Alkyne

Alkynes

- Hydrocarbons that contain carbon-carbon triple bonds
- Acetylene, the simplest alkyne is produced industrially from methane and steam at high temperature
- Our study of alkynes provides an introduction to organic synthesis, the preparation of organic molecules from simpler organic molecules

physical properties:

- weakly or non-polar,

- no H-bonding

- relatively low mp/bp

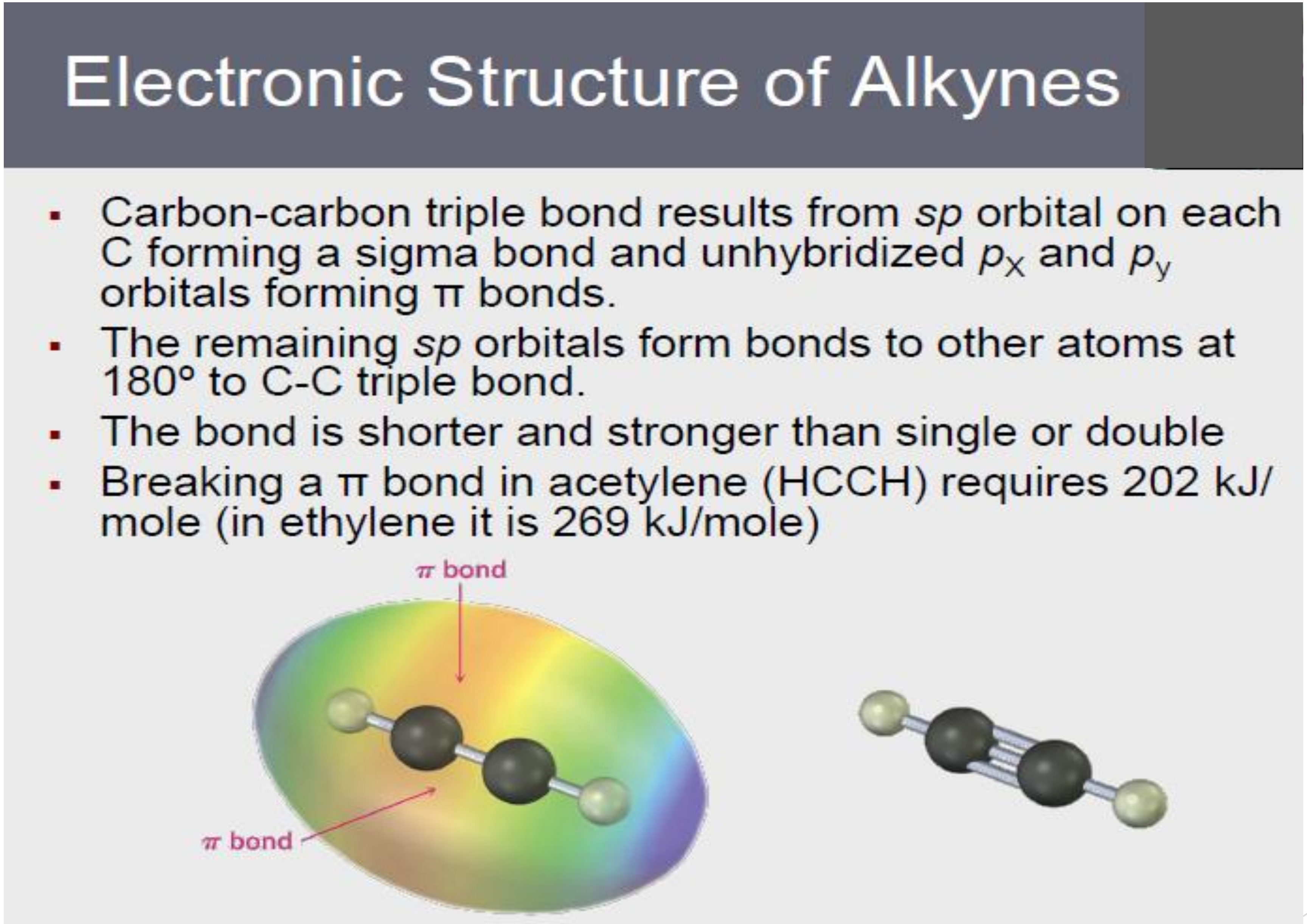
- water insoluble

Alkynes. C_nH_{2n-2}

C_2H_2 H:C:::C:H $H—C \equiv C—H$ sp => linear, 180°

acetylene (ethyne)

C_3H_4 $CH_3C{\equiv}CH$ methylacetylene (propyne)

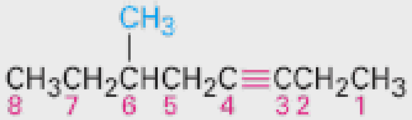


Electronic Structure of Alkynes

- Carbon-carbon triple bond results from *sp* orbital on each C forming a sigma bond and unhybridized p_X and p_y orbitals forming π bonds.
- The remaining *sp* orbitals form bonds to other atoms at 180° to C-C triple bond.
- The bond is shorter and stronger than single or double
- Breaking a π bond in acetylene (HCCH) requires 202 kJ/mole (in ethylene it is 269 kJ/mole)

Naming Alkynes

- General hydrocarbon rules apply with “*-yne*” as a suffix indicating an alkyne
- Numbering of chain with triple bond is set so that the smallest number possible is assigned to the first carbon of the triple bond



$\underset{8}{CH_3}\underset{7}{CH_2}\overset{CH_3}{\underset{6}{CH}}\underset{5}{CH_2}\underset{4}{C}\equiv\underset{3}{C}\underset{2}{CH_2}\underset{1}{CH_3}$

Begin numbering at the end nearer the triple bond.

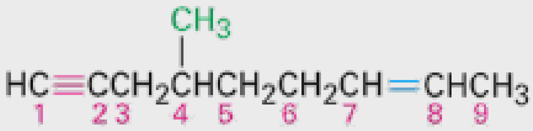
6-Methyl-3-octyne

(New: 6-Methyloct-3-yne)

$\underset{7}{HC}\equiv\underset{6}{C}\underset{5}{CH_2}\underset{4}{CH_2}\underset{3}{CH_2}\underset{2}{CH}=\underset{1}{CH_2}$

1-Hepten-6-yne

(New: Hept-1-en-6-yne)



$\underset{1}{HC}\equiv\underset{2}{C}\underset{3}{CH_2}\overset{CH_3}{\underset{4}{CH}}\underset{5}{CH_2}\underset{6}{CH_2}\underset{7}{CH}=\underset{8}{CH}\underset{9}{CH_3}$

4-Methyl-7-nonen-1-yne

(New: 4-Methylnon-7-en-1-yne)

$CH_3CH_2CH_2CH_2-$

Butyl
(an alkyl group)

$CH_3CH_2CH=CH-$

1-Butenyl
(a vinylic group)

(New: But-1-enyl)

$CH_3CH_2C\equiv C-$

1-Butynyl
(an alkynyl group)

(New: But-1-ynyl)

Nomenclature:

common names: “alkylacetylene”

IUPAC: parent chain = longest continuous carbon chain that contains the triple bond.

alkane drop –ane add -yne

prefix locant for the triple bond, etc.

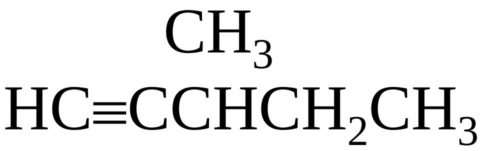
$CH_3CH_2C{\equiv}CCH_3$ 2-pentyne (ethylmethylacetylene)

“terminal” alkynes have the triple bond at the end of the chain:

$CH_3CH_2C{\equiv}CH$

1-butyne

ethylacetylene



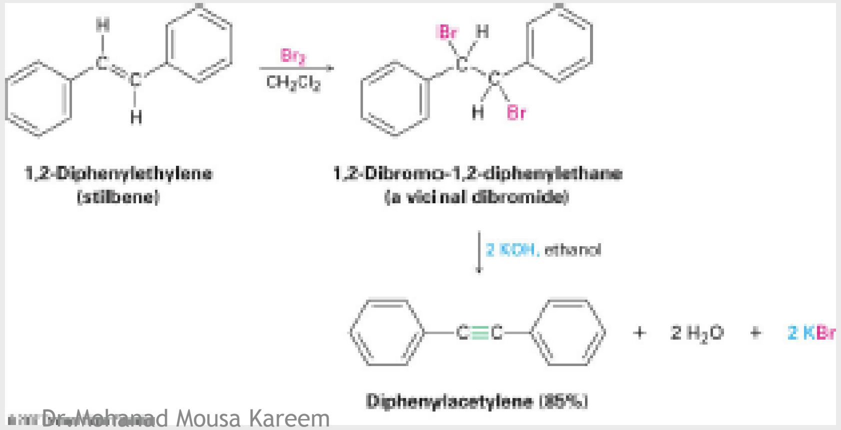
$HC{\equiv}C\overset{CH_3}{C}HCH_2CH_3$

3-methyl-1-pentyne

sec-butylacetylene

9.2 Preparation of Alkynes: Elimination Reactions of Dihalides

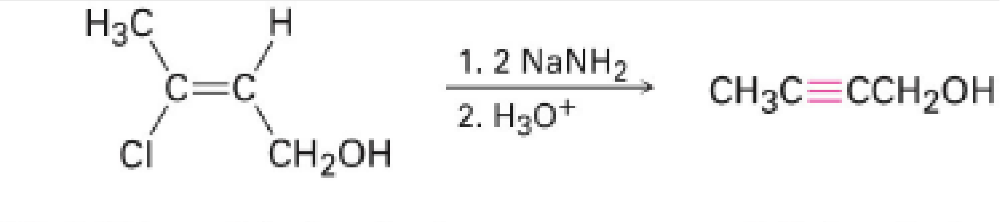
- Treatment of a 1,2-dihaloalkane with KOH or NaOH produces a two-fold elimination of HX
- Vicinal dihalides are available from addition of bromine or chlorine to an alkene
- Intermediate is a vinyl halide



1,2-Diphenylethylene (stilbene)

1,2-Dibromo-1,2-diphenylethane (a vicinal dibromide)

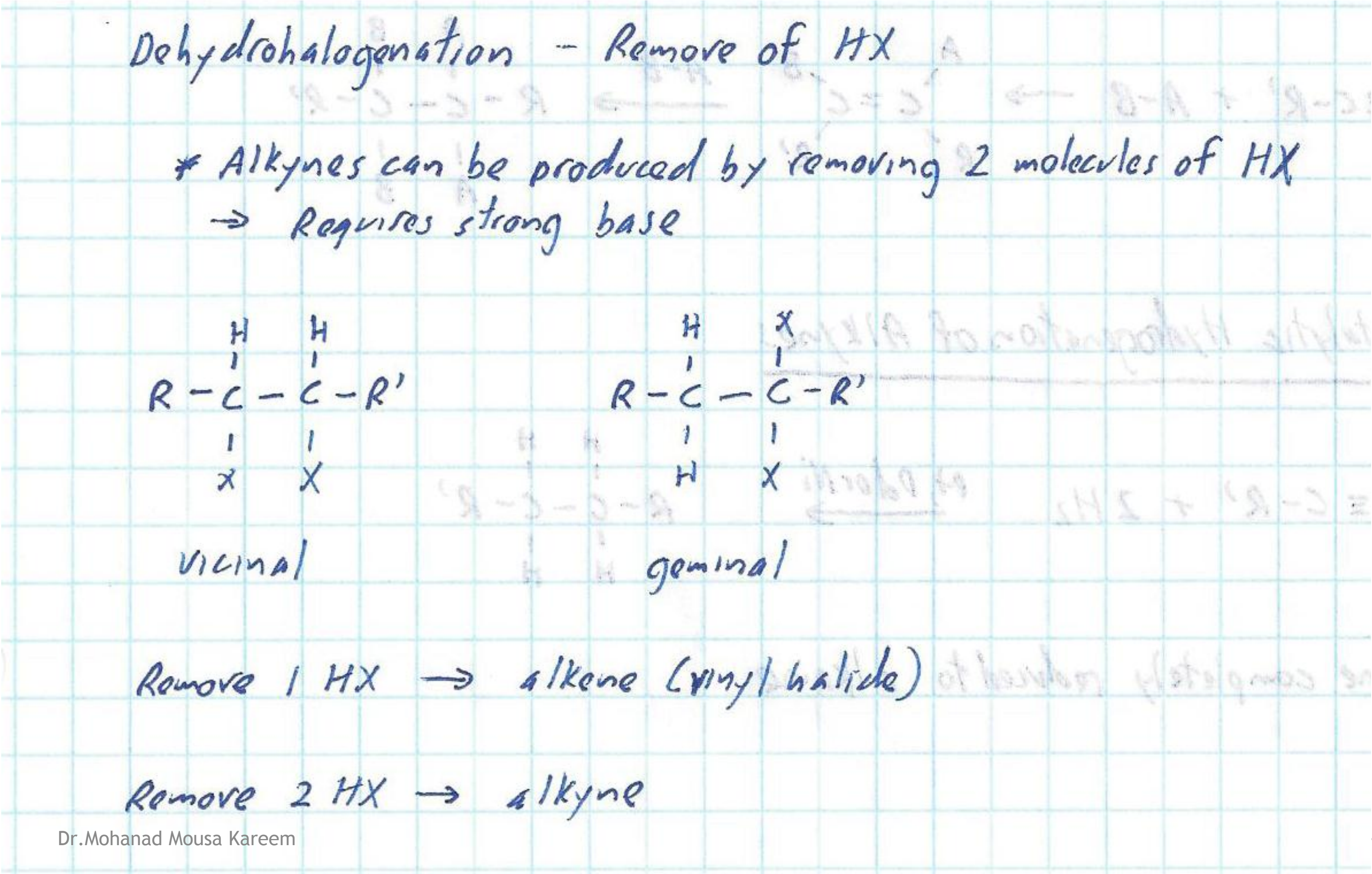
Diphenylacetylene (85%)



(*Z*)-3-Chloro-2-buten-1-ol

2-Butyn-1-ol

9.2 Preparation of Alkynes:
Elimination Reactions of Dihalides



Dehydrohalogenation - Remove of HX

* Alkynes can be produced by removing 2 molecules of HX
→ Requires strong base

$$R-\underset{X}{\overset{H}{C}}-\underset{X}{\overset{H}{C}}-R' \qquad R-\underset{H}{\overset{H}{C}}-\underset{X}{\overset{X}{C}}-R'$$

vicinal

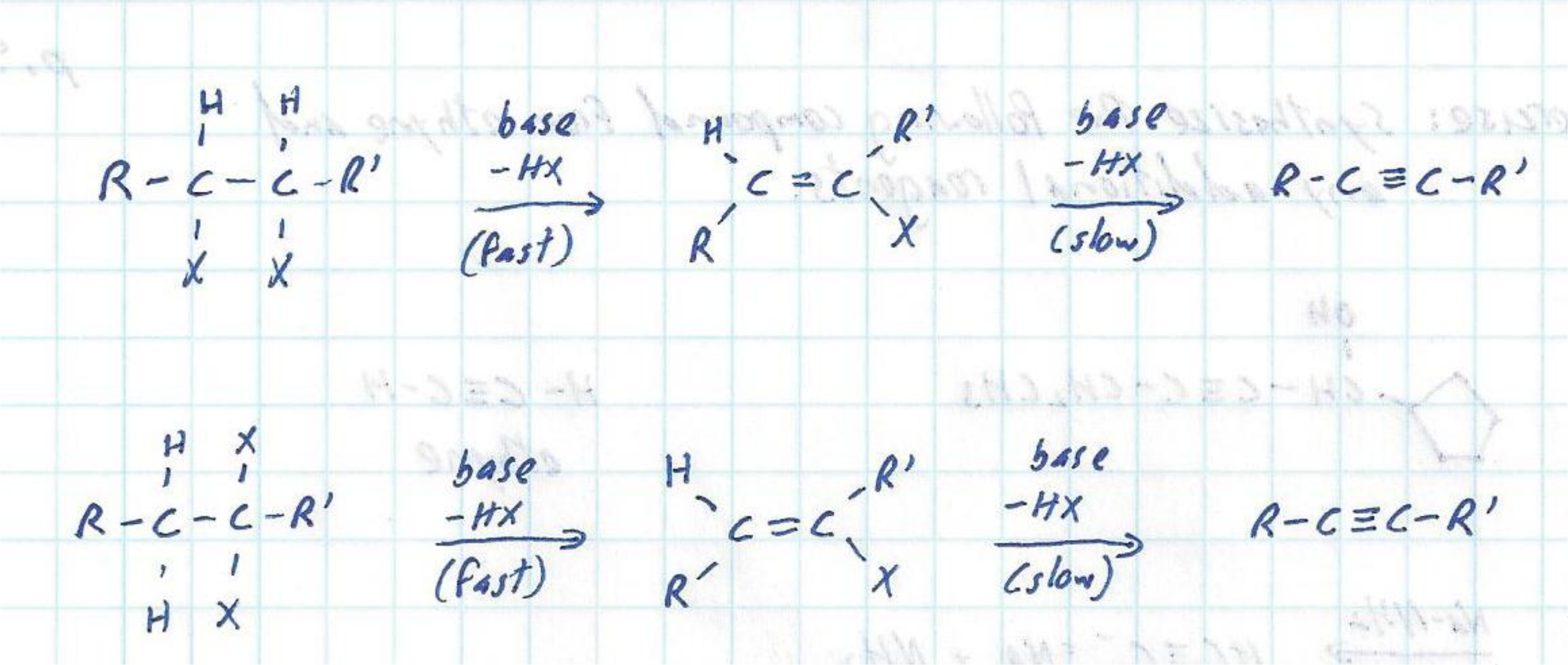
geminal

Remove 1 HX → alkene (vinyl halide)

Remove 2 HX → alkyne

9.2 Preparation of Alkynes: Elimination Reactions of Dihalides

- Works with vicinal or geminal dihalides

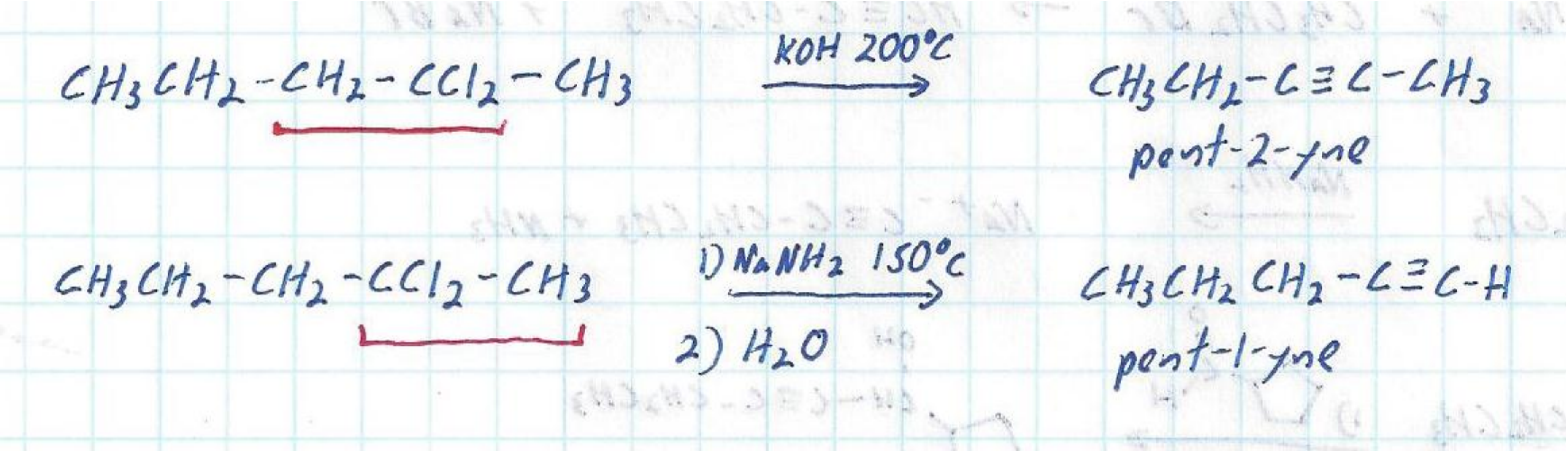


9.2 Preparation of Alkynes: Elimination Reactions of Dihalides

- Works with vicinal or geminal dihalides

9.2 Preparation of Alkynes: Elimination Reactions of Dihalides

- For geminal dihalides (on C2), can produce either internal or terminal alkyne



$$CH_3CH_2-\underline{CH_2-CCl_2}-CH_3 \xrightarrow{KOH\ 200°C} CH_3CH_2-C\equiv C-CH_3$$

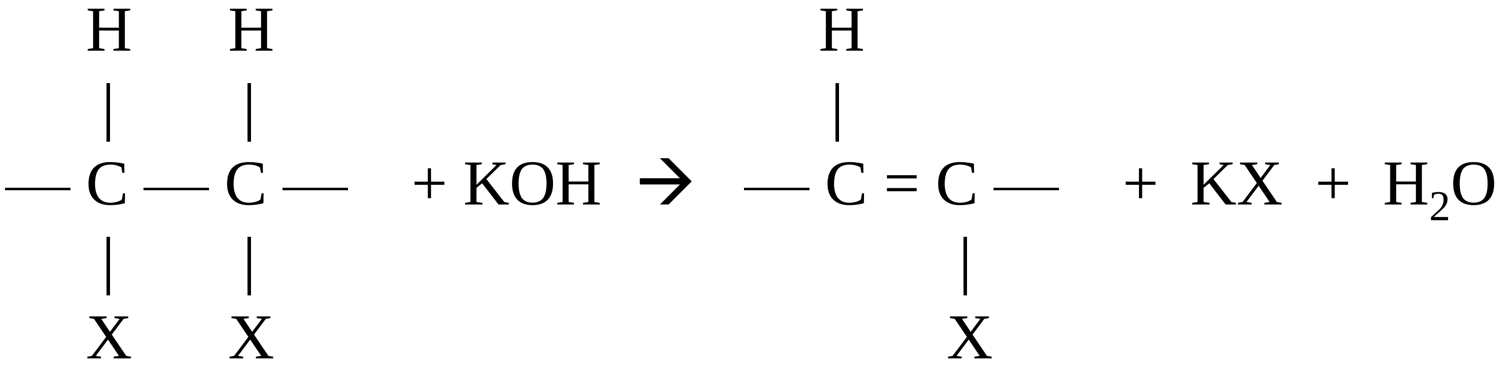
pent-2-yne

$$CH_3CH_2-CH_2-\underline{CCl_2-CH_3} \xrightarrow[2)\ H_2O]{1)\ NaNH_2\ 150°C} CH_3CH_2CH_2-C\equiv C-H$$

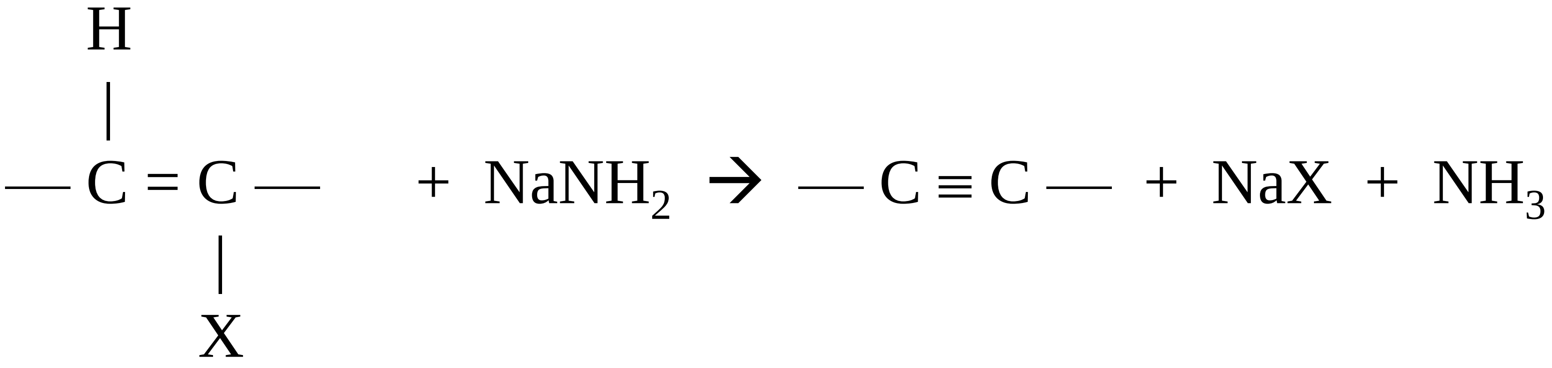
pent-1-yne

Synthesis, alkynes:

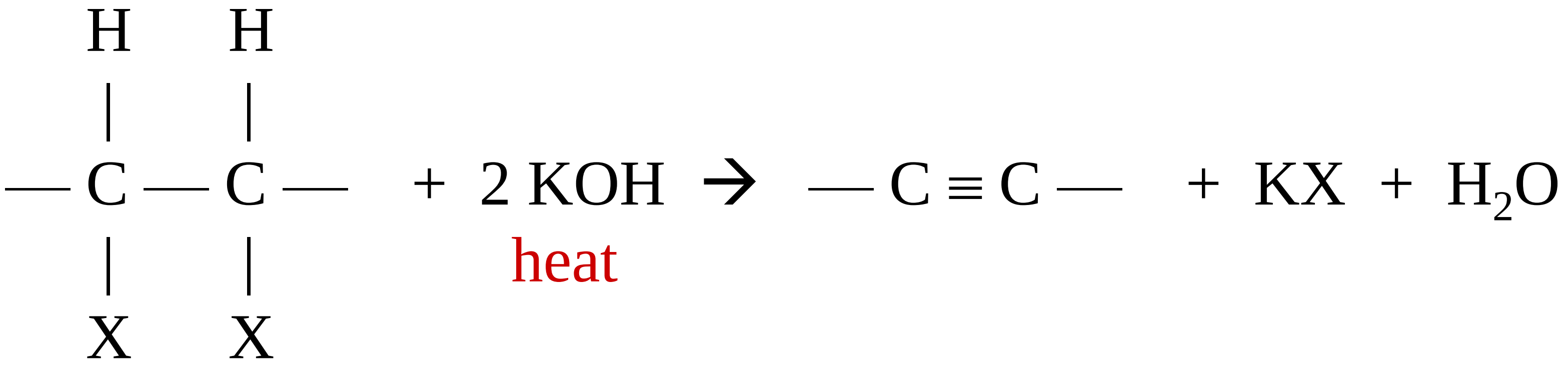
1. dehydrohalogenation of vicinal dihalides



$$-\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}- + KOH \rightarrow -\overset{\overset{H}{|}}{C}=\underset{\underset{X}{|}}{C}- + KX + H_2O$$



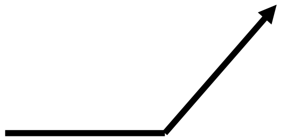
$$-\overset{\overset{H}{|}}{C}=\underset{\underset{X}{|}}{C}- + NaNH_2 \rightarrow -C\equiv C- + NaX + NH_3$$



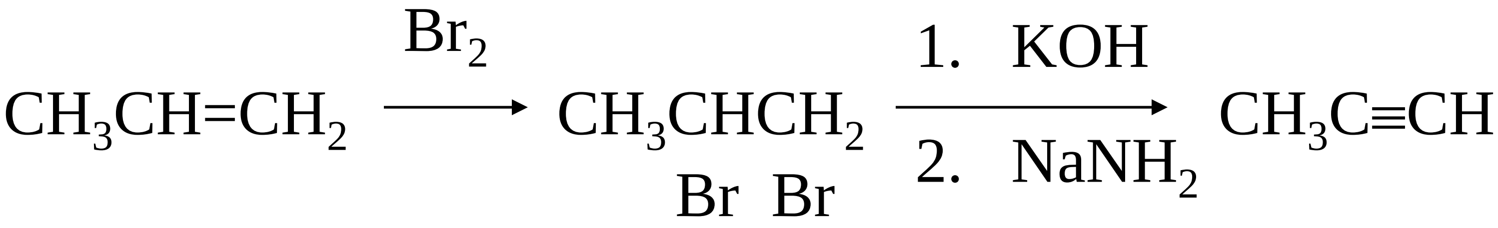
$$\begin{array}{c} H\quad H \\ |\quad\ | \\ -C-C- \\ |\quad\ | \\ X\quad X \end{array} + \underset{heat}{2\,KOH} \rightarrow -C\equiv C- + KX + H_2O$$

$$CH_3CH_2\underset{Br}{CH}\underset{Br}{CH_2} + KOH;\ then\ NaNH_2 \rightarrow CH_3CH_2C\equiv CH$$

“ + 2 KOH, heat

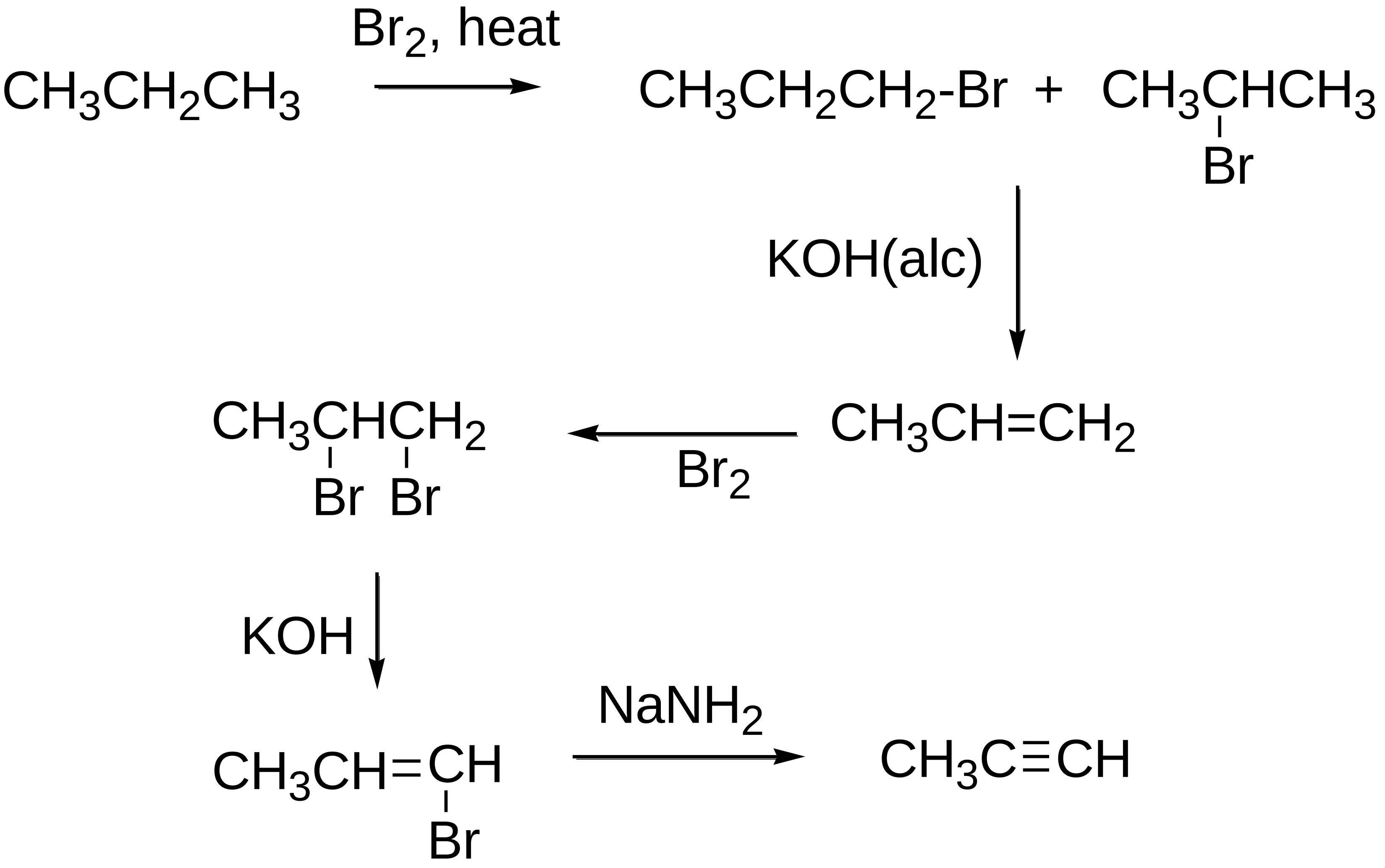


$$\boxed{\text{alkene}} \xrightarrow{X_2} \boxed{\text{vicinal dihalide}} \xrightarrow[\text{2. NaNH}_2]{\text{1. KOH}} \boxed{\text{alkyne}}$$



$$CH_3CH{=}CH_2 \xrightarrow{Br_2} \underset{\text{Br}\ \ \text{Br}}{CH_3CHCH_2} \xrightarrow[\text{2.}\ \ \text{NaNH}_2]{\text{1.}\ \ \text{KOH}} CH_3C{\equiv}CH$$

Synthesis of propyne from propane



$$CH_3CH_2CH_3 \xrightarrow{Br_2,\ heat} CH_3CH_2CH_2\text{-}Br + CH_3\underset{\underset{Br}{|}}{C}HCH_3$$

$$\xrightarrow{KOH(alc)} CH_3CH{=}CH_2$$

$$CH_3CH{=}CH_2 \xrightarrow{Br_2} CH_3\underset{\underset{Br}{|}}{C}H\underset{\underset{Br}{|}}{C}H_2$$

$$\xrightarrow{KOH} CH_3CH{=}\underset{\underset{Br}{|}}{C}H$$

$$CH_3CH{=}\underset{\underset{Br}{|}}{C}H \xrightarrow{NaNH_2} CH_3C{\equiv}CH$$

2. coupling of metal acetylides with 1º/CH_3 alkyl halides

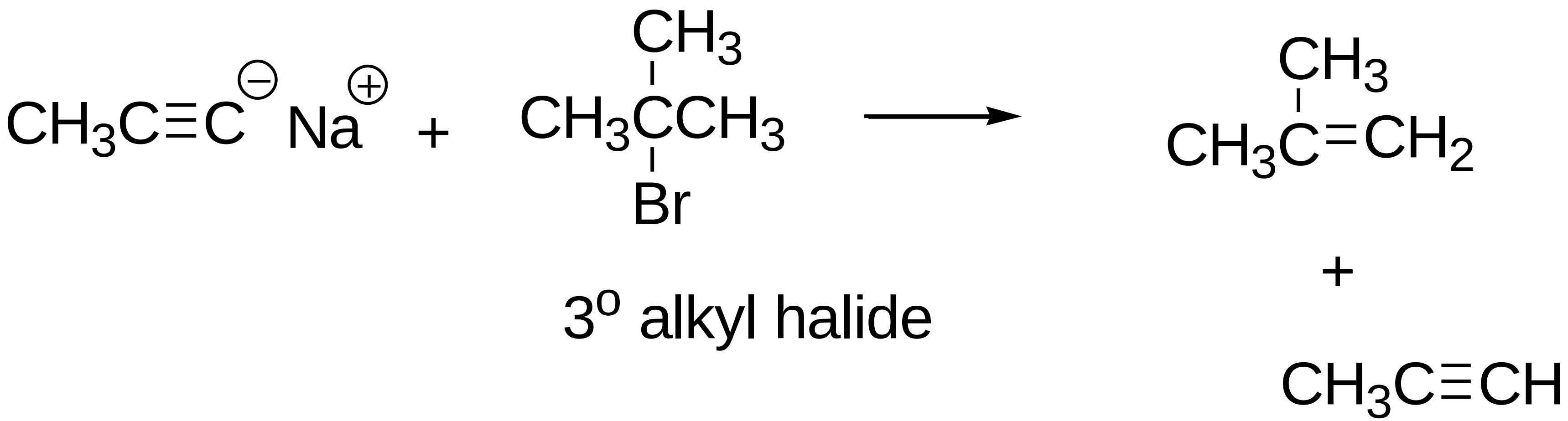
$$R\text{-}C{\equiv}C^{-}Na^{+} + R'X \rightarrow R\text{-}C{\equiv}C\text{-}R' + NaX$$

a) S_N2

b) R´X must be 1º or CH_3X

$$CH_3C{\equiv}C^{-}Li^{+} + CH_3CH_2\text{-}Br \rightarrow CH_3C{\equiv}CCH_2CH_3$$

note: R-X must be 1° or CH_3 to get S_N2!



$$CH_3C\equiv C^{\ominus}\ Na^{\oplus} + \underset{Br}{\overset{CH_3}{CH_3CCH_3}} \longrightarrow \overset{CH_3}{CH_3C{=}CH_2} + CH_3C\equiv CH$$

3^{o} alkyl halide

E2 elimination!

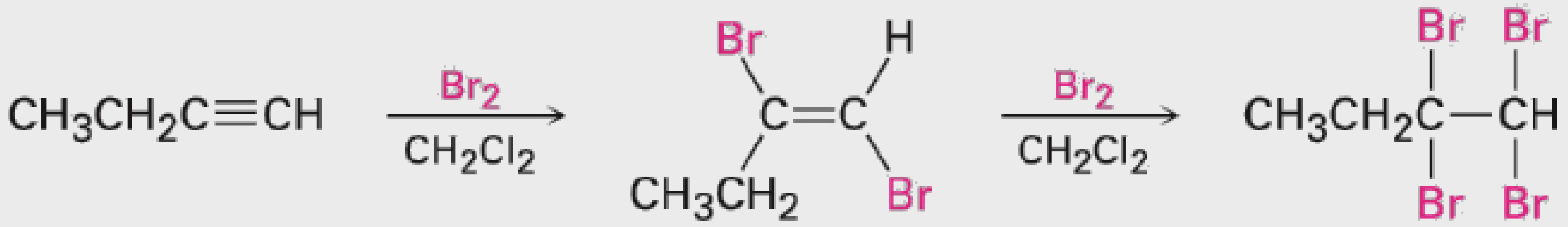
	alkynes	
acids	✓	
bases	✓ some	terminal only
metals	✓	terminal only
oxid.	✓	
reduct.	✓	
halogens	✓	

Reactions, alkynes:

1. addition of H_2 (reduction)
2. addition of X_2
3. addition of HX
4. addition of H_2O, H^+
5. as acids
6. Ag^+
7. oxidation

9.3 Reactions of Alkynes: Addition of HX and X_2

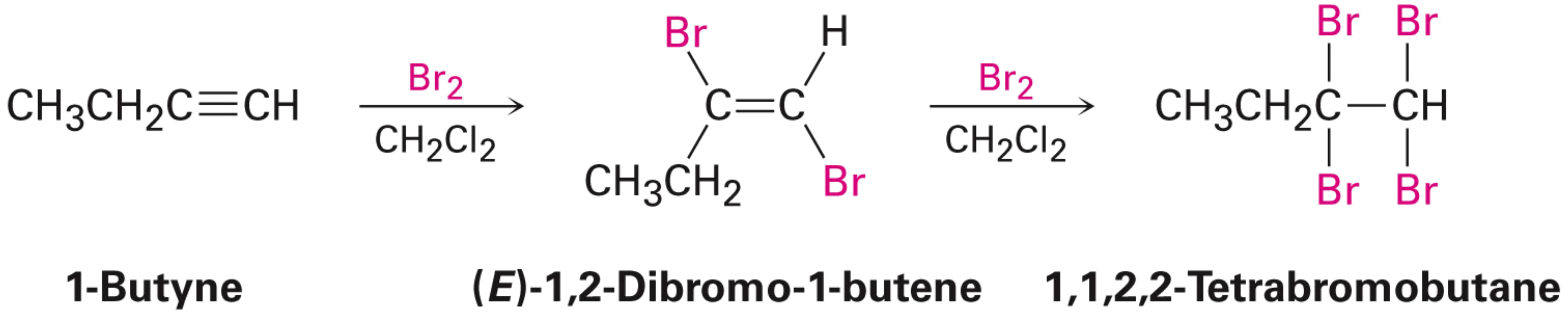
- Addition reactions of alkynes are similar to those of alkenes
- Intermediate alkene reacts further with excess reagent
- Regioselectivity according to Markovnikov



1-Butyne **(*E*)-1,2-Dibromo-1-butene** **1,1,2,2-Tetrabromobutane**

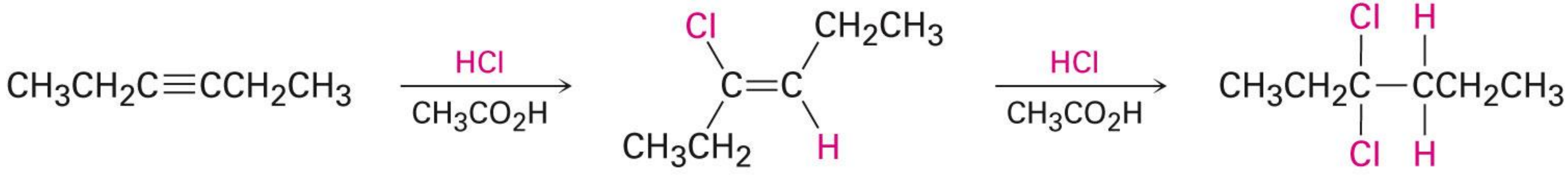
Addition of Bromine and Chlorine

- Initial addition gives *trans* intermediate
- Product with excess reagent is tetrahalide



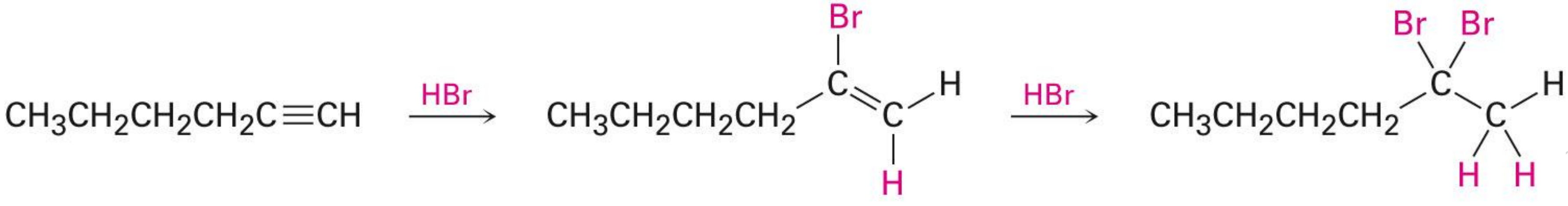
Addition of HX to Alkynes Involves Markovnikov Products

Internal alkynes produce mixture of halogenated alkenes, then Markovnikov product



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

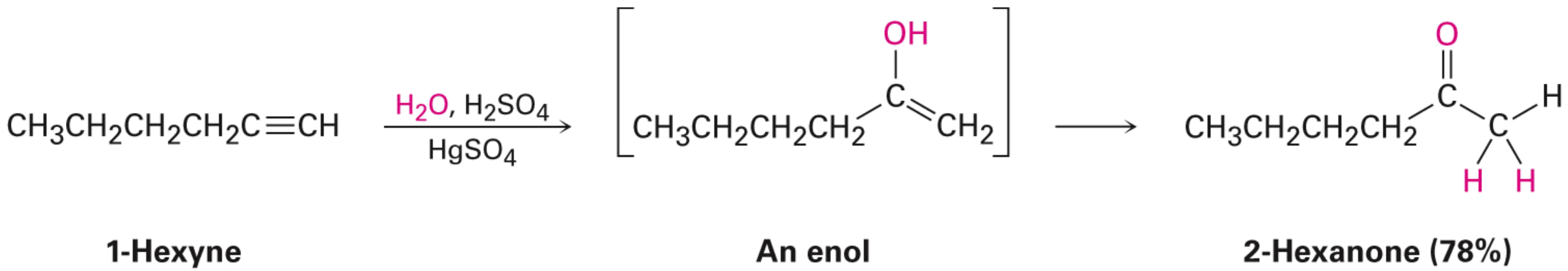
Terminal alkynes produce Markovnikov product



1-Hexyne **2-Bromo-1-hexene** **2,2-Dibromohexane**

Hydration of Alkynes

- Addition of H-OH as in alkenes
    - Mercury (II) catalyzes Markovnikov oriented addition
    - Hydroboration-oxidation gives the anti-Markovnikov product



Mercury(II)-Catalyzed Hydration of Alkynes

- Alkynes do not react with aqueous protic acids
- Mercuric ion (as the sulfate) is a Lewis acid catalyst that promotes addition of water with Markovnikov orientation
- The immediate product is a vinylic alcohol, or **enol**, which spontaneously transforms to a ketone or to an aldehyde in the event that acetylene is employed.

Mechanism of Mercury(II)-Catalyzed Hydration of Alkynes

- Addition of Hg(II) to alkyne gives a vinylic cation
- Water adds and loses a proton
- A proton from aqueous acid replaces Hg(II)

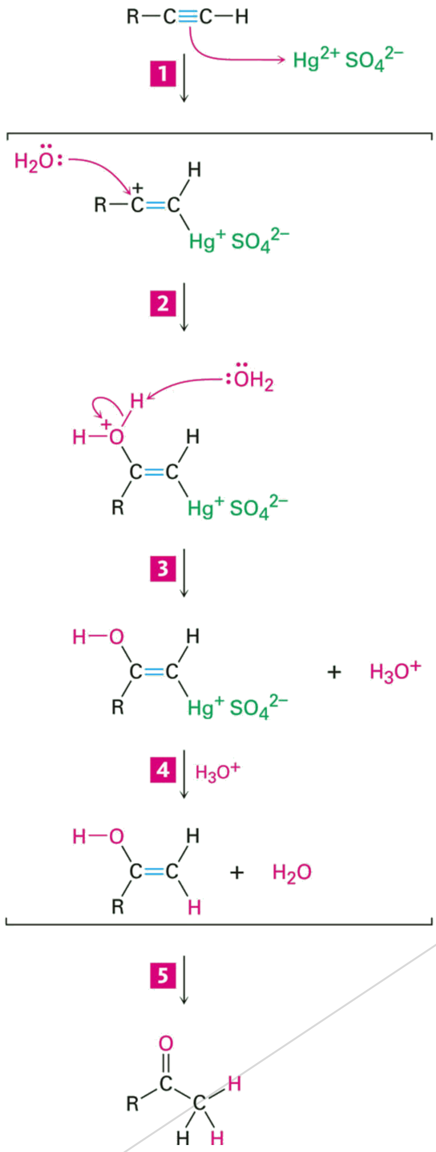
1 The alkyne uses a pair of electrons to attack the electrophilic mercury(II) ion, yielding a mercury-containing vinylic carbocation intermediate.

2 Nucleophilic attack of water on the carbocation forms a C–O bond and yields a protonated mercury-containing enol.

3 Abstraction of H^+ from the protonated enol by water gives an organomercury compound.

4 Replacement of Hg^{2+} by H^+ occurs to give a neutral enol.

5 The enol undergoes tautomerization to give the final ketone product.



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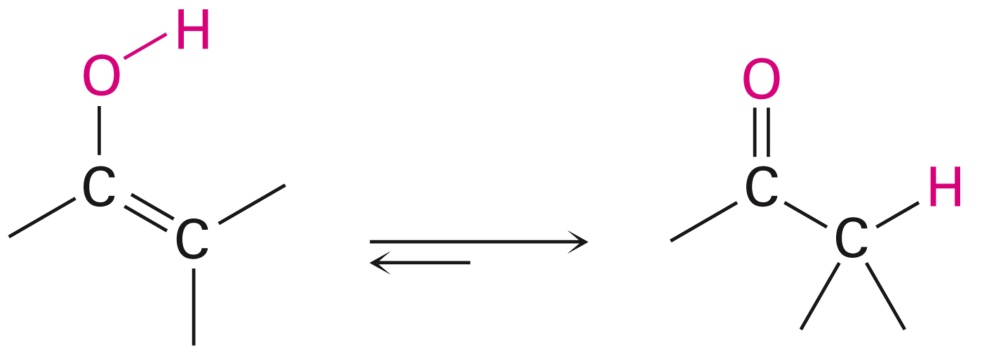
Keto-enol Tautomerism

- Isomeric compounds that can rapidily interconvert by the movement of a proton are called **tautomers** and the phenomenon is called tautomerism
- Enols rearrange to the isomeric ketone by the rapid transfer of a proton from the hydroxyl to the alkene carbon
- The keto form is usually so stable compared to the enol that only the keto form can be observed



Enol tautomer
(less favored)

Keto tautomer
(more favored)

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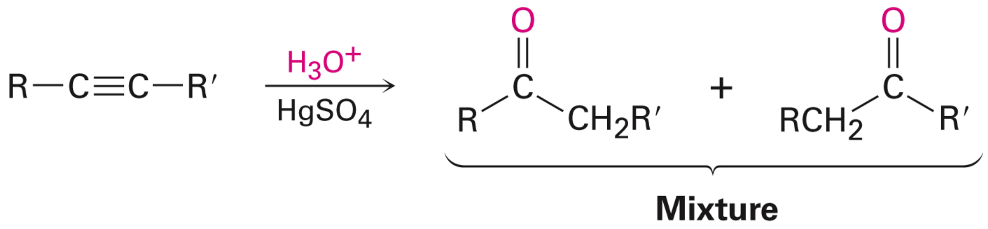
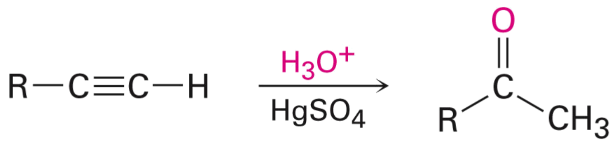
Hydration of Unsymmetrical Alkynes

- If the alkyl groups at either end of the C-C triple bond are not the same, both products can form and this is not normally useful
- If the triple bond is at the first carbon of the chain (then H is what is attached to one side) this is called a **terminal** alkyne
- Hydration of a terminal alkyne always gives the methyl ketone, which is useful

An internal alkyne



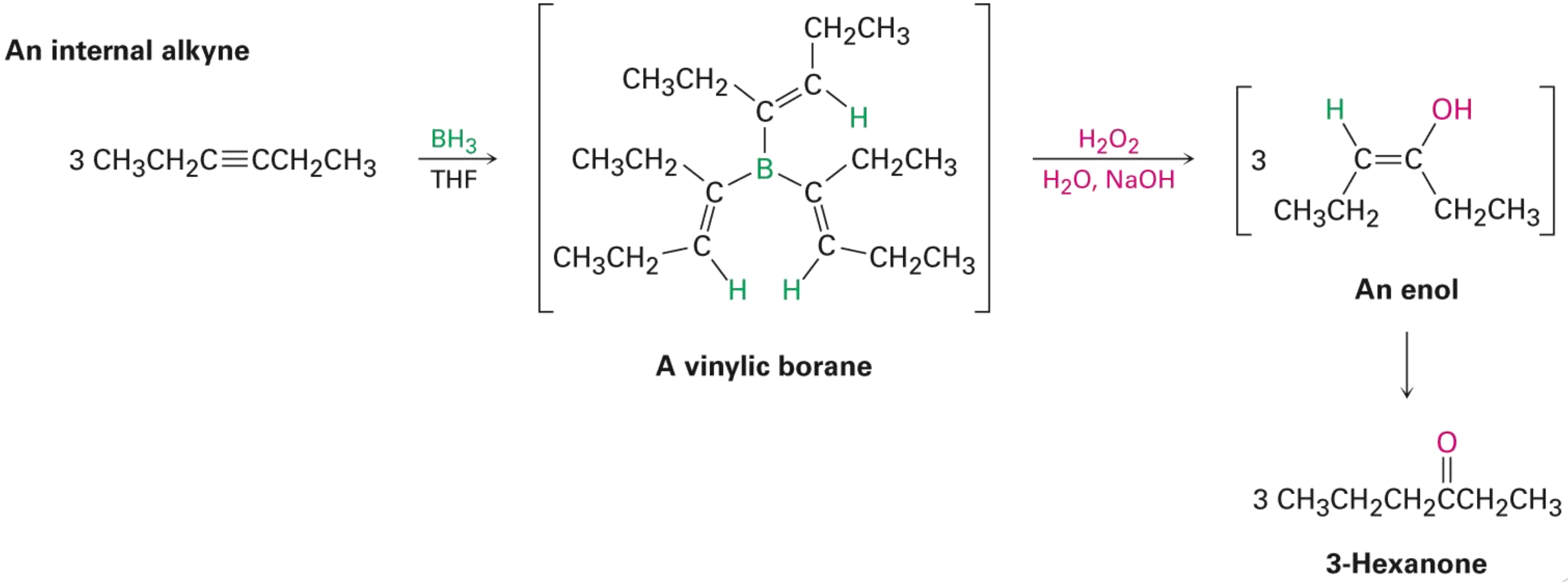
A terminal alkyne



A methyl ketone

Hydroboration/Oxidation of Alkynes

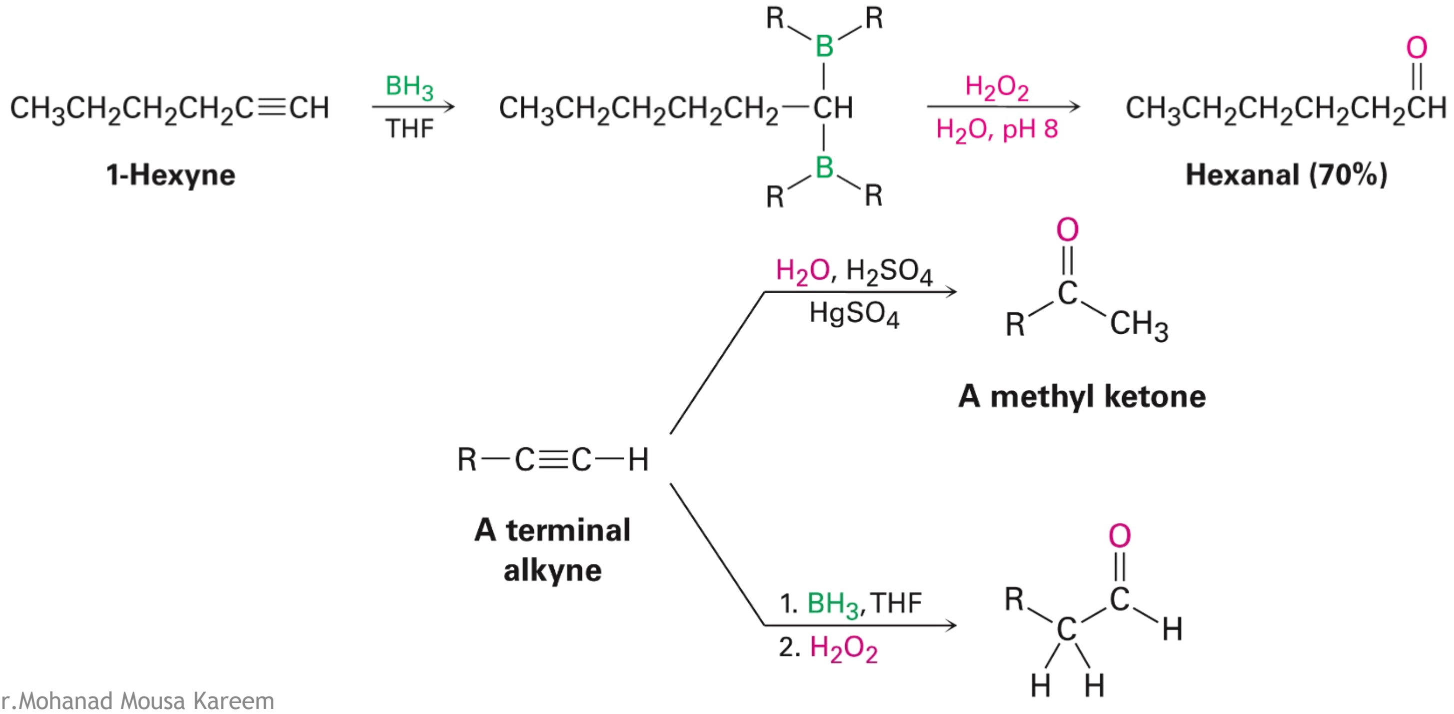
- BH_3 (borane) adds to alkynes to give a vinylic borane
- Oxidation with H_2O_2 produces an enol that converts to the ketone or aldehyde
- Process converts alkyne to ketone or aldehyde with orientation opposite to mercuric ion catalyzed hydration



Comparison of Hydration of Terminal Alkynes

- Hydroboration/oxidation converts terminal alkynes to aldehydes because addition of water is anti-Markovnikov
- The product from the mercury(II) catalyzed hydration converts terminal alkynes to methyl ketones

A terminal alkyne



1-Hexyne

Hexanal (70%)

A methyl ketone

A terminal alkyne

An aldehyde

Reduction of Alkynes

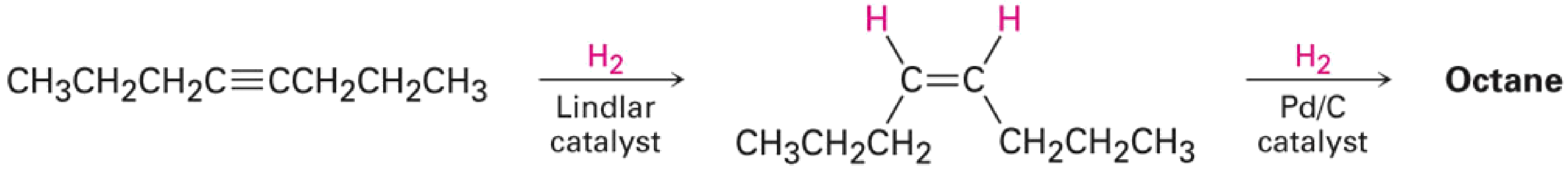
- Addition of H_2 over a metal catalyst (such as palladium on carbon, Pd/C) converts alkynes to alkanes (complete reduction)
- The addition of the first equivalent of H_2 produces an alkene, which is more reactive than the alkyne so the alkene is not observed

$$\mathrm{HC{\equiv}CH} \xrightarrow[\text{Catalyst}]{H_2} \mathrm{H_2C{=}CH_2} \qquad \Delta H^\circ_{\text{hydrog}} = -176\ \text{kJ/mol}\ (-42\ \text{kcal/mol})$$

$$\mathrm{H_2C{=}CH_2} \xrightarrow[\text{Catalyst}]{H_2} \mathrm{CH_3{-}CH_3} \qquad \Delta H^\circ_{\text{hydrog}} = -137\ \text{kJ/mol}\ (-33\ \text{kcal/mol})$$

Conversion of Alkynes to *cis*-Alkenes

- Addition of H_2 using chemically deactivated palladium on calcium carbonate as a catalyst (the *Lindlar catalyst*) produces a *cis* alkene
- The two hydrogens add *syn* (from the same side of the triple bond)

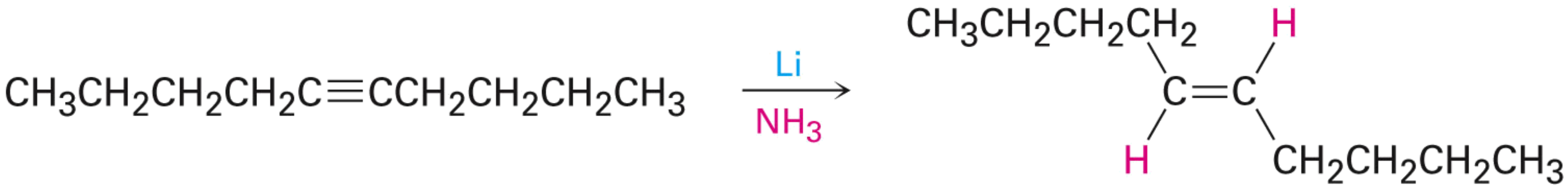


4-Octyne

***cis*-4-Octene**

Conversion of Alkynes to *trans*-Alkenes

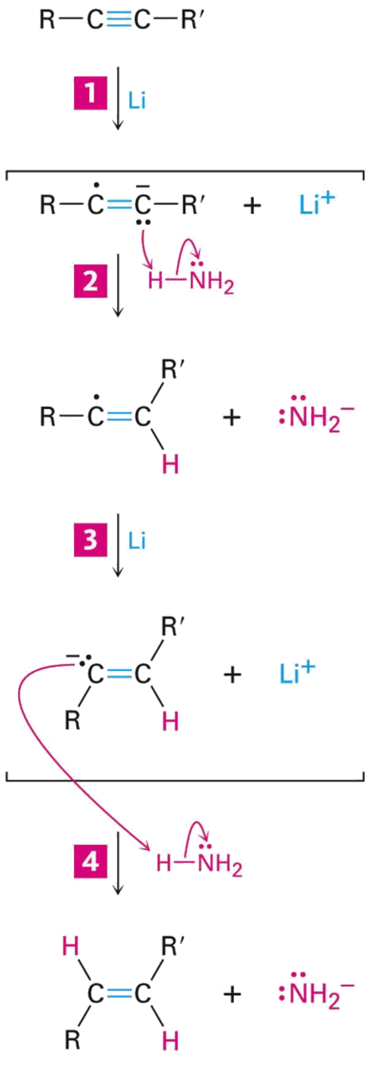
- Anhydrous ammonia (NH_3) is a liquid below –33 °C
  - Alkali metals dissolve in liquid ammonia and function as reducing agents
- Alkynes are reduced to *trans* alkenes with sodium or lithium in liquid ammonia
- The reaction involves a *radical anion* intermediate



5-Decyne

***trans*-5-Decene (78%)**

Mechanism of Li/NH_3 Reduction of an Alkyne



A trans alkene

1 Lithium metal donates an electron to the alkyne to give an anion radical . . .

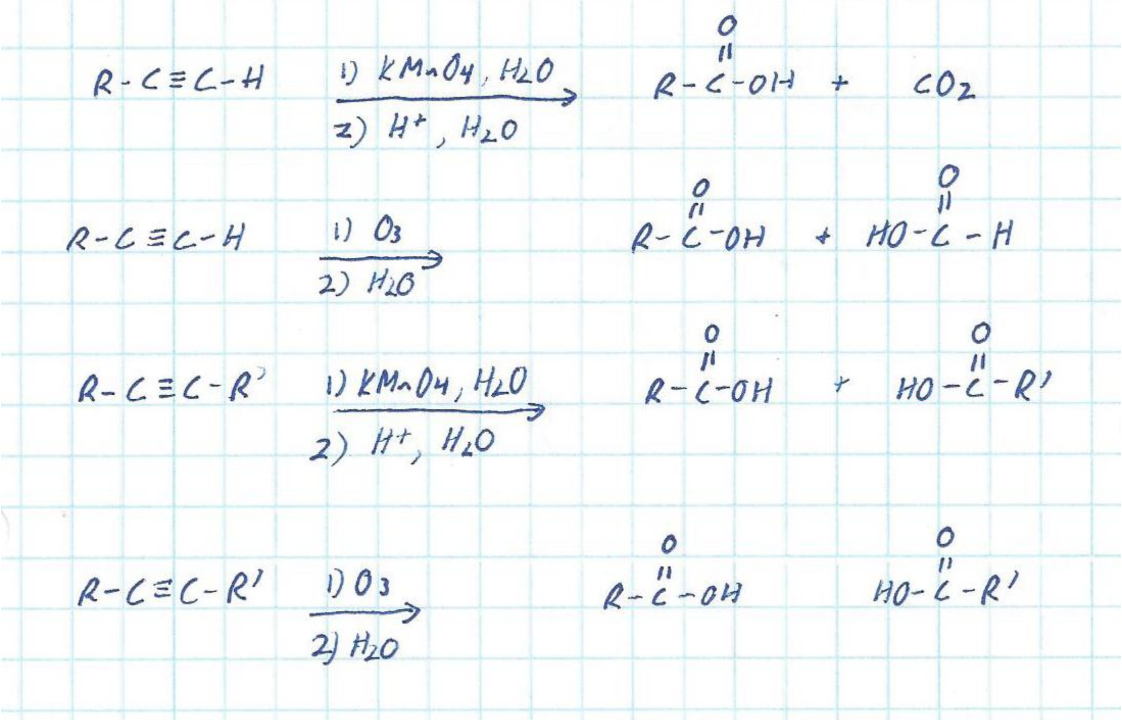
2 . . . which abstracts a proton from ammonia solvent to yield a vinylic radical.

3 The vinylic radical accepts another electron from a second lithium atom to produce a vinylic anion . . .

4 . . . which abstracts another proton from ammonia solvent to yield the final trans alkene product.

Oxidative Cleavage of Alkynes

- Strong oxidizing reagents (O_3 or $KMnO_4$) cleave internal alkynes and terminal alkynes
- Neither process is useful in modern synthesis – were used to elucidate structures because the products indicate the structure of the alkyne precursor



$$R-C\equiv C-H \xrightarrow[2)\ H^+,\ H_2O]{1)\ KMnO_4,\ H_2O} R-\overset{\overset{O}{\|}}{C}-OH + CO_2$$

$$R-C\equiv C-H \xrightarrow[2)\ H_2O]{1)\ O_3} R-\overset{\overset{O}{\|}}{C}-OH + HO-\overset{\overset{O}{\|}}{C}-H$$

$$R-C\equiv C-R' \xrightarrow[2)\ H^+,\ H_2O]{1)\ KMnO_4,\ H_2O} R-\overset{\overset{O}{\|}}{C}-OH + HO-\overset{\overset{O}{\|}}{C}-R'$$

$$R-C\equiv C-R' \xrightarrow[2)\ H_2O]{1)\ O_3} R-\overset{\overset{O}{\|}}{C}-OH \quad HO-\overset{\overset{O}{\|}}{C}-R'$$

Alkyne Acidity: Formation of Acetylide Anions

- Terminal alkynes are weak Brønsted acids (alkenes and alkanes are much less acidic (pK_a ~ 25. See Table 9.1 for comparisons))
- Reaction of strong anhydrous bases (e.g., sodium amide) with a terminal alkyne produces an **acetylide ion**
- The *sp*-hydbridization at carbon holds negative charge relatively close to the positive nucleus (Figure 9.5 in text)

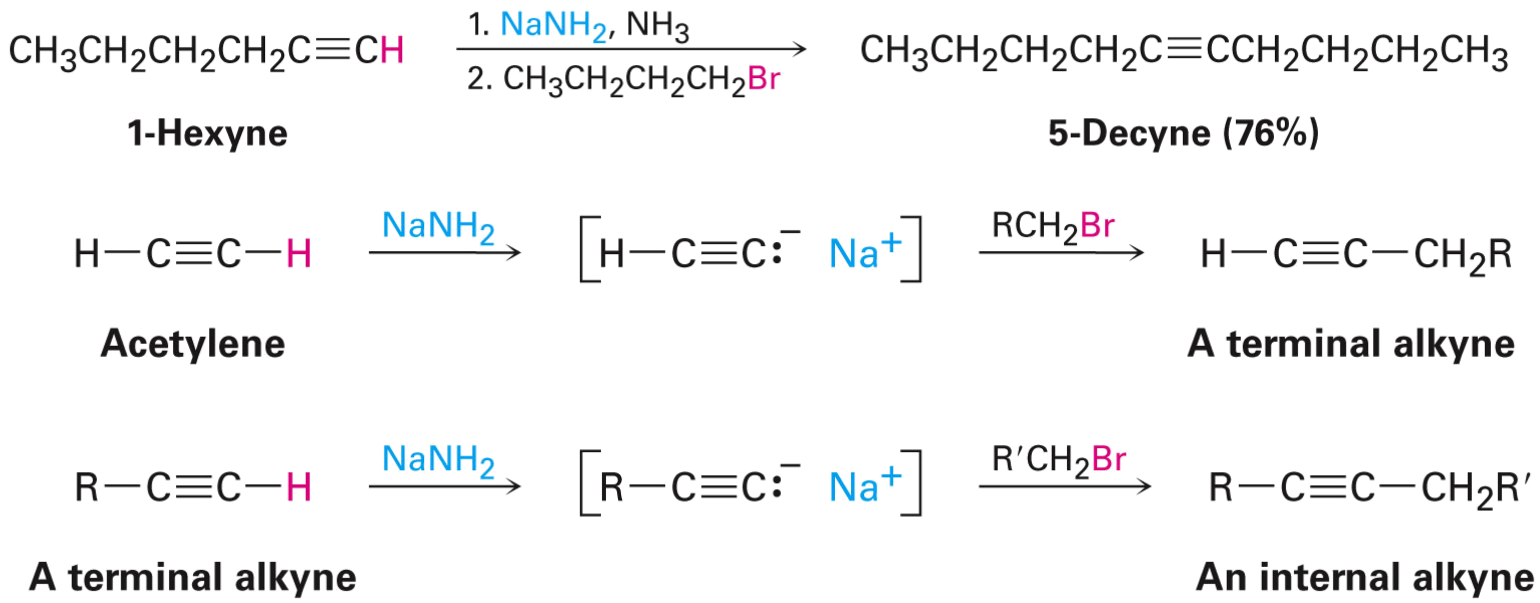
$$R-C\equiv C-H \xrightarrow{:\ddot{N}H_2^{-}\ Na^{+}} R-C\equiv C:^{-}\ Na^{+} + :NH_3$$

A terminal alkyne

An acetylide anion

Alkylation of Acetylide Anions

- Acetylide ions can react as nucleophiles as well as bases (see Figure 9-6 for mechanism)
- Reaction with a primary alkyl halide produces a hydrocarbon that contains carbons from both partners, providing a general route to larger alkynes



$$CH_3CH_2CH_2CH_2C{\equiv}CH \xrightarrow[2.\ CH_3CH_2CH_2CH_2Br]{1.\ NaNH_2,\ NH_3} CH_3CH_2CH_2CH_2C{\equiv}CCH_2CH_2CH_2CH_3$$

1-Hexyne **5-Decyne (76%)**

$$H{-}C{\equiv}C{-}H \xrightarrow{NaNH_2} \left[H{-}C{\equiv}C{:}^{-}\ Na^{+}\right] \xrightarrow{RCH_2Br} H{-}C{\equiv}C{-}CH_2R$$

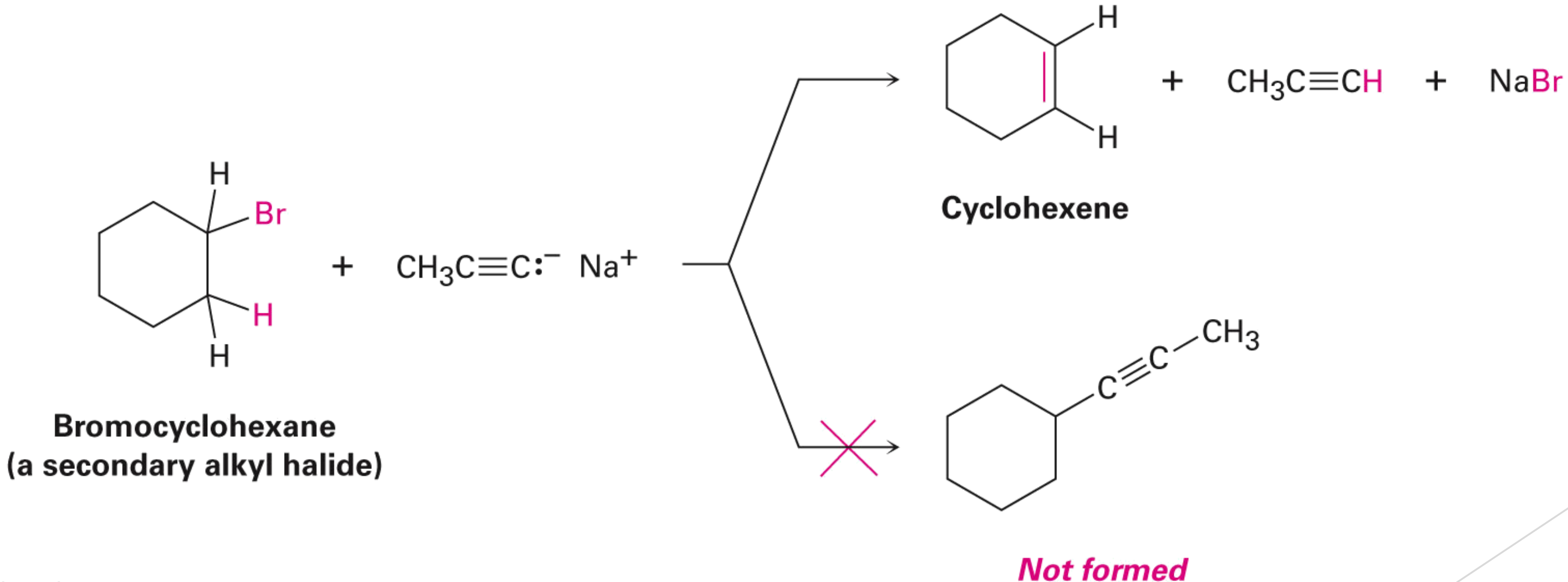
Acetylene **A terminal alkyne**

$$R{-}C{\equiv}C{-}H \xrightarrow{NaNH_2} \left[R{-}C{\equiv}C{:}^{-}\ Na^{+}\right] \xrightarrow{R'CH_2Br} R{-}C{\equiv}C{-}CH_2R'$$

A terminal alkyne **An internal alkyne**

Limitations of Alkyation of Acetylide Ions

- Reactions only are efficient with 1° alkyl bromides and alkyl iodides
- Acetylide anions can behave as bases as well as nucelophiles
- Reactions with 2° and 3° alkyl halides gives dehydrohalogenation, converting alkyl halide to alkene



An Introduction to Organic Synthesis

- Organic synthesis creates molecules by design
- Synthesis can produce new molecules that are needed as drugs or materials
- Syntheses can be designed and tested to improve efficiency and safety for making known molecules
- Highly advanced synthesis is used to test ideas and methods, answering challenges
- Chemists who engage in synthesis may see some work as *elegant* or *beautiful* when it uses novel ideas or combinations of steps – this is very subjective and not part of an introductory course

Synthesis as a Tool for Learning Organic Chemistry

- In order to propose a synthesis you must be familiar with reactions
    - What they begin with
    - What they lead to
    - How they are accomplished
    - What the limitations are
- A synthesis combines a series of proposed steps to go from a defined set of reactants to a specified product
    - Questions related to synthesis can include partial information about a reaction of series that the student completes

Strategies for Synthesis

- Compare the target and the starting material
- Consider reactions that efficiently produce the outcome. Look at the product and think of what can lead to it
- Read the practice problems in the text

Let’s Work a Problem

Prepare *n*-octane from 1-pentyne.

The best strategy to approach this problem is to use acetylide coupling: