset{Br}{\overset{|}{C}}HCH_2Br \xrightarrow[2.\ H_2O]{1.\ NaNH_2,\ NH_3} CH_3CH_2C{\equiv}CH$$

1-Butene 1-Butyne

Reaction of the anion of 1-butyne with ethyl bromide completes the synthesis.

$$CH_3CH_2C{\equiv}CH \xrightarrow[NH_3]{NaNH_2} CH_3CH_2C{\equiv}C\!:^- \ Na^+ \xrightarrow{CH_3CH_2Br} CH_3CH_2C{\equiv}CCH_2CH_3$$

1-Butyne 3-Hexyne

(*b*) Dehydrohalogenation of 1,1-dichlorobutane yields 1-butyne. The synthesis is completed as in part (*a*).

$$CH_3CH_2CH_2CHCl_2 \xrightarrow[2.\ H_2O]{1.\ NaNH_2,\ NH_3} CH_3CH_2C{\equiv}CH$$

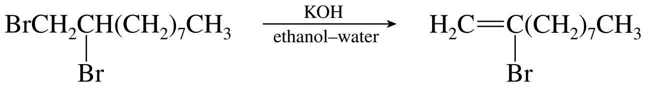
1,1-Dichlorobutane 1-Butyne

(*c*) $$HC{\equiv}CH \xrightarrow[NH_3]{NaNH_2} HC{\equiv}C\!:^- Na^+ \xrightarrow{CH_3CH_2Br} HC{\equiv}CCH_2CH_3$$

Acetylene 1-Butyne

1-Butyne is converted to 3-hexyne as in part (*a*).

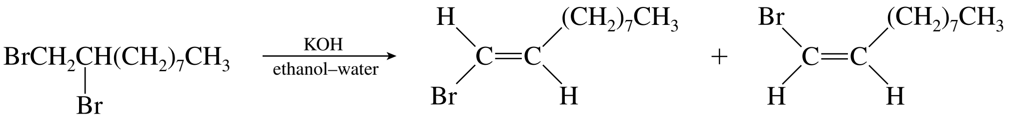
9.25 A single dehydrobromination step occurs in the conversion of 1,2-dibromodecane to $C_{10}H_{19}Br$. Bromine may be lost from C-1 to give 2-bromo-1-decene.



$$BrCH_2\underset{Br}{\underset{|}{C}}H(CH_2)_7CH_3 \xrightarrow[\text{ethanol–water}]{KOH} H_2C{=}\underset{Br}{\underset{|}{C}}(CH_2)_7CH_3$$

1,2-Dibromodecane 2-Bromo-1-decene

Loss of bromine from C-2 gives (*E*)- and (*Z*)-1-bromo-1-decene.



1,2-Dibromodecane (*E*)-1-Bromo-1-decene (*Z*)-1-Bromo-1-decene

9.26 (*a*) $$CH_3CH_2CH_2CH_2C{\equiv}CH + 2H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_2CH_2CH_3$$

1-Hexyne Hexane

(*b*) $$CH_3CH_2CH_2CH_2C{\equiv}CH + H_2 \xrightarrow{\text{Lindlar Pd}} CH_3CH_2CH_2CH_2CH{=}CH_2$$

1-Hexyne 1-Hexene

(*c*) $$CH_3CH_2CH_2CH_2C{\equiv}CH \xrightarrow[NH_3]{Li} CH_3CH_2CH_2CH_2CH{=}CH_2$$

1-Hexyne 1-Hexene

(*d*) $CH_3CH_2CH_2CH_2C\equiv CH \xrightarrow[NH_3]{NaNH_2} CH_3CH_2CH_2CH_2C\equiv C\!:^-Na^+$

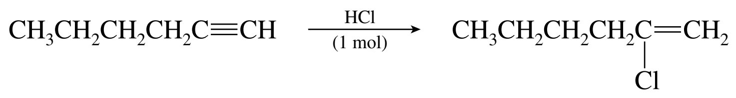
1-Hexyne — Sodium 1-hexynide

(*e*)
$CH_3CH_2CH_2CH_2C\equiv C\!:^-\ Na^+ + CH_3CH_2CH_2CH_2Br \longrightarrow CH_3CH_2CH_2CH_2C\equiv CCH_2CH_2CH_2CH_3$

Sodium 1-hexynide — 1-Bromobutane — 5-Decyne

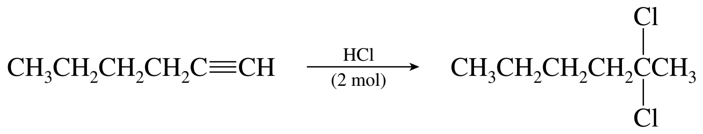
(*f*)
$CH_3CH_2CH_2CH_2C\equiv C\!:^-\ Na^+ + (CH_3)_3CBr \longrightarrow CH_3CH_2CH_2CH_2C\equiv CH + (CH_3)_2C{=}CH_2$

Sodium 1-hexynide — *tert*-Butyl bromide — 1-Hexyne — 2-Methylpropene

(*g*)


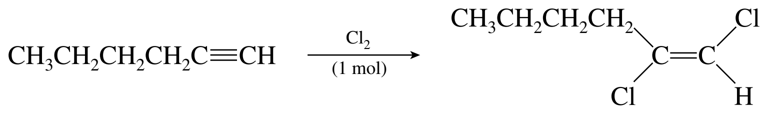
$$CH_3CH_2CH_2CH_2C\equiv CH \xrightarrow[(1\text{ mol})]{HCl} CH_3CH_2CH_2CH_2\underset{\displaystyle Cl}{C}{=}CH_2$$

1-Hexyne — 2-Chloro-1-hexene

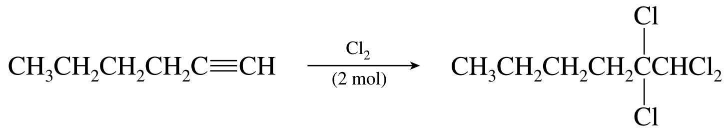
(*h*)


$$CH_3CH_2CH_2CH_2C\equiv CH \xrightarrow[(2\text{ mol})]{HCl} CH_3CH_2CH_2CH_2\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}CH_3$$

1-Hexyne — 2,2-Dichlorohexane

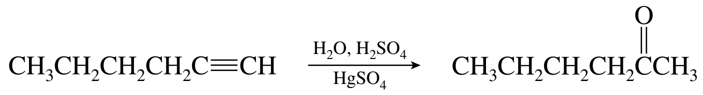
(*i*)


1-Hexyne — (*E*)-1,2-Dichloro-1-hexene

(*j*)


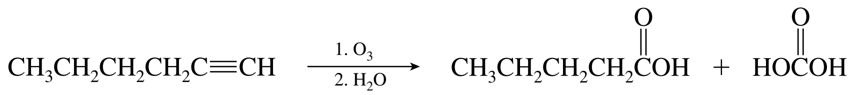
$$CH_3CH_2CH_2CH_2C\equiv CH \xrightarrow[(2\text{ mol})]{Cl_2} CH_3CH_2CH_2CH_2\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}CHCl_2$$

1-Hexyne — 1,1,2,2-Tetrachlorohexane

(*k*)


$$CH_3CH_2CH_2CH_2C\equiv CH \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} CH_3CH_2CH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}CH_3$$

1-Hexyne — 2-Hexanone

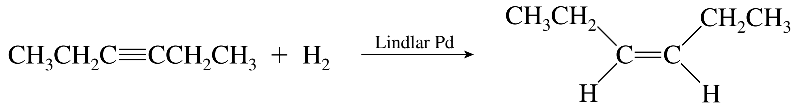
(*l*)


$$CH_3CH_2CH_2CH_2C\equiv CH \xrightarrow[2.\ H_2O]{1.\ O_3} CH_3CH_2CH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}OH + HO\overset{\displaystyle O}{\overset{\|}{C}}OH$$

1-Hexyne — Pentanoic acid — Carbonic acid

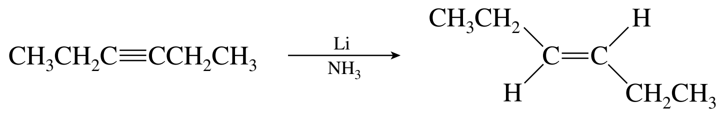
9.27 (*a*) $CH_3CH_2C\equiv CCH_2CH_3 + 2H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_2CH_2CH_3$

3-Hexyne — Hexane

(*b*)


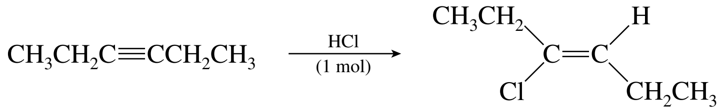
3-Hexyne — (*Z*)-3-Hexene

(*c*)



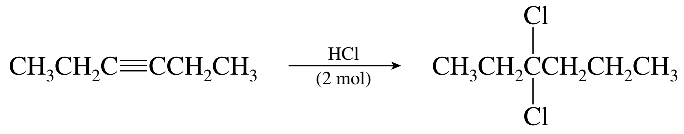
3-Hexyne (*E*)-3-Hexene

(*d*)



3-Hexyne (*Z*)-3-Chloro-3-hexene

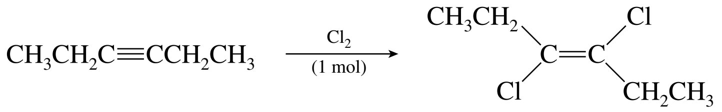
(*e*)



$$\mathrm{CH_3CH_2C{\equiv}CCH_2CH_3 \xrightarrow[\text{(2 mol)}]{\text{HCl}} CH_3CH_2\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}CH_2CH_2CH_3}$$

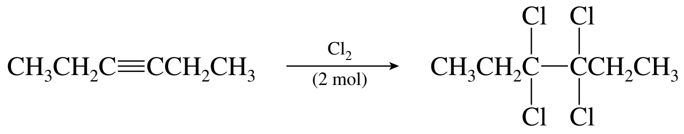
3-Hexyne 3,3-Dichlorohexane

(*f*)



3-Hexyne (*E*)-3,4-Dichloro-3-hexene

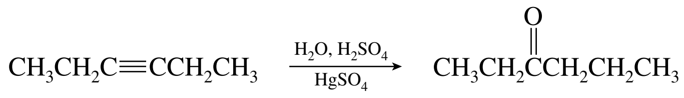
(*g*)



$$\mathrm{CH_3CH_2C{\equiv}CCH_2CH_3 \xrightarrow[\text{(2 mol)}]{Cl_2} CH_3CH_2\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}{-}\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}CH_2CH_3}$$

3-Hexyne 3,3,4,4-Tetrachlorohexane

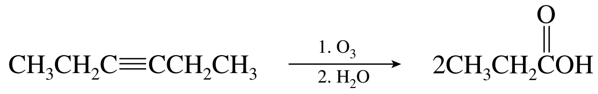
(*h*)



$$\mathrm{CH_3CH_2C{\equiv}CCH_2CH_3 \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_2CH_3}$$

3-Hexyne 3-Hexanone

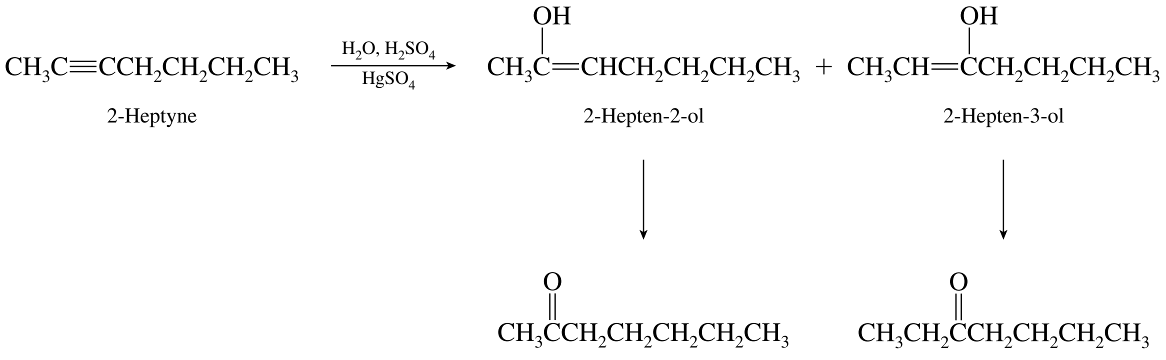
(*i*)



$$\mathrm{CH_3CH_2C{\equiv}CCH_2CH_3 \xrightarrow[2.\ H_2O]{1.\ O_3} 2CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}OH}$$

3-Hexyne Propanoic acid

9.28 The two carbons of the triple bond are similarly but not identically substituted in 2-heptyne, $\mathrm{CH_3C{\equiv}CCH_2CH_2CH_2CH_3}$. Two regioisomeric enols are formed, each of which gives a different ketone.



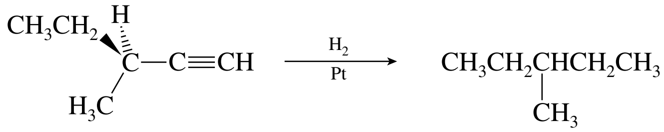
$$\mathrm{CH_3C{\equiv}CCH_2CH_2CH_2CH_3 \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} CH_3\overset{\overset{\displaystyle OH}{|}}{C}{=}CHCH_2CH_2CH_2CH_3 + CH_3CH{=}\overset{\overset{\displaystyle OH}{|}}{C}CH_2CH_2CH_2CH_3}$$

2-Heptyne 2-Hepten-2-ol 2-Hepten-3-ol

$$\mathrm{CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_2CH_2CH_2CH_3 \qquad CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_2CH_2CH_3}$$

2-Heptanone 3-Heptanone

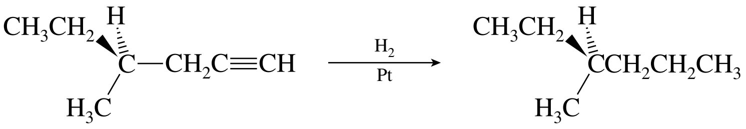
9.29 The alkane formed by hydrogenation of (*S*)-3-methyl-1-pentyne is achiral; it cannot be optically active.



(*S*)-3-Methyl-1-pentyne

3-Methylpentane
(does not have a stereogenic
center; optically inactive)

The product of hydrogenation of (*S*)-4-methyl-1-hexyne is optically active because a stereogenic center is present in the starting material and is carried through to the product.



(*S*)-4-Methyl-1-hexyne

(*S*)-3-Methylhexane

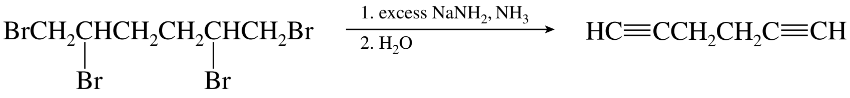
Both (*S*)-3-methyl-1-pentyne and (*S*)-4-methyl-1-hexyne yield optically active products when their triple bonds are reduced to double bonds.

9.30 (*a*) The dihaloalkane contains both a primary alkyl chloride and a primary alkyl iodide functional group. Iodide is a better leaving group than chloride and is the one replaced by acetylide.

$$NaC{\equiv}CH + ClCH_2CH_2CH_2CH_2CH_2CH_2I \longrightarrow ClCH_2CH_2CH_2CH_2CH_2CH_2C{\equiv}CH$$

Sodium acetylide — 1-Chloro-6-iodohexane — 8-Chloro-1-octyne

(*b*) Both vicinal dibromide functions are converted to alkyne units on treatment with excess sodium amide.

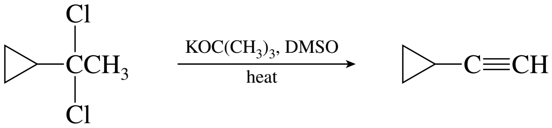


$$BrCH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_2CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_2Br \xrightarrow[\text{2. } H_2O]{\text{1. excess } NaNH_2,\ NH_3} HC{\equiv}CCH_2CH_2C{\equiv}CH$$

1,2,5,6-Tetrabromohexane

1,5-Hexadiyne

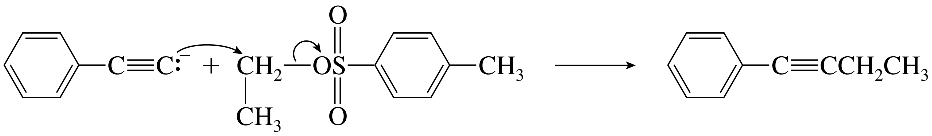
(*c*) The starting material is a geminal dichloride. Potassium *tert*-butoxide in dimethyl sulfoxide is a sufficiently strong base to convert it to an alkyne.



1,1-Dichloro-1-cyclopropylethane

Ethynylcyclopropane

(*d*) Alkyl *p*-toluenesulfonates react similarly to alkyl halides in nucleophilic substitution reactions. The alkynide nucleophile displaces the *p*-toluenesulfonate leaving group from ethyl *p*-toluenesulfonate.

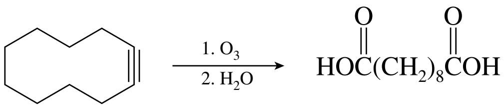


Phenylacetylide ion

Ethyl *p*-toluenesulfonate

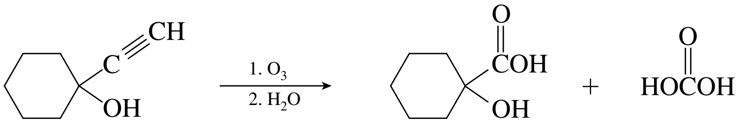
1-Phenyl-1-butyne

(*e*) Both carbons of a —C≡C— unit are converted to carboxyl groups (—CO_2H) on ozonolysis.



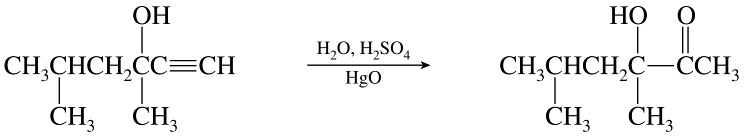
Cyclodecyne Decanedioic acid

(*f*) Ozonolysis cleaves the carbon–carbon triple bond.



1-Ethynylcyclohexanol 1-Hydroxycyclohexanecarboxylic acid Carbonic acid

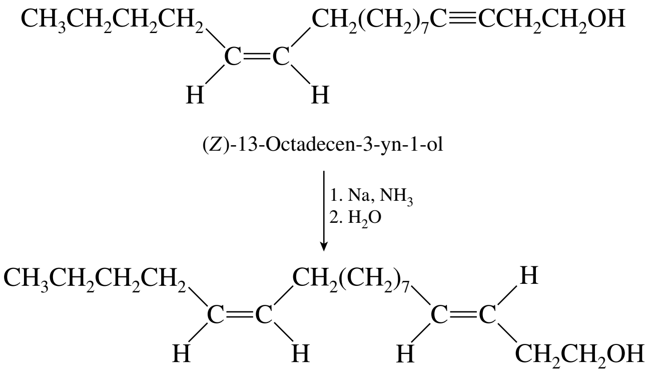
(*g*) Hydration of a terminal carbon–carbon triple bond converts it to a $—\overset{O}{\overset{\|}{C}}CH_3$ group.



$$CH_3\underset{CH_3}{\underset{|}{C}}HCH_2\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}C\equiv CH \xrightarrow[HgO]{H_2O,\ H_2SO_4} CH_3\underset{CH_3}{\underset{|}{C}}HCH_2\overset{HO}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}—\overset{O}{\overset{\|}{C}}CH_3$$

3,5-Dimethyl-1-hexyn-3-ol 3-Hydroxy-3,5-dimethyl-2-hexanone

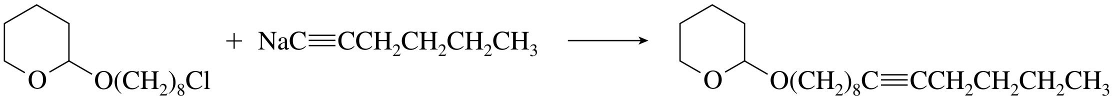
(*h*) Sodium-in-ammonia reduction of an alkyne yields a trans alkene. The stereochemistry of a double bond that is already present in the molecule is not altered during the process.



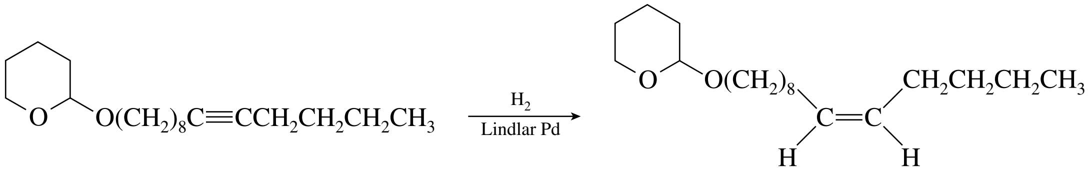
(*Z*)-13-Octadecen-3-yn-1-ol

(3*E*,13*Z*)-3,13-Octadecadien-1-ol

(*i*) The primary chloride leaving group is displaced by the alkynide nucleophile.

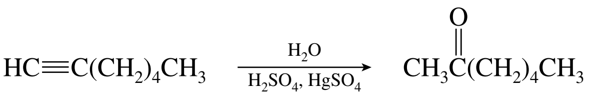


8-Chlorooctyl tetrahydropyranyl ether Sodium 1-hexynide 9-Tetradecyn-1-yl tetrahydropyranyl ether (*j*) Hydrogenation of the triple bond over the Lindlar catalyst converts the compound to a cis alkene.



9-Tetradecyn-1-yl tetrahydropyranyl ether (*Z*)-9-Tetradecen-1-yl tetrahydropyranyl ether

9.31 Ketones such as 2-heptanone may be readily prepared by hydration of terminal alkynes. Thus, if we had 1-heptyne, it could be converted to 2-heptanone.



$$HC{\equiv}C(CH_2)_4CH_3 \xrightarrow[H_2SO_4,\ HgSO_4]{H_2O} CH_3\overset{\overset{\large O}{\|}}{C}(CH_2)_4CH_3$$

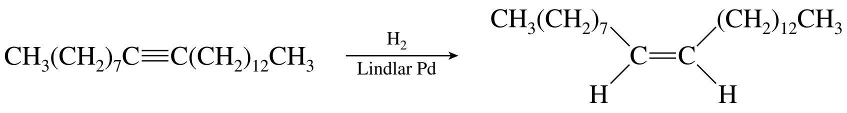
1-Heptyne 2-Heptanone

Acetylene, as we have seen in earlier problems, can be converted to 1-heptyne by alkylation.

$$HC{\equiv}CH \xrightarrow[NH_3]{NaNH_2} HC{\equiv}C{:}^-\ \ Na^+$$

$$HC{\equiv}C{:}^-\ \ Na^+ + CH_3CH_2CH_2CH_2CH_2Br \longrightarrow HC{\equiv}C(CH_2)_4CH_3$$

9.32 Apply the technique of reasoning backward to gain a clue to how to attack this synthesis problem. A reasonable final step is the formation of the *Z* double bond by hydrogenation of an alkyne over Lindlar palladium.



9-Tricosyne (*Z*)-9-Tricosene

The necessary alkyne 9-tricosyne can be prepared by a double alkylation of acetylene.

$$\underset{\text{Acetylene}}{HC{\equiv}CH} \xrightarrow[2.\ CH_3(CH_2)_7Br]{1.\ NaNH_2,\ NH_3} \underset{\text{1-Decyne}}{CH_3(CH_2)_7C{\equiv}CH} \xrightarrow[2.\ CH_3(CH_2)_{12}Br]{1.\ NaNH_2,\ NH_3} \underset{\text{9-Tricosyne}}{CH_3(CH_2)_7C{\equiv}C(CH_2)_{12}CH_3}$$

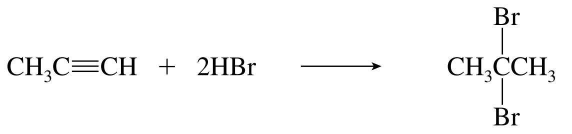
It does not matter which alkyl group is introduced first.

The alkyl halides are prepared from the corresponding alcohols.

$$\underset{\text{1-Octanol}}{CH_3(CH_2)_7OH} \xrightarrow[\text{or } PBr_3]{HBr} \underset{\text{1-Bromooctane}}{CH_3(CH_2)_7Br}$$

$$\underset{\text{1-Tridecanol}}{CH_3(CH_2)_{12}OH} \xrightarrow[\text{or } PBr_3]{HBr} \underset{\text{1-Bromotridecane}}{CH_3(CH_2)_{12}Br}$$

9.33 (*a*) 2,2-Dibromopropane is prepared by addition of hydrogen bromide to propyne.



$$CH_3C{\equiv}CH \;+\; 2HBr \longrightarrow CH_3\overset{Br}{\underset{Br}{C}}CH_3$$

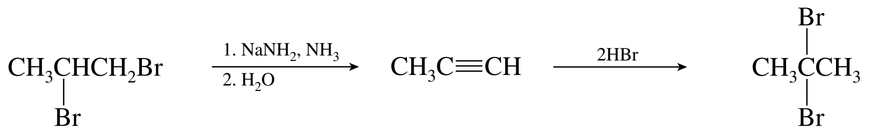
Propyne Hydrogen bromide 2,2-Dibromopropane

The designated starting material, 1,1-dibromopropane, is converted to propyne by a double dehydrohalogenation.

$$CH_3CH_2CHBr_2 \xrightarrow[2.\ H_2O]{1.\ NaNH_2,\ NH_3} CH_3C{\equiv}CH$$

1,1-Dibromopropane Propyne

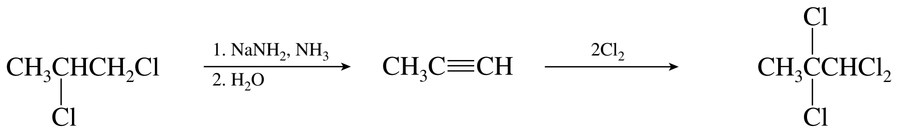
(*b*) As in part (*a*), first convert the designated starting material to propyne, and then add hydrogen bromide.



$$CH_3\underset{Br}{C}HCH_2Br \xrightarrow[2.\ H_2O]{1.\ NaNH_2,\ NH_3} CH_3C{\equiv}CH \xrightarrow{2HBr} CH_3\overset{Br}{\underset{Br}{C}}CH_3$$

1,2-Dibromopropane Propyne 2,2-Dibromopropane

(*c*) Instead of trying to introduce two additional chlorines into 1,2-dichloropropane by free-radical substitution (a mixture of products would result), convert the vicinal dichloride to propyne, and then add two moles of Cl_2.



$$CH_3\underset{Cl}{C}HCH_2Cl \xrightarrow[2.\ H_2O]{1.\ NaNH_2,\ NH_3} CH_3C{\equiv}CH \xrightarrow{2Cl_2} CH_3\overset{Cl}{\underset{Cl}{C}}CHCl_2$$

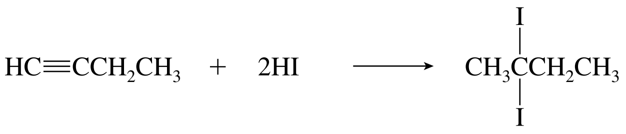
1,2-Dichloropropane Propyne 1,1,2,2-Tetrachloropropane

(*d*) The required carbon skeleton can be constructed by alkylating acetylene with ethyl bromide.

$$HC{\equiv}CH \xrightarrow[NH_3]{NaNH_2} HC{\equiv}C{:}^-\ \ Na^+ \xrightarrow{CH_3CH_2Br} HC{\equiv}CCH_2CH_3$$

Acetylene Sodium acetylide 1- Butyne

Addition of 2 mol of hydrogen iodide to 1-butyne gives 2,2-diiodobutane.



$$HC{\equiv}CCH_2CH_3 \;+\; 2HI \longrightarrow CH_3\overset{I}{\underset{I}{C}}CH_2CH_3$$

1-Butyne Hydrogen iodide 2,2-Diiodobutane

(*e*) The six-carbon chain is available by alkylation of acetylene with 1-bromobutane.

$$HC{\equiv}CH \xrightarrow[2.\ CH_3CH_2CH_2CH_2Br]{1.\ NaNH_2,\ NH_3} HC{\equiv}CCH_2CH_2CH_2CH_3$$

Acetylene 1-Hexyne

The alkylating agent, 1-bromobutane, is prepared from 1-butene by free-radical (anti-Markovnikov) addition of hydrogen bromide.

$$\mathrm{CH_3CH_2CH{=}CH_2} \;+\; \mathrm{HBr} \xrightarrow{\text{peroxides}} \mathrm{CH_3CH_2CH_2CH_2Br}$$

1-Butene Hydrogen bromide 1-Bromobutane

Once 1-hexyne is prepared, it can be converted to 1-hexene by hydrogenation over Lindlar palladium or by sodium–ammonia reduction.

$$\mathrm{CH_3CH_2CH_2CH_2C{\equiv}CH} \xrightarrow[\text{or Na, NH}_3]{\text{H}_2\text{, Lindlar Pd}} \mathrm{CH_3CH_2CH_2CH_2CH{=}CH_2}$$

1-Hexyne 1-Hexene

(*f*) Dialkylation of acetylene with 1-bromobutane, prepared in part (*f*), gives the necessary ten-carbon chain.

$$\mathrm{HC{\equiv}CH} \xrightarrow[\text{2. CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}]{\text{1. NaNH}_2\text{, NH}_3} \mathrm{CH_3CH_2CH_2CH_2C{\equiv}CH} \xrightarrow[\text{2. CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}]{\text{1. NaNH}_2\text{, NH}_3} \mathrm{CH_3CH_2CH_2CH_2C{\equiv}CCH_2CH_2CH_2CH_3}$$

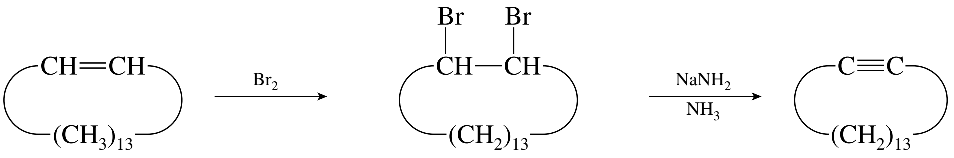
Acetylene 1-Hexyne 5-Decyne

Hydrogenation of 5-decyne yields decane.

$$\mathrm{CH_3(CH_2)_3C{\equiv}C(CH_2)_3CH_3} \xrightarrow[\text{Pt}]{2\text{H}_2} \mathrm{CH_3(CH_2)_3CH_2CH_2(CH_2)_3CH_3}$$

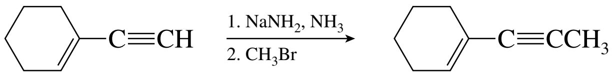
5-Decyne Decane

(*g*) A standard method for converting alkenes to alkynes is to add Br_2 and then carry out a double dehydrohalogenation.



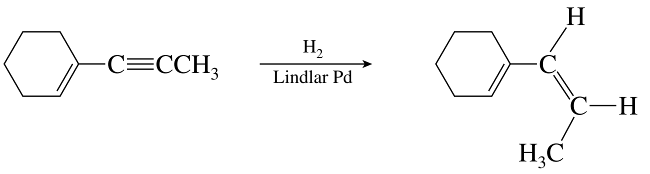
Cyclopentadecene 1,2-Dibromocyclopentadecane Cyclopentadecyne

(*h*) Alkylation of the triple bond gives the required carbon skeleton.

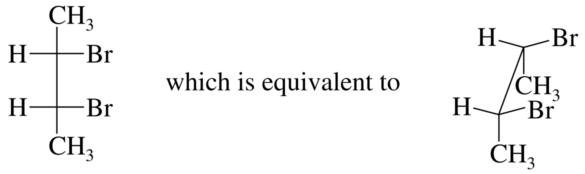


1-Ethynylcyclohexene 1-(1-Propynyl)cyclohexene

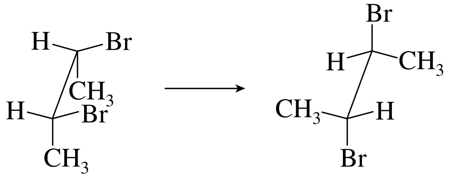
Hydrogenation over the Lindlar catalyst converts the carbon–carbon triple bond to a cis double bond.



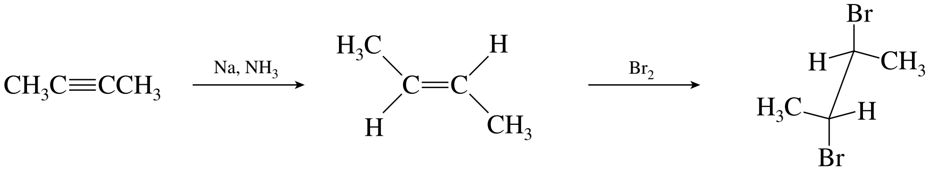
1-(1-Propynyl)cyclohexene (*Z*)-1-(1-Propenyl)cyclohexene (*i*) The stereochemistry of *meso*-2,3-dibromobutane is most easily seen with a Fischer projection:



Recalling that the addition of Br_2 to alkenes occurs with anti stereochemistry, rotate the sawhorse diagram so that the bromines are anti to each other:



Thus, the starting alkene must be *trans*-2-butene. *trans*-2-Butene is available from 2-butyne by metal-ammonia reduction:



2-Butyne *trans*-2-Butene *meso*-2,3-Dibromobutane

9.34 Attack this problem by first planning a synthesis of 4-methyl-2-pentyne from any starting material in a single step. Two different alkyne alkylations suggest themselves:

$$CH_3C{\equiv}CCH(CH_3)_2 \quad \begin{cases} (a) & \text{from } CH_3C{\equiv}C{:}^- \text{ and } BrCH(CH_3)_2 \\ (b) & \text{from } CH_3I \text{ and } {}^-{:}C{\equiv}CCH(CH_3)_2 \end{cases}$$

4-Methyl-2-pentyne

Isopropyl bromide is a secondary alkyl halide and cannot be used to alkylate $CH_3C{\equiv}C{:}^-$ according to reaction (*a*). A reasonable last step is therefore the alkylation of $(CH_3)_2CHC{\equiv}CH$ via reaction of its anion with methyl iodide.

The next question that arises from this analysis is the origin of $(CH_3)_2CHC{\equiv}CH$. One of the available starting materials is 1,1-dichloro-3-methylbutane. It can be converted to $(CH_3)_2CHC{\equiv}CH$ by a double dehydrohalogenation. The complete synthesis is therefore:

$$(CH_3)_2CHCH_2CHCl_2 \xrightarrow[\text{2. } H_2O]{\text{1. } NaNH_2,\, NH_3} (CH_3)_2CHC{\equiv}CH \xrightarrow[\text{2. } CH_3I]{\text{1. } NaNH_2} (CH_3)_2CHC{\equiv}CCH_3$$

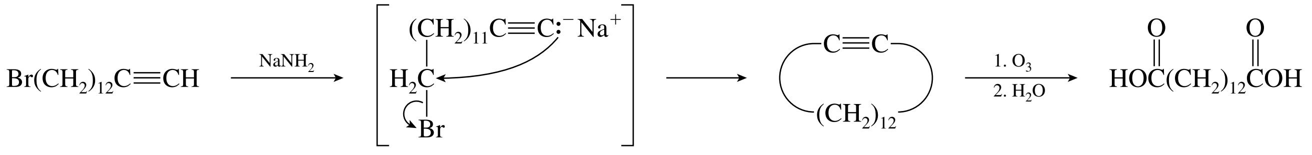
1,1-Dichloro-3-methylbutane 3-Methyl-1-butyne 4-Methyl-2-pentyne

9.35 The reaction that produces compound A is reasonably straightforward. Compound A is 14-bromo-1-tetradecyne.

$$NaC{\equiv}CH + Br(CH_2)_{12}Br \longrightarrow Br(CH_2)_{12}C{\equiv}CH$$

Sodium acetylide 1,12-Dibromododecane Compound A ($C_{14}H_{25}Br$)

Treatment of compound A with sodium amide converts it to compound B. Compound B on ozonolysis gives a diacid that retains all the carbon atoms of B. Compound B must therefore be a cyclic alkyne, formed by an intramolecular alkylation.

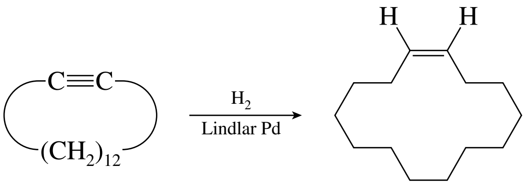


Compound A

Compound B

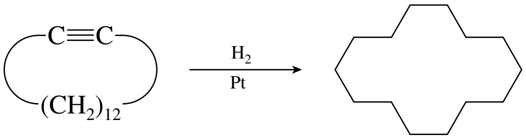
Compound B is cyclotetradecyne.

Hydrogenation of compound B over Lindlar palladium yields *cis*-cyclotetradecene (compound C).



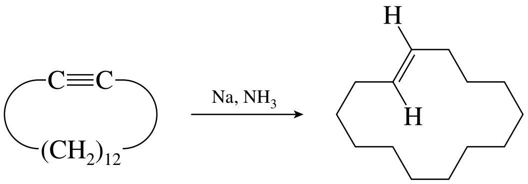
Compound C ($C_{14}H_{26}$)

Hydrogenation over platinum gives cyclotetradecane (compound D).



Compound D ($C_{14}H_{28}$)

Sodium–ammonia reduction of compound B yields *trans*-cyclotetradecene.



Compound E ($C_{14}H_{26}$)

The cis and trans isomers of cyclotetradecene are both converted to $O{=}CH(CH_2)_{12}CH{=}O$ on ozonolysis, whereas cyclotetradecane does not react with ozone.

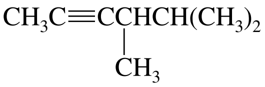
9.36–9.37 Solutions to molecular modeling exercises are not provided in this *Study Guide and Solutions Manual.* You should use *Learning By Modeling* for these exercises.

SELF-TEST

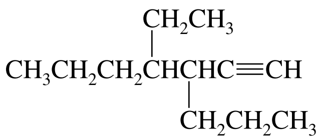
PART A

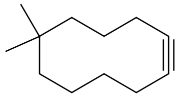
A-1. Provide the IUPAC names for the following:

(*a*)



$CH_3C{\equiv}C\underset{\displaystyle CH_3}{\underset{|}{C}}HCH(CH_3)_2$

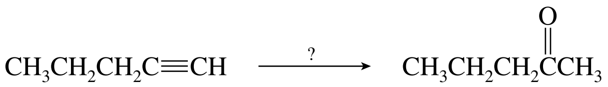
(*b*)

$CH_3CH_2CH_2\overset{\displaystyle CH_2CH_3}{\overset{|}{C}}H\underset{\displaystyle CH_2CH_2CH_3}{\underset{|}{C}}HC\equiv CH$

(*c*)


A-2. Give the structure of the reactant, reagent, or product omitted from each of the following reactions.

(*a*) $CH_3CH_2CH_2C\equiv CH \xrightarrow{HCl\ (1\ mol)} ?$

(*b*) $CH_3CH_2CH_2C\equiv CH \xrightarrow{HCl\ (2\ mol)} ?$

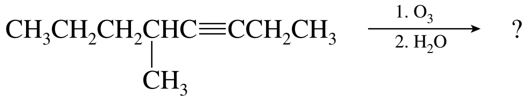
(*c*)

$CH_3CH_2CH_2C\equiv CH \xrightarrow{?} CH_3CH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}CH_3$

(*d*) $CH_3C\equiv CCH_3 \xrightarrow[\text{Lindlar Pd}]{H_2} ?$

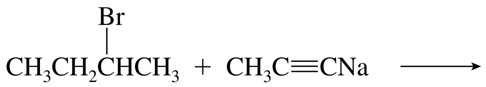
(*e*) $? \xrightarrow[2.\ CH_3CH_2Br]{1.\ NaNH_2} (CH_3)_2CHC\equiv CCH_2CH_3$

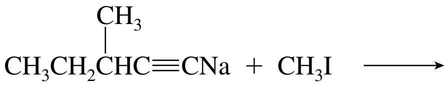
(*f*) $CH_3C\equiv CCH_2CH_3 \xrightarrow{?}$ (*E*)-2-pentene

(*g*) $CH_3C\equiv CCH_2CH_3 \xrightarrow{Cl_2\ (1\ mol)} ?$

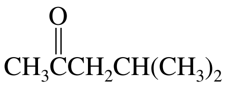
(*h*)

$CH_3CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HC\equiv CCH_2CH_3 \xrightarrow[2.\ H_2O]{1.\ O_3} ?$

A-3. Which one of the following two reactions is effective in the synthesis of 4-methyl-2-hexyne? Why is the other not effective?

1.

$CH_3CH_2\overset{\displaystyle Br}{\overset{|}{C}}HCH_3 + CH_3C\equiv CNa \longrightarrow$

2.

$CH_3CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}HC\equiv CNa + CH_3I \longrightarrow$

A-4. Outline a series of steps, using any necessary organic and inorganic reagents, for the preparation of:

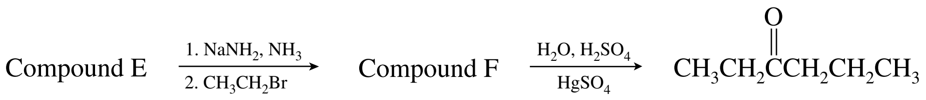
(*a*) 1-Butyne from ethyl bromide as the source of all carbon atoms
(*b*) 3-Hexyne from 1-butyne
(*c*) 3-Hexyne from 1-butene
(*d*)

$CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH(CH_3)_2$ from acetylene

A-5. Treatment of propyne in successive steps with sodium amide, 1-bromobutane, and sodium in liquid ammonia yields as the final product ______.

A-6. Give the structures of compounds A through D in the following series of equations.

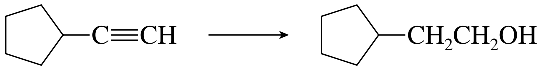
$$A \xrightarrow{NaNH_2,\ NH_3} B$$
$$C \xrightarrow{HBr,\ heat} D$$
$$B + D \longrightarrow CH_3CH_2CH_2C\equiv CC(CH_3)_3$$

A-7. What are the structures of compounds E and F in the following sequence of reactions?



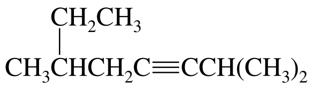
$$\text{Compound E} \xrightarrow[\text{2. } CH_3CH_2Br]{\text{1. } NaNH_2,\ NH_3} \text{Compound F} \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_2CH_3$$

A-8. Give the reagents that would be suitable for carrying out the following transformation. Two or more reaction steps are necessary.



PART B

B-1. The IUPAC name for the compound shown is



$$CH_3\underset{}{\overset{\overset{\displaystyle CH_2CH_3}{|}}{C}}HCH_2C{\equiv}CCH(CH_3)_2$$

(*a*) 2,6-Dimethyl-3-octyne
(*b*) 6-Ethyl-2-methyl-3-heptyne
(*c*) 2-Ethylpropyl isopropyl acetylene
(*d*) 2-Ethyl-6-methyl-4-heptyne

B-2. Which of the following statements best explains the greater acidity of terminal alkynes ($RC{\equiv}CH$) compared with monosubstituted alkenes ($RCH{=}CH_2$)?

(*a*) The *sp*-hybridized carbons of the alkyne are less electronegative than the sp^2 carbons of the alkene.
(*b*) The two π bonds of the alkyne are better able to stabilize the negative charge of the anion by resonance.
(*c*) The *sp*-hybridized carbons of the alkyne are more electronegative than the sp^2 carbons of the alkene.
(*d*) The question is incorrect—alkenes are more acidic than alkynes.

B-3. Referring to the following equilibrium (R = alkyl group)

$$RCH_2CH_3 + RC{\equiv}\ddot{C}:^- \rightleftharpoons RCH_2\ddot{C}H_2^- + RC{\equiv}C{-}H$$

(*a*) $K < 1$; the equilibrium would lie to the left.
(*b*) $K > 1$; the equilibrium would lie to the right.
(*c*) $K = 1$; equal amounts of all species would be present.
(*d*) Not enough information is given; the structure of R must be known.

B-4. Which of the following is an effective way to prepare 1-pentyne?

(*a*) 1-Pentene $\xrightarrow[\text{2. } NaNH_2\text{, heat}]{\text{1. } Cl_2}$

(*b*) Acetylene $\xrightarrow[\text{2. } CH_3CH_2CH_2Br]{\text{1. } NaNH_2}$

(*c*) 1,1-Dichloropentane $\xrightarrow[\text{2. } H_2O]{\text{1. } NaNH_2,\ NH_3}$

(*d*) All these are effective.

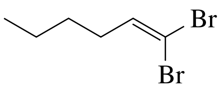
B-5. Which alkyne yields butanoic acid ($CH_3CH_2CH_2CO_2H$) as the only organic product on treatment with ozone followed by hydrolysis?

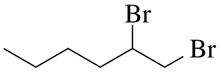
(*a*) 1-Butyne (*c*) 1-Pentyne
(*b*) 4-Octyne (*d*) 2-Hexyne

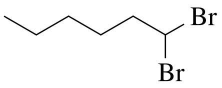
B-6. Which of the following produces a significant amount of acetylide ion on reaction with acetylene?

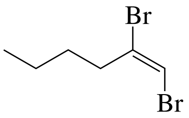
(*a*) Conjugate base of CH_3OH (pK_a16)
(*b*) Conjugate base of H_2 (pK_a35)
(*c*) Conjugate base of H_2O (pK_a16)
(*d*) Both (*a*) and (*c*).

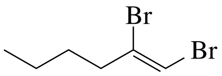
B-7. Which of the following is the product of the reaction of 1-hexyne with 1 mol of Br_2?

(*a*)


(*d*)


(*b*)


(*e*)


(*c*)


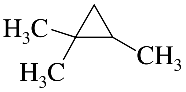
B-8. Choose the sequence of steps that describes the best synthesis of 1-butene from ethanol.

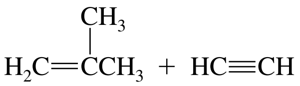
(*a*) (1) $NaC\equiv CH$; (2) H_2, Lindlar Pd
(*b*) (1) $NaC\equiv CH$; (2) Na, NH_3
(*c*) (1) HBr, heat; (2) $NaC\equiv CH$; (3) H_2, Lindlar Pd
(*d*) (1) HBr, heat; (2) $KOC(CH_3)_3$, DMSO; (3) $NaC\equiv CH$; (4) H_2, Lindlar Pd

B-9. What is (are) the major product(s) of the following reaction?

$$(CH_3)_3CBr + HC\equiv C\!:^{-}Na^{+} \longrightarrow ?$$

(*a*) $(CH_3)_3CC\equiv CH$

(*c*)


(*b*)


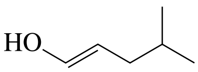
$H_2C{=}\overset{\displaystyle CH_3}{\overset{|}{C}}CH_3 + HC\equiv CH$

(*d*) $HC\equiv CCH_2CH(CH_3)_2$

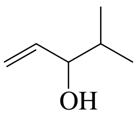
B-10. Which would be the best sequence of reactions to use to prepare *cis*-3-nonene from 1-butyne?

(*a*) (1) $NaNH_2$ in NH_3; (2) 1-bromopentane; (3) H_2, Lindlar Pd
(*b*) (1) $NaNH_2$ in NH_3; (2) 1-bromopentane; (3) Na, NH_3
(*c*) (1) H_2, Lindlar Pd; (2) $NaNH_2$ in NH_3; (3) 1-bromopentane
(*d*) (1) Na, NH_3; (2) $NaNH_2$ in NH_3; (3) 1-bromopentane

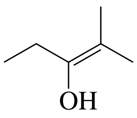
B-11. Which one of the following is the intermediate in the preparation of a ketone by hydration of an alkyne in the presence of sulfuric acid and mercury(II) sulfate?



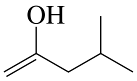
(*a*)



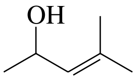
(*b*)



(*c*)

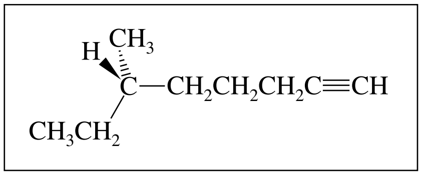


(*d*)

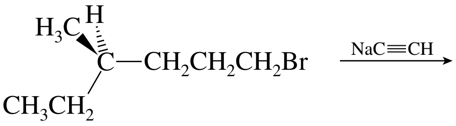


(*e*)

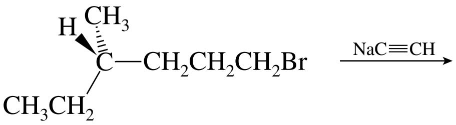
B-12. Which combination is best for preparing the compound shown in the box?



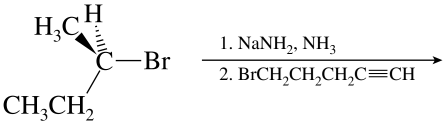
(*a*)



(*b*)



(*c*)



(*d*)