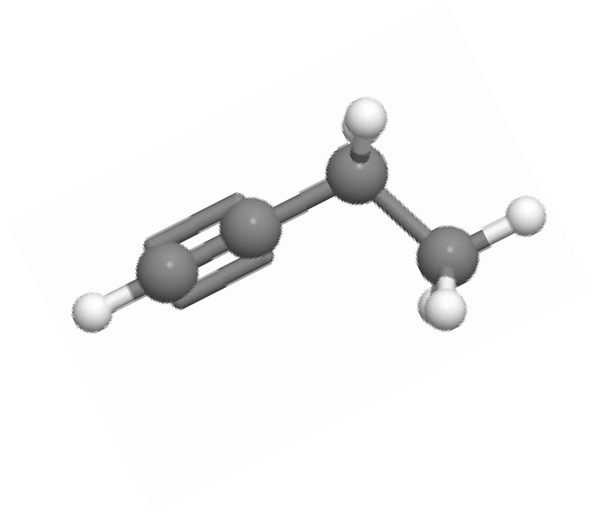
2302263 – Organic Chemistry I – Part III

Lecture 2-5

Alkynes



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Recommended Textbook:
Chapter 8 in *Organic Chemistry*, 8th Edition, L. G. Wade, Jr., **2010**, Prentice Hall (Pearson Education)

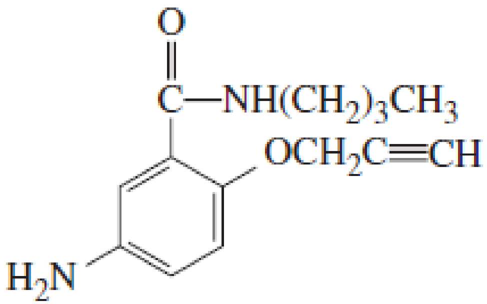
Alkynes

Alkynes are hydrocarbons that contain carbon–carbon **triple bonds**.

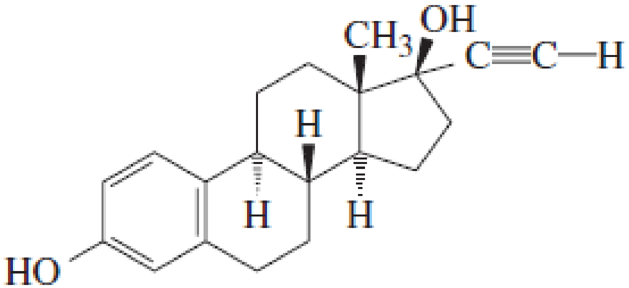
$H-C\equiv C-H$	$CH_3CH_2-C\equiv C-H$	$CH_3-C\equiv C-CH_3$
acetylene	ethylacetylene	dimethylacetylene
ethyne	but-1-yne	but-2-yne

The chemistry of the carbon–carbon triple bond is similar to that of the double bond.

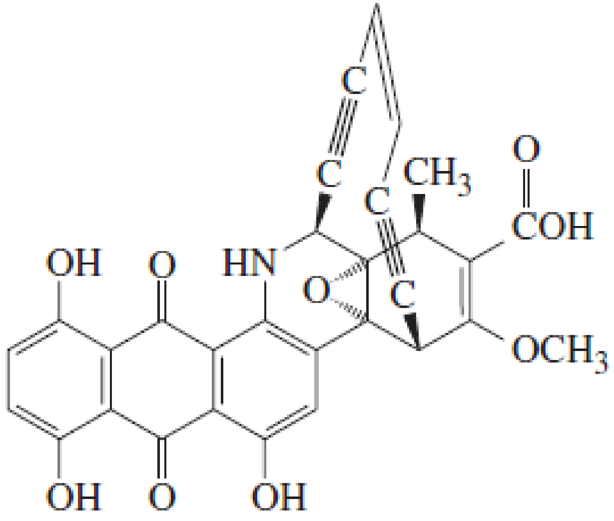
Alkynes are not as common in nature as alkenes



parsalmide



ethynyl estradiol



dynemicin A

IUPAC Nomenclature

Alkanes

Suffix: -ane

H_3C-CH_3

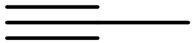
ethane

Alkynes

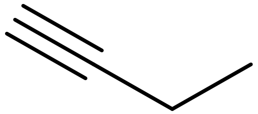
Suffix: -yne

$HC\equiv CH$

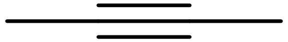
ethyne



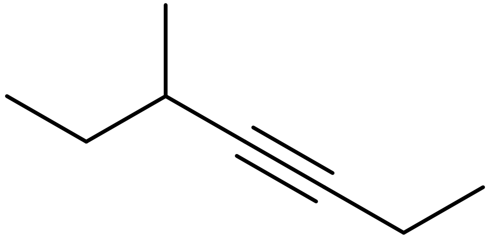
propyne

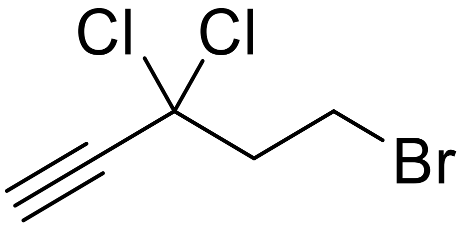


but-1-yne

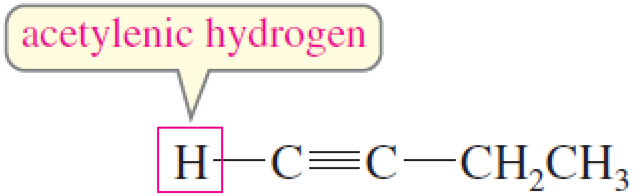


but-2-yne





Terminal alkynes



but-1-yne, a *terminal* alkyne

Physical Properties

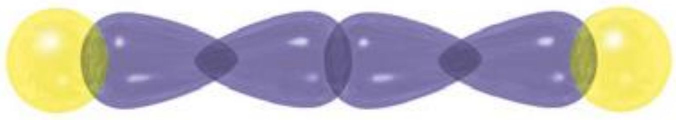
The physical properties of alkynes are **similar to those of alkanes and alkenes** of similar molecular weights.

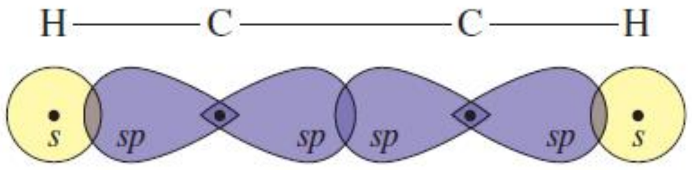
Name	Structure	mp (°C)	bp (°C)	Density (g/cm^3)
ethyne (acetylene)	$H-C\equiv C-H$	−82	−84	0.62
propyne	$H-C\equiv C-CH_3$	−101	−23	0.67
but-1-yne	$H-C\equiv C-CH_2CH_3$	−126	8	0.67
but-2-yne	$CH_3-C\equiv C-CH_3$	−32	27	0.69
pent-1-yne	$H-C\equiv C-CH_2CH_2CH_3$	−90	40	0.70
pent-2-yne	$CH_3-C\equiv C-CH_2CH_3$	−101	55	0.71
3-methylbut-1-yne	$CH_3-CH(CH_3)-C\equiv C-H$		28	0.67
hex-1-yne	$H-C\equiv C-(CH_2)_3-CH_3$	−132	71	0.72
hex-2-yne	$CH_3-C\equiv C-CH_2CH_2CH_3$	−90	84	0.73
hex-3-yne	$CH_3CH_2-C\equiv C-CH_2CH_3$	−101	82	0.73
3,3-dimethylbut-1-yne	$(CH_3)_3C-C\equiv C-H$	−81	38	0.67
hept-1-yne	$H-C\equiv C-(CH_2)_4CH_3$	−81	100	0.73
oct-1-yne	$H-C\equiv C-(CH_2)_5CH_3$	−79	125	0.75
non-1-yne	$H-C\equiv C-(CH_2)_6CH_3$	−50	151	0.76
dec-1-yne	$H-C\equiv C-(CH_2)_7CH_3$	−36	174	0.77

Nonpolar and nearly **insoluble in water**

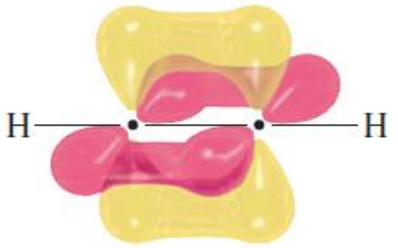
Electronic structure

Hybridization of the *s* orbital with one *p* orbital gives two hybrid orbitals, directed 180° apart, for each carbon atom. Overlap of these ***sp* hybrid orbitals** with each other gives the sigma bond framework

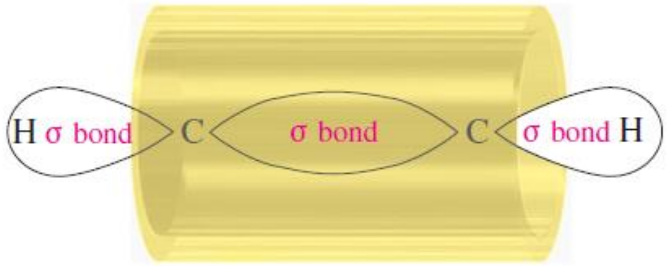




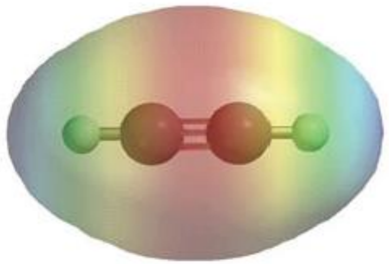
Two pi bonds result from overlap of the two remaining unhybridized ***p* orbitals** on each carbon atom.



overlap of *p* orbitals

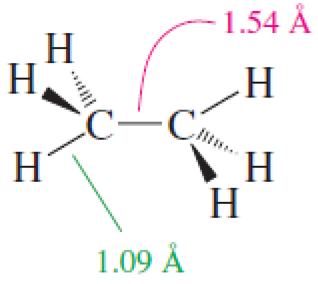


cylinder of electron density

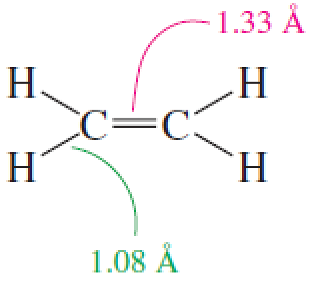


EPM of acetylene

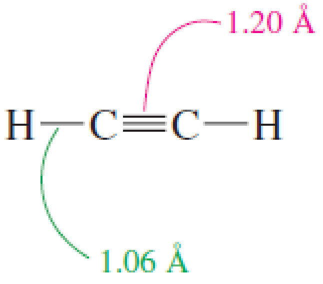
The triple bond is relatively **short** because of the attractive overlap of three bonding pairs of electrons and the high ***s* character** of the *sp* hybrid orbitals



ethane



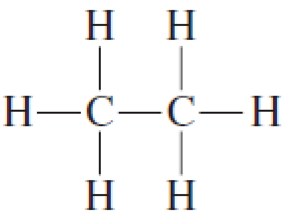
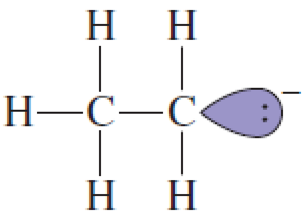
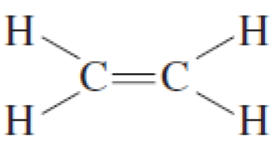
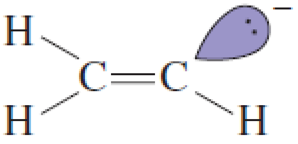
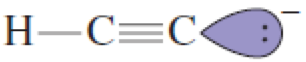
ethene

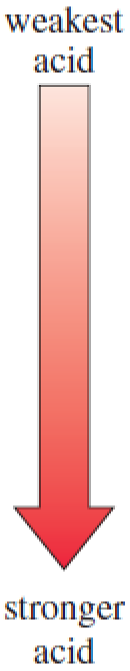


ethyne

Acidity of Terminal Alkynes

Terminal alkynes are much more acidic than other hydrocarbons (although still very weak acid)

Compound	Conjugate Base	Hybridization	*s* Character	pK_a
		sp^3	25%	50
		sp^2	33%	44
$:NH_3$	$^{-}:\ddot{N}H_2$	(ammonia)		35
H—C≡C—H		sp	50%	25
R—OH	R—$\ddot{\underset{..}{O}}$:$^-$	(alcohols)		16–18



Abstraction of an acetylenic proton gives a carbanion that has the lone pair of electrons in the ***sp* hybrid orbital**

Very strong bases (such as sodium amide, NH_2^-) deprotonate terminal acetylenes to form carbanions called acetylide ions

Acidity of Terminal Alkynes

Very strong bases (such as sodium amide, NH_2^-) deprotonate terminal acetylenes to form carbanions called **acetylide ions**

Acetylide ions are **strong nucleophiles**.
One of the best methods for synthesizing substituted alkynes is a nucleophilic attack by an acetylide ion on an unhindered alkyl halide.

Acidity of Terminal Alkynes

Example 1 Predict the products of the following reactions, or indicate if no significant reaction would take place.

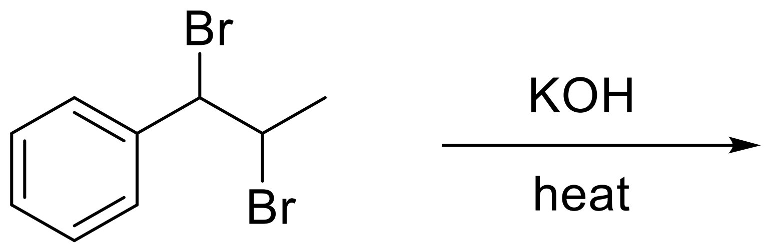
(a)

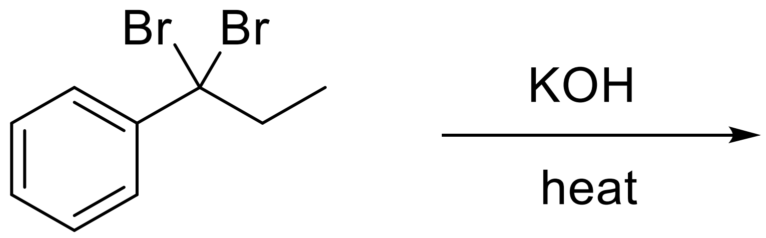
(b)

(c)

Preparation of Alkynes

We can generate a carbon–carbon triple bond by **eliminating two molecules of HX** from a ***geminal*** or ***vicinal*** dihalide.



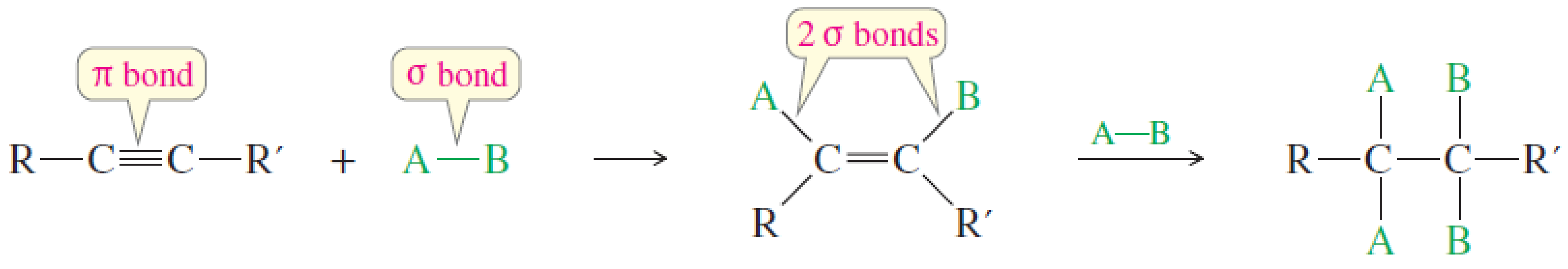


Reactions of Alkynes: Addition

Many of the reactions of alkynes are **similar to** the corresponding reactions of **alkenes** because both involve pi bonds between two carbon atoms

Bond	Total Energy	Class of Bond	Approximate Energy
C—C	347 kJ (83 kcal)	alkane sigma bond	347 kJ (83 kcal)
C=C	611 kJ (146 kcal)	alkene pi bond	264 kJ (63 kcal)
C≡C	837 kJ (200 kcal)	second alkyne pi bond	226 kJ (54 kcal)

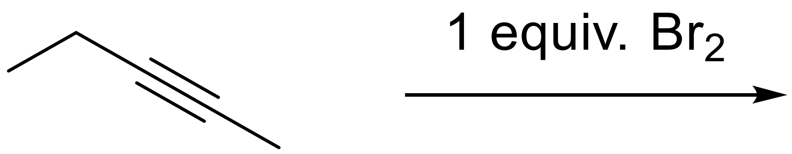
Alkynes have two pi bonds, so **up to two molecules** can add across the triple bond

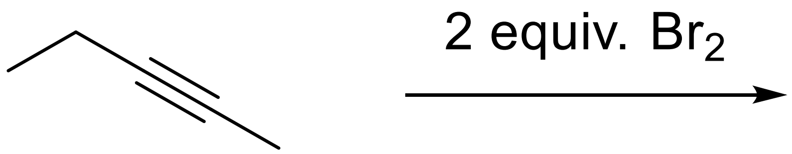


Sigma bonds are generally stronger than pi bonds, the reaction is usually **exothermic**.

Reactions of Alkynes: Addition

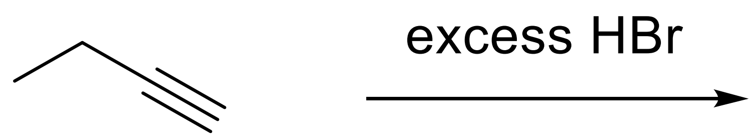
- **Addition of Halogens**

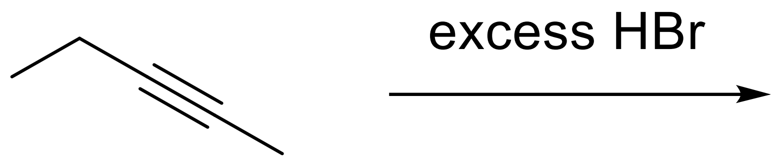




Reactions of Alkynes: Addition

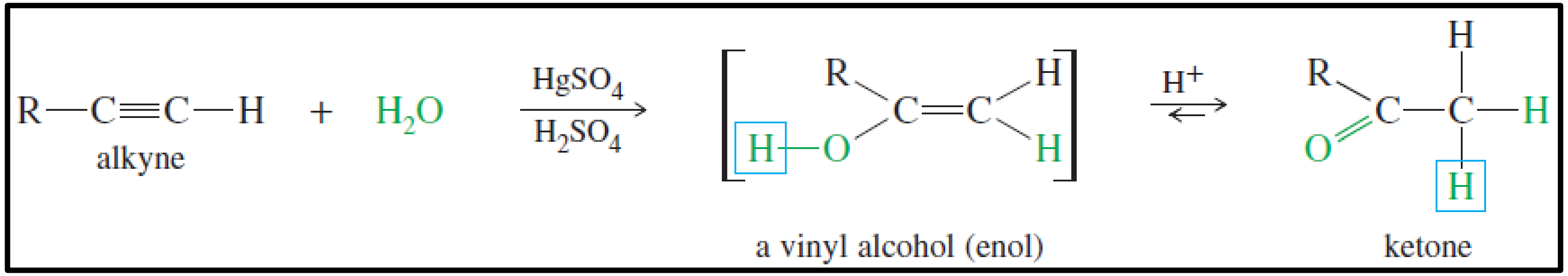
- **Addition of Hydrogen Halides**

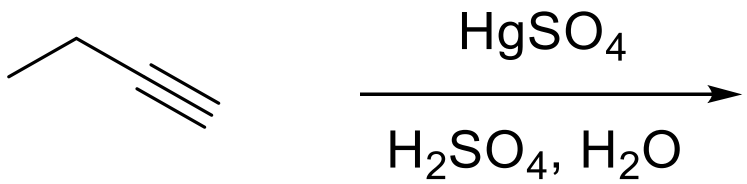




Reactions of Alkynes: Addition

- **Hydration** Alkynes undergo acid-catalyzed addition of water in the presence of **mercuric ion** as a **catalyst**

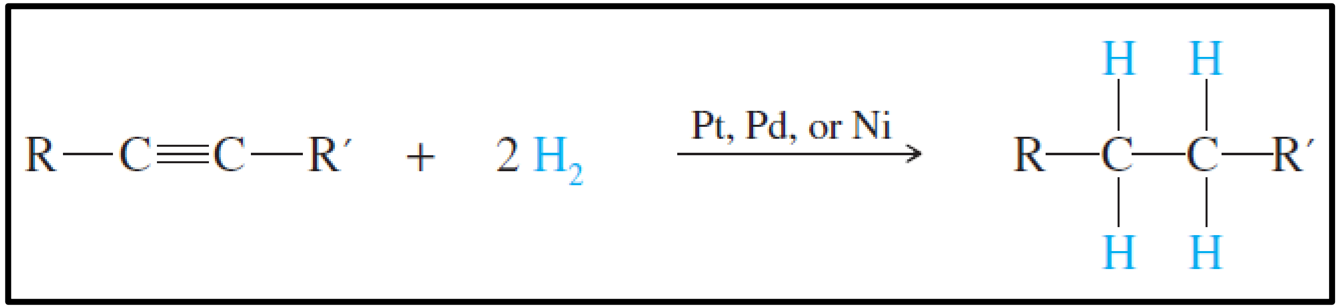


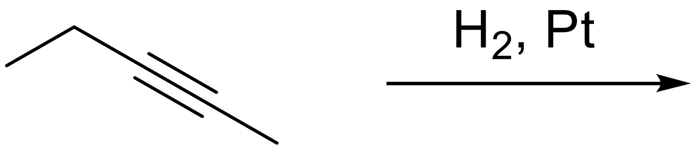


Reactions of Alkynes: Addition

- **Catalytic Hydrogenation**

  In the presence of a **suitable catalyst**, hydrogen adds to an alkyne, reducing it to an **alkane**.

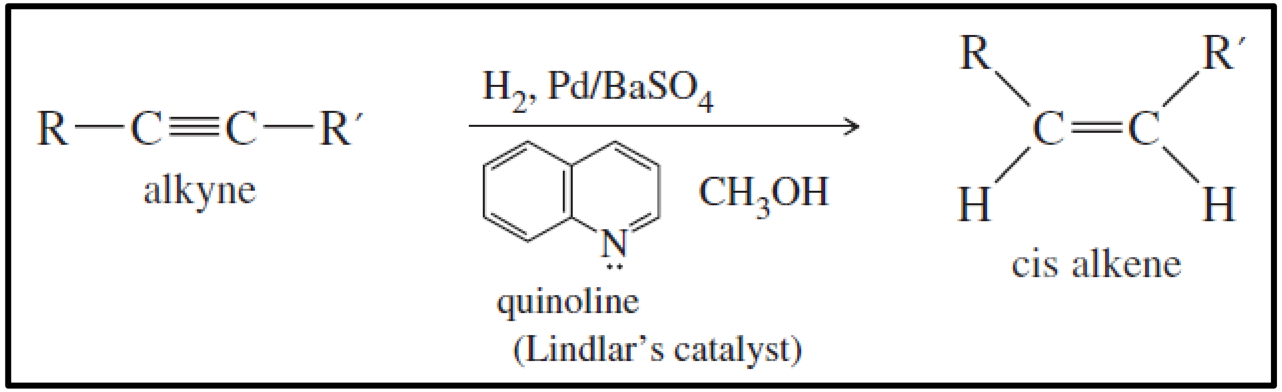


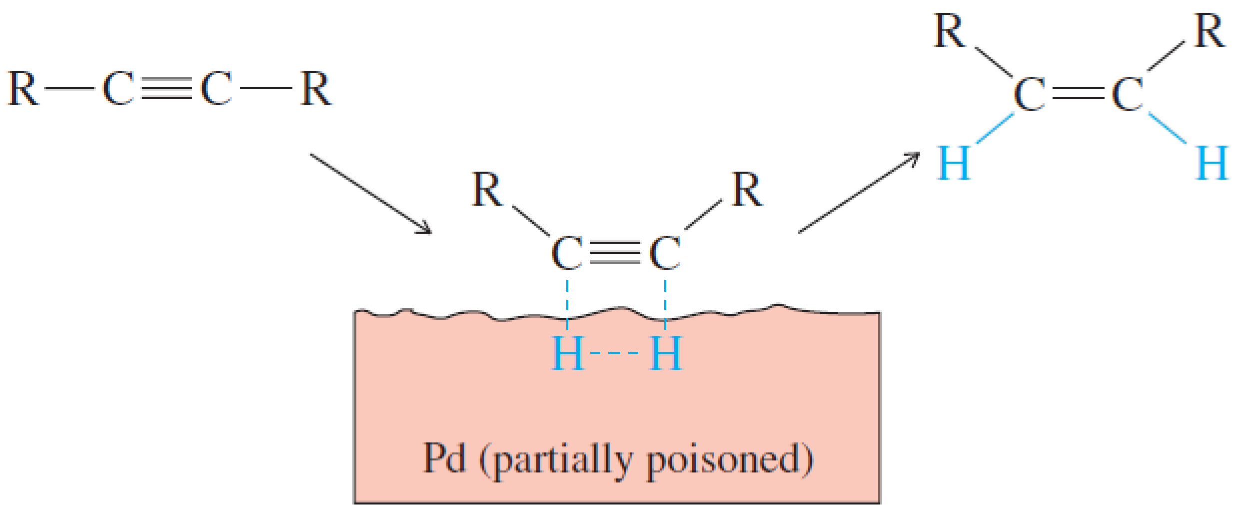


Reactions of Alkynes: Addition

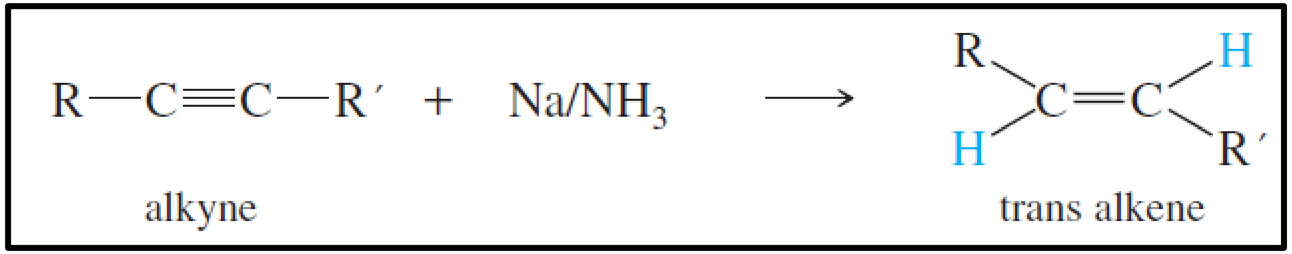
- **Catalytic Hydrogenation**

Hydrogenation of an alkyne can be stopped at the **alkene** stage by using a "**poisoned**" (partially deactivated) catalyst: such as **Lindlar's catalyst** (powdered barium sulfate coated with palladium, poisoned with quinoline)





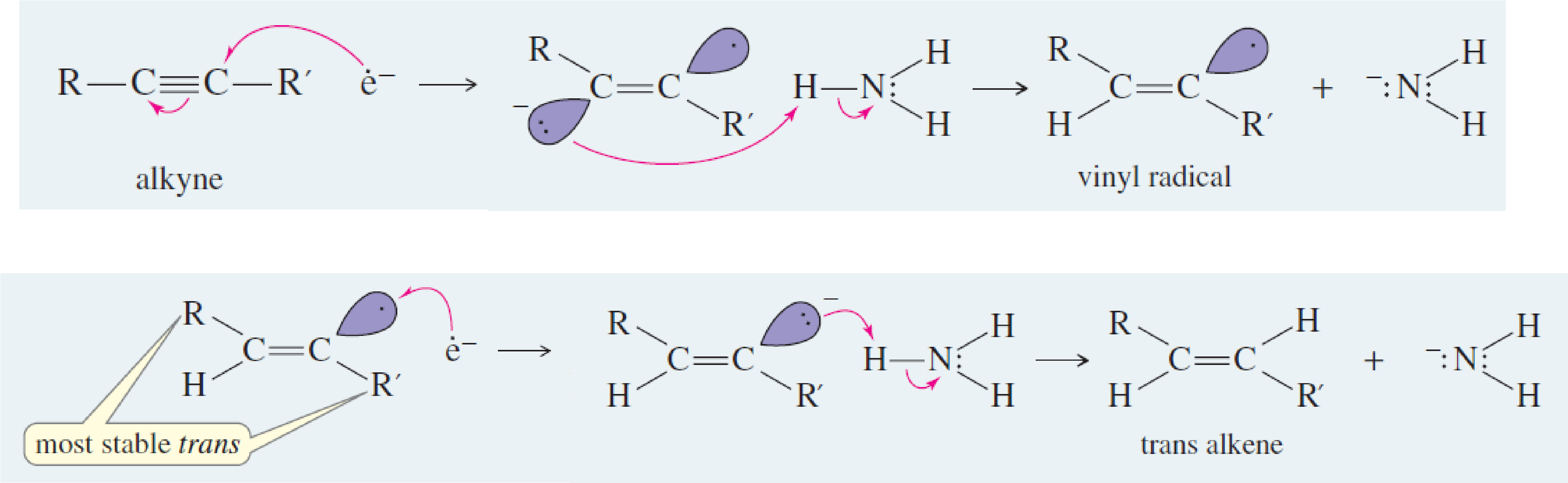
- **Metal–Ammonia Reduction to *trans* Alkenes**



Mechanism

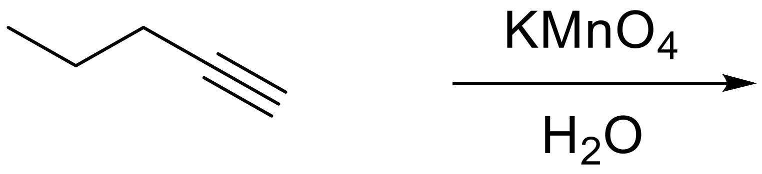
$$NH_3 + Na \longrightarrow NH_3\cdot e^- \text{ (deep blue solution)} + Na^+$$

solvated electron



Reactions of Alkynes: Oxidation

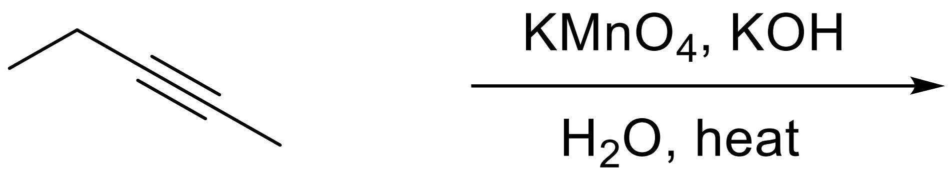
- **With $KMnO_4$ under mild conditions**

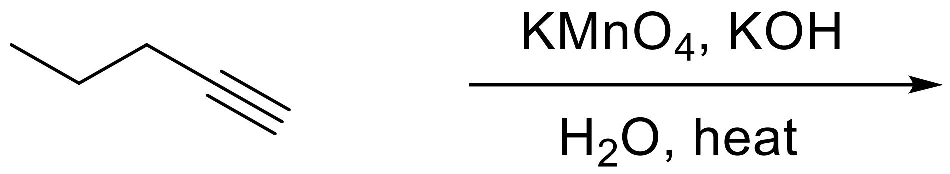


Reactions of Alkynes: Oxidation

- **With $KMnO_4$ under harsh conditions**

If the reaction mixture becomes **warm** or too **basic**, the diketone undergoes **oxidative cleavage**.





Example 2 Predict the products of the following reactions