Alkynes

- General formula is C_nH_{2n-2}
- Alkynes contain a triple bond.
- Carbon-carbon triple bond result from sp orbital on each C forming a sigma bond and unhybridized p_X and p_y orbitals forming a π bond
- The remaining sp orbitals form bonds to other atoms at 180º to C-C triple bond.

H−C≡C−H

1

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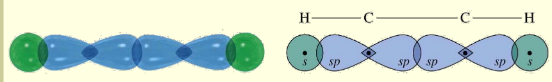
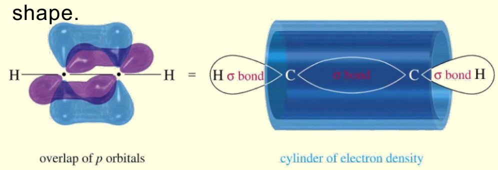
Electronic Structure

- The sigma bond is *sp-sp* overlap.



• The two pi bonds are unhybridized *p* overlaps at 90°, which blend into a cylindrical shape.



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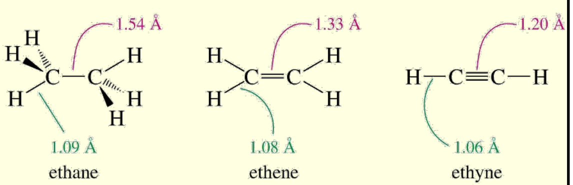
Bond Lengths

- More *s* character, so shorter length.
- Three bonding overlaps, so shorter.



Bond angle is 180°, so linear geometry.

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Nomenclature

- General hydrocarbon rules apply with "-*yne*" as a suffix indicating an alkyne.

C_2H_2 H:C:::C:H H—C ≡ C—H sp => linear, 180o
acetylene
ethyne

C_3H_4 $CH_3C{\equiv}CH$ methylacetylene
propyne

$H_3C{-}H_2C{-}C{\equiv}C{-}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$ 3-Nonyne

4

4

Nomenclature: IUPAC

- Find the longest chain containing the triple bond.
- Change ***-ane*** ending to ***-yne***.
- Number the chain, starting at the end closest to the triple bond.
- Give branches or other substituents a number to locate their position.

5

5

Nomenclature

$CH_3—C\equiv CH$

propyne

$CH_3—C\equiv C—CH_2—CH_2—Br$

5-bromo-2-pentyne

CH_3 (on C-2), CH_3 (on C-6)

$CH_3—CH—CH_2—C\equiv C—CH—CH_3$

2,6-dimethyl-3-heptyn

6

6

Nomenclature

Additional Functional Groups

- All other functional groups, except ethers and halides have a higher priority than alkynes.

CH_3 (on C-4)

$CH_2=CH—CH_2—CH—C\equiv CH$

4-methyl-1-hexen-5-yne

OH (on C-2)

$CH_3—C\equiv C—CH_2—CH—CH_3$

4-hexyn-2-ol

7

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Diyines and Triynes

- A compound with two triple bonds is a diyine.
  - A triyne has three triple bonds.
- Number from chain that ends nearest a double of triple bond – double bonds is preferred if both are present in the same relative position.

$H_3C-CH_2-C\equiv C-CH_2\cdot C\equiv CH$

1,4-Heptdiyne

8

8

Acidity of Alkynes

- Terminal alkynes, R-C≡C-H, are more acidic than other hydrocarbons.
- Acetylene → acetylide by NH_2^-, but not by OH^- or RO^-.
- More *s* character, so pair of electrons in anion is held more closely to the nucleus. Less charge separation, so more stable.

9

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Acidity Table

Compound	Conjugate Base	Hybridization	*s* Character	pK_a
H_3C-CH_3	$H_3C-CH_2^-$	sp^3	25%	50
$H_2C=CH_2$	$H_2C=CH^-$	sp^2	33%	44
$:NH_3$	$:\ddot{N}H_2^-$	(ammonia)		35
$H-C\equiv C-H$	$H-C\equiv C:^-$	sp	50%	25
$R-OH$	$R-\ddot{O}:^-$	(alcohols)		16–18

weakest acid → stronger acid

10

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Acidity of Alkynes

Formation of Acetylide Anions

- Terminal alkynes are weak Brønsted acids (alkenes and alkanes are much less acidic, p*K*a ~ 25.)
- Reaction of strong anhydrous bases (sodium amide) with a terminal acetylene produces an **acetylide ion**
- The sp-hydbridization at carbon holds negative charge relatively close to the positive nucleus

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

Acetylide anion

- $NaNH_2$ is produced by the reaction of ammonia with sodium metal.

$$H-\ddot{N}H-H + Na \xrightarrow{Fe^{+3}} H-\ddot{N}H^{\ominus}Na^+ + 1/2\ H_2$$

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Alkynes from Acetylides

- Acetylide ions are good nucleophiles.
- S_N2 reaction with 1° alkyl halides lengthens the alkyne chain.

$$CH_3-C\equiv C:^-\ Na^+ + CH_3CH_2-Br \longrightarrow CH_3-C\equiv C-CH_2-CH_3 + NaBr$$

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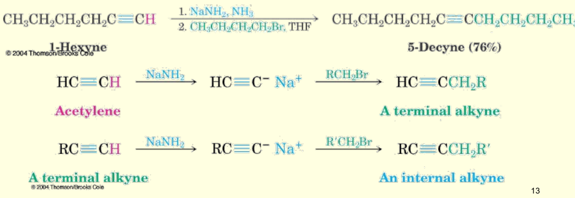
Alkylation of Acetylide Anions

- Acetylide ions can react as nucleophiles as well as bases
- Reaction with a primary alkyl halide produces a hydrocarbon that contains carbons from both partners, providing a general route to larger alkynes



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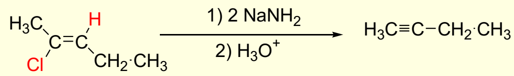
Preparation of Alkynes:

Elimination Reactions of Dihalides

- Treatment of a 1,2 dihaloalkane with KOH or NaOH (strong Base) produces a two-fold elimination of HX



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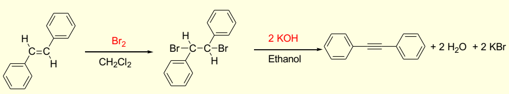
Preparation of Alkynes

From Vicinal Dihalides

- Vicinal dihalides are available from addition of bromine or chlorine to an alkene.
- Intermediate is a vinyl halide.



A vicinal dibromide

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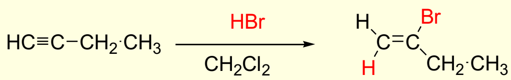
Reactions of Alkynes

Addition of HX

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



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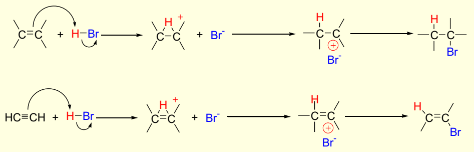
Reactions of Alkynes

- Addition of H-X to alkyne should produce a vinylic carbocation intermediate
  - Secondary vinyl carbocations form less readily than primary alkyl carbocations
  - Primary vinyl carbocations probably do not form at all



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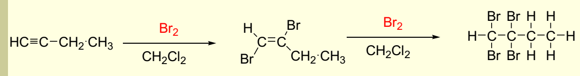
Reactions of Alkynes

Addition of Bromine and Chlorine

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



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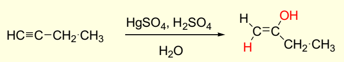
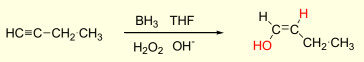
Hydration of Alkynes

- Addition of H-OH as in alkenes
  - Mercury (II) catalyzes Markovinikov oriented addition



  - Hydroboration-oxidation gives the non-Markovnikov product



Anti- Markinov

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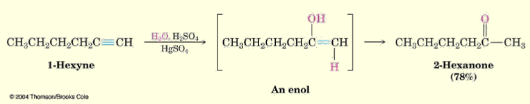
Reactions of Alkynes

Mercury(II)-Catalyzed Hydration

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



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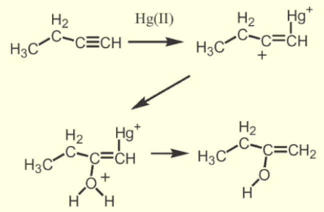
Reactions of Alkynes

Mechanism of Mercury(II)-Catalyzed Hydration

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



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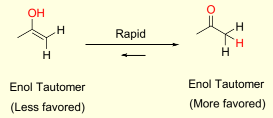
Keto-enol Tautomerism

- Isomeric compounds that can rapidly 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



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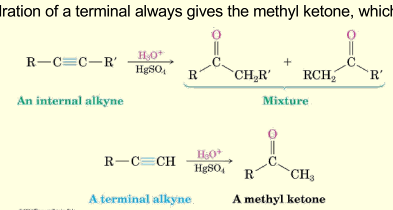
Reactions of Alkynes

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 always gives the methyl ketone, which is useful



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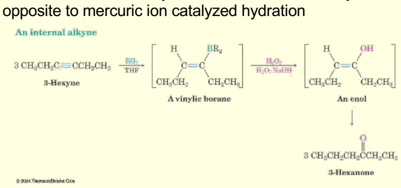
Reactions of Alkynes

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



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Reactions of Alkynes

Reduction

- 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

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

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

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Lindlar catalyst

- A Lindlar catalyst is a heterogeneous catalyst that consists of palladium deposited on calcium carbonate which is then poisoned with various forms of lead or sulphur.
- It is used for the hydrogenation of alkynes to alkenes
  - Without further reduction into alkanes
- Named after its inventor **Herbert Lindlar**

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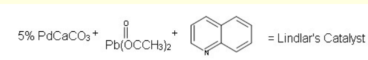
Lindlar catalyst

- Lindlar's catalyst is a palladium catalyst poisoned with traces of lead and quinoline,
  - Lead and Quinoline acts as poison that reduce its activity such that it can only reduce alkynes, not alkenes.
  - It always gives the cis-alkene, in contrast to Na/NH3, which gives the trans alkenes.
  - Lindlar's catalyst doesn't really have a “structure.



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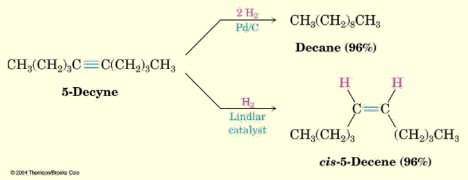
Reactions of Alkynes

Conversion of Alkynes to cis-Alkenes

- Addition of H2 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)



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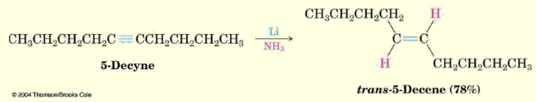
Reactions of Alkynes

Conversion of Alkynes to trans-Alkenes

- Anhydrous ammonia (NH_3) is a liquid below -33 ºC
  - 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



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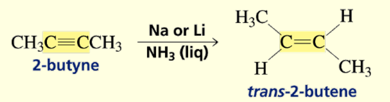
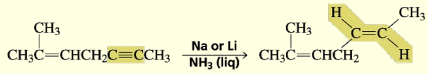
Dissolving-Metal Reduction





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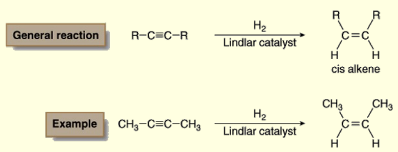
Dissolving-Metal Reduction

Alkyne reduction to a Cis Alkene

- Reduction of an alkyne to a cis alkene is a stereoselective reaction, because only one stereoisomer is formed.
- Hydroboration-acidification instead of Lindlar's catalyst can be used to get a cis alkene.



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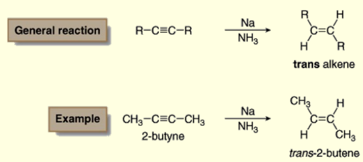
Dissolving-Metal Reduction

Alkyne reduction to a Trans Alkene

- In a dissolving metal reduction (such as Na in NH_3), the elements of H_2 are added in an anti fashion to form a trans alkene.
  - Na has only one electron, so, electrons for the reduction are added sequentially from 2 Na atoms.



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Dissolving-Metal Reduction

Alkyne reduction to a Trans Alkene

- Dissolving metal reduction of a triple bond with Na in NH_3 is a stereoselective reaction because it forms a trans product exclusively.
- Dissolving metal reductions always form the more stable trans product preferentially.

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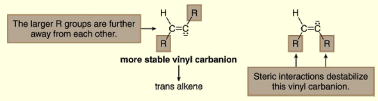
Dissolving-Metal Reduction

Alkyne reduction to a Trans Alkene

- The trans alkene is formed because the vinyl carbanion intermediate that is formed is more stable when the larger R groups are further away from each other to avoid steric interactions. Protonation of this anion leads to the more stable trans adduct.



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Dissolving-Metal Reduction

- Metal (Li, Na, K) is reducing agent;
  - H_2 is not involved
  - There are four steps
    - Electron transfer
    - Proton transfer
    - Electron transfer
    - Proton transfer

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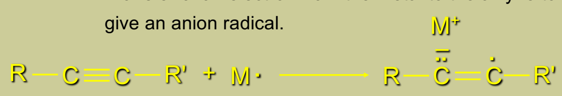
Dissolving-Metal Reduction

Mechanism

- **Step 1 (Electron Transfer)**

  Transfer of an electron from the metal to the alkyne to give an anion radical.



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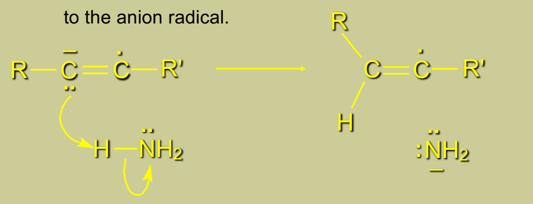
Dissolving-Metal Reduction

Mechanism

- **Step 2 (Proton Transfer)**

  Transfer of a proton from the solvent (liquid ammonia) to the anion radical.



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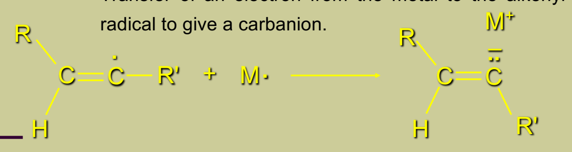
Dissolving-Metal Reduction

Mechanism

- **Step 3 (Electron Transfer)**

  Transfer of an electron from the metal to the alkenyl radical to give a carbanion.



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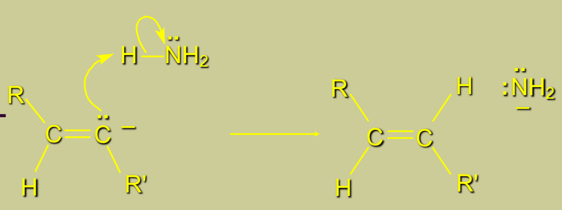
Dissolving-Metal Reduction

Mechanism

- **Step 4 (Proton Transfer)**

  Transfer of a proton from the solvent (liquid ammonia) to the carbanion .



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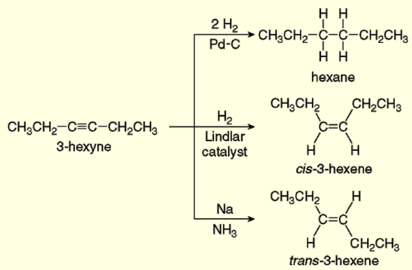
Dissolving-Metal Reduction

Summary of Alkyne Reductions

- Three methods to reduce a triple bond



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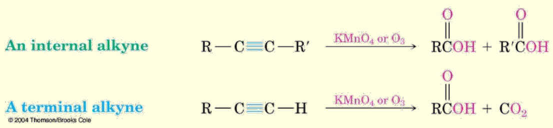
Reactions of Alkynes

Oxidative Cleavage of Alkynes

- Strong oxidizing reagents (O_3 or $KMnO_4$) cleave internal alkynes, producing two carboxylic acids
- Terminal alkynes are oxidized to a carboxylic acid and carbon dioxide
- Neither process is useful in modern synthesis – were used to elucidate structures because the products indicate the structure of the alkyne precursor



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