

Chapter 9: Alkynes

9.1: Sources of Alkynes (please read)

9.2: Nomenclature

Systematic Nomenclature: Prefix-Parent-Suffix

Naming Alkynes: Suffix: -yne

Many of the same rules for alkenes apply to alkynes

1. Number the carbon chain from the end of the carbon nearest the triple bond
2. The alkyne position is indicated by the number of the alkyne carbon in the chain
3. Compounds with two triple bonds are referred to as diynes, three triple bonds as triynes, etc

9.3: Physical Properties of Alkynes (please read)

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9.4: Structure and Bonding in Alkynes: *sp* Hybridization



acetylene
(ethyne)

bond angles:

H-C-C = 180° (linear geometry)

bond distances:

C-H = 106 pm

C≡C = 120 pm

Each carbon is *sp* hybridized – linear geometry

C≡C bond consists of one σ -bond (*sp* hybridized orbitals) and two π -bond (unhybridized p-orbitals) (see ch. 2 notes)

Bond dissociation energies ($\Delta H^\circ_{\text{C-C}}$)

$\Delta H^\circ \text{C}=\text{C} = 611 \text{ KJ/mol}$ $\Delta H^\circ \text{C}\equiv\text{C} = 820 \text{ KJ/mol}$

$\Delta H^\circ \text{C}-\text{C} = 368 \text{ KJ/mol}$ $\Delta H^\circ \text{C}-\text{C} = 368 \text{ KJ/mol}$

π -bond = 243 KJ/mol π -bonds = 452 KJ/mol

226 KJ/mol per π -bond

The π -bond of an alkene is ~17 KJ/mol more stable than the π -bond of an alkyne.

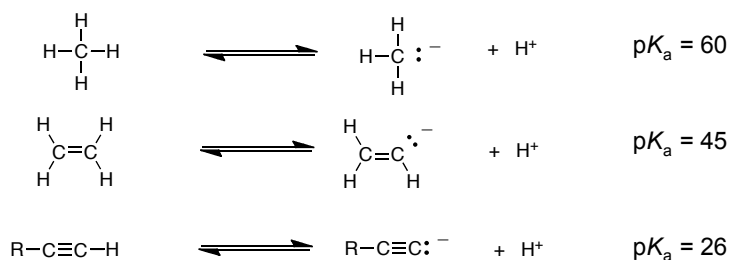
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hybridization of C	sp^3	sp^2	sp
geometry	tetrahedral	trigonal planar	linear
ΔH°_{C-C}	368 kJ/mol	611 kJ/mol	820 kJ/mol
ΔH°_{C-H}	410 kJ/mol	452 kJ/mol	536 kJ/mol
% s character	25%	33%	50%
pK_a	62	45	26

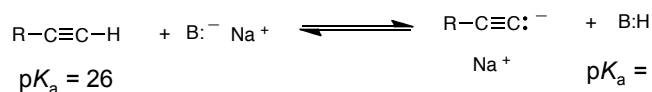
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9.5: Acidity of Acetylene and Terminal Alkynes

In general, the C-H bond of hydrocarbons are very weak acids. The R-C≡C-H bond of a terminal acetylene is weakly acid, $pK_a \sim 26$.

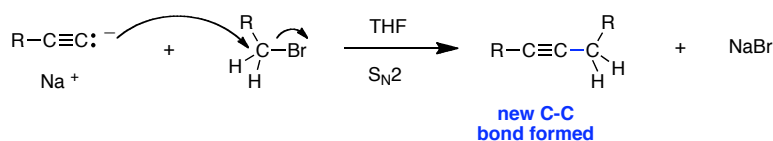


A strong base can deprotonate terminal acetylenes to generate an acetylide anion.

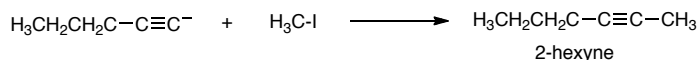
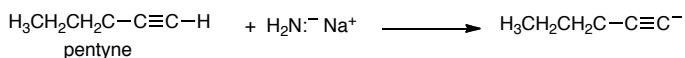
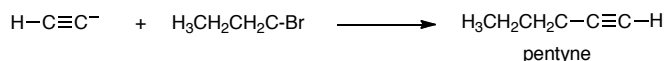
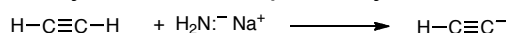


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9.6: Preparation of Alkynes by Alkylation of Acetylene and Terminal Alkynes - Acetylide anions are strong nucleophiles and will undergo nucleophilic substitution reactions with primary alkyl halides, resulting in the formation of a C-C bond.



Alkylation of acetylide anions is a general method of making higher alkynes from simpler alkynes.

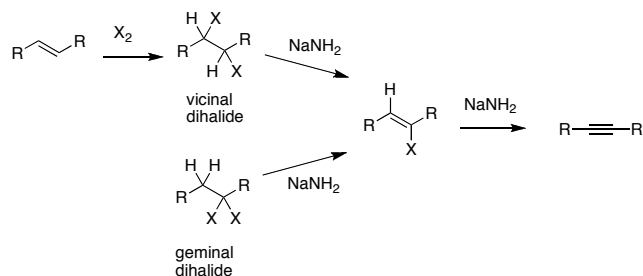


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Alkylation of acetylide anions is generally limited to primary alkyl halides. Acetylide anions act as a base with secondary and tertiary alkyl halides resulting in E2 elimination.

9.7: Preparation of Alkynes by Elimination Reactions

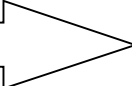
Double dehydrohalogenation reaction

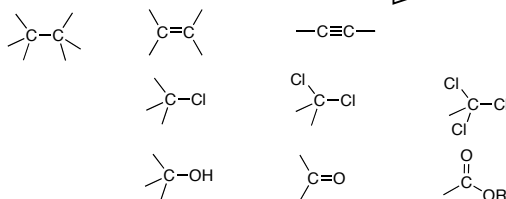


3 equivalents of NaNH_2 are required for preparing terminal alkynes from 1,2- or 1,1-dihaloalkane.

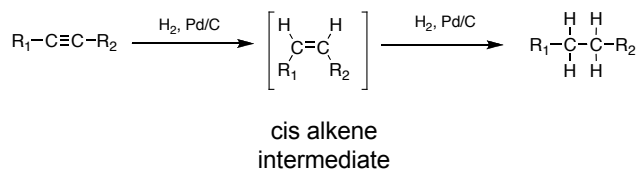
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9.8: Reactions of Alkynes - alkynes undergo addition reactions similar to alkenes.

Increasing oxidation state 



9.9: Hydrogenation of Alkynes - The hydrogenation of an alkyne cannot be stopped at the alkene stage under normal hydrogenation conditions (H_2 , metal catalyst)



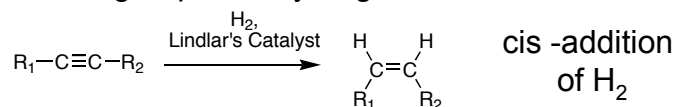
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The π -bonds of alkynes are slightly more reactive toward hydrogenation than the π -bond of an alkene.

Lindlar's catalyst: "poisoned" palladium catalyst

Pd on $CaCO_3$ + $Pb(OAc)_4$ + quinoline (amine)

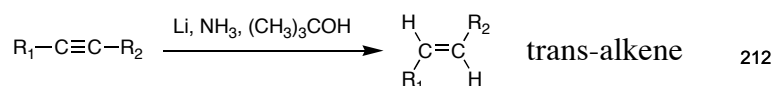
"poisons" reduce the catalysts activity so only the most reactive functional groups are hydrogenated



Hydrogenation can be stopped at the cis-alkene stage with Lindlar's catalyst

9.10: Metal-Ammonia Reduction of Alkynes - Dissolving Metal Reduction: $Li(0)$ metal in liquid ammonia (NH_3)

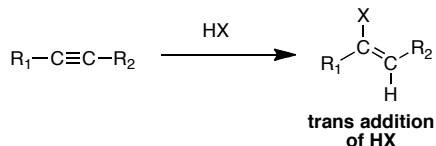
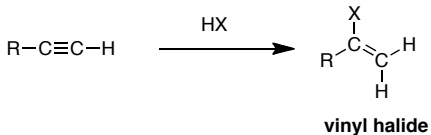
$Li(0)$ in $NH_3 \longrightarrow e^-$ (solvated electron)



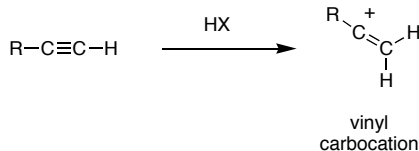
9.11: Addition of Hydrogen Halides to Alkynes

Addition of HX to acetylenes: Markovnikov addition

only useful for
terminal or
symmetrical
acetylenes
($R_1 = R_2$)



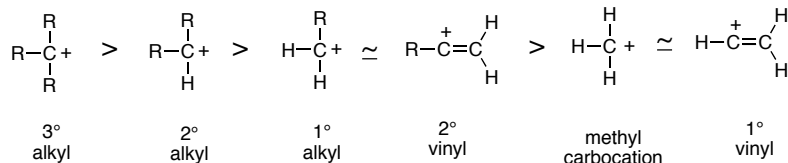
Mechanism ?



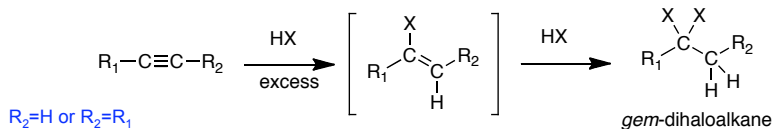
$$\text{rate} = k [\text{alkyne}][\text{HX}]^2$$

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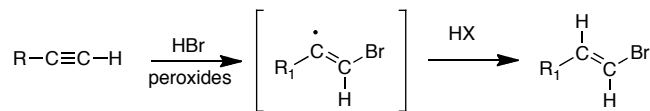
Carbocation Stability



gem-dihaloalkanes are obtained with excess HX - addition follows Markovnikov's rule

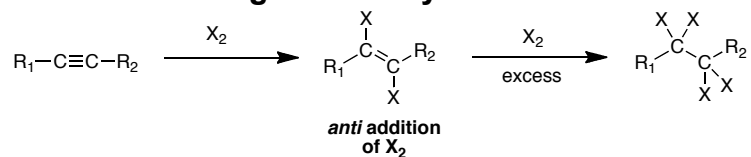


Anti-Markovnikov addition of HBr to terminal alkynes in the Presence of peroxides (radical mechanism)

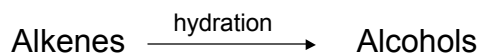


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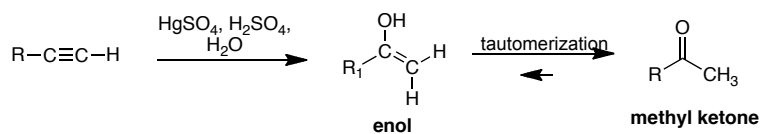
9.13: Addition of Halogens to Alkynes



9.12: Hydration of Alkynes



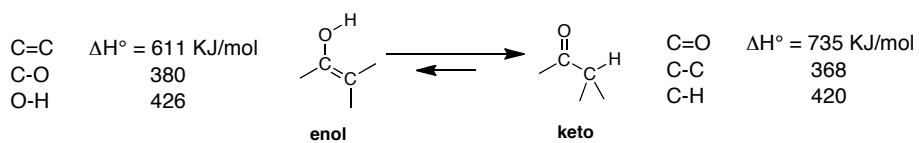
Hg (II) catalyzed hydration of alkynes: similar to oxymercuration
- Markovnikov Addition



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Tautomerization - equilibrium between two isomers (tautomer), which differ by the migration of a proton and a π -bond.

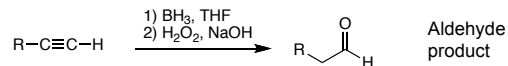
Keto-enol tautomerization - normally favors the keto form (C=O)



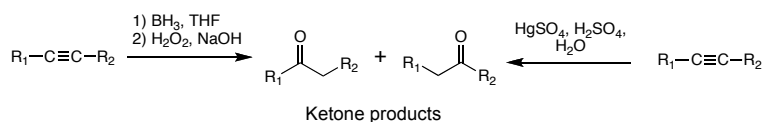
Keto-enol tautomerization is acid-catalyzed

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Hydroboration of Alkynes - anti-Markovnikov hydration of an alkyne (complementary to the Hg(II) catalyzed method)



Hg(II)-catalyzed hydration and hydroboration are equivalent for internal alkynes

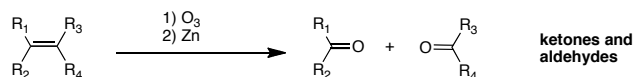


Hydration of an internal alkyne is only useful for symmetrical acetylenes ($\text{R}_1 = \text{R}_2$)

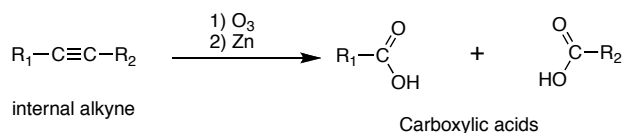
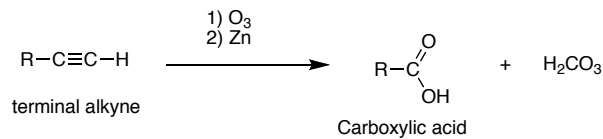
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9.14: Ozonolysis of Alkynes

Ozonolysis of alkenes (sect. XX):



Ozonolysis of Alkynes

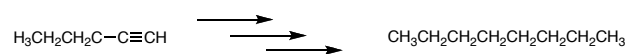


Alkynes are less reactive toward ozonolysis than alkenes. An alkenes can be oxidatively cleaved by ozone in the presence of an alkyne.

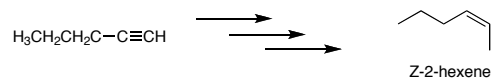
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C-C bond forming reactions are important for organic synthesis

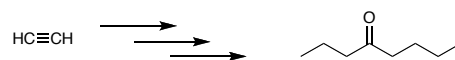
Prepare octane from 1-pentyne



Prepare (Z)-2-hexene from 1-pentyne



Prepare 4-octanone from acetylene



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