Reactions of Alkynes - Chapter 9 (Klein)

Chapter 9 Outline

I. Structure, Properties and Nomenclature of Alkynes (9.1, 9.2) ***SkillBuilder 9.1***
II. Reductions of alkynes (9.5)
III. Ozonolysis of alkynes (9.9)
IV. Addition reactions
  A. Br_2 (9.8)
  B. HBr (9.6)
  C. Hydration of alkynes (9.7) ***SkillBuilders 9.3, 9.4***
V. Alkyne synthesis
  A. by E2/dehydrohalogenation (9.4)
  B. by alkylation reaction (9.3, 9.10) ***SkillBuilders 9.2, 9.5***
VII. Synthesis strategies (9.11) ***SkillBuilder 9.6***

$HC\equiv CH$

ethyne
(acetylene)

I. Alkyne structure

(Nomenclature, section 9.2, was covered in Chapter 8 skeleton notes)

$-C\equiv C-$

3-D sketch: *p* orbitals are orthogonal to *sp* linear

Types of alkynes:

$RC\equiv CR$

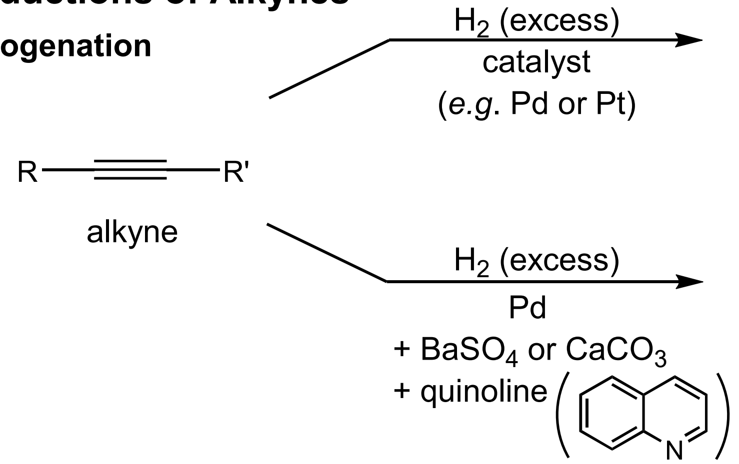
internal

$RC\equiv CH$

terminal

II. Reductions of Alkynes

Hydrogenation



(add 2 equivalents of H_2)

(syn addition of 1 equiv. of H_2)

Dissolving Metal Reduction

$$R-C\equiv C-R' \xrightarrow[NH_3]{\text{Na or Li}}$$

alkyne

Na° metal is a reducing agent (single electron donor)

III. Ozonolysis of Alkynes (9.9)

$$R{-}{\equiv}{-}R' \xrightarrow[\text{2) } H_2O\text{ (workup)}]{\text{1) } O_3}$$

alkyne

an oxidation reaction: 3 C–C bonds ⇨

IV. Addition Reactions

A. Bromination (9.8)

$$CH_3C\equiv CH \xrightarrow[\text{["xs" = "excess"]}]{Br_2\text{ (xs)}}$$

* adds 2 equivalents

* no regiochemistry

* no stereochemistry

* *FYI 1 eq.* Br_2 *gives (E)-dibromoalkene*

B. Addition of HBr (9.6)

$$CH_3C\equiv CH \xrightarrow{\text{HBr (xs)}}$$

* adds 2 equivalents HX

* Markovnikov addition of both

* same mechanism as alkene

Mechanism:

Practice: Provide reagents to achieve the following transformation.

retrosynthesis asks *"what starting material do I need?"* ⟹

C. Hydration of Alkynes (9.7)

$$CH_3C\equiv CH \xrightarrow[\substack{H_2SO_4 \\ HgSO_4}]{H_2O}$$

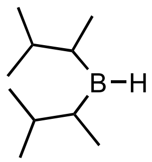
Mechanism:

"Hydration" via Hydroboration-Oxidation

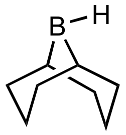
$$CH_3C\equiv CH \xrightarrow[\substack{2)\ H_2O_2 \\ NaOH}]{1)\ Sia_2BH}$$

BULKY boron reagents:

Sia_2BH **9-BBN**



disiamylborane

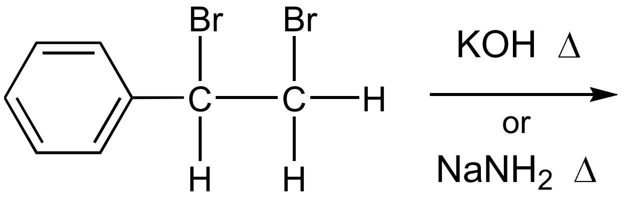


SkillBuilders 9.3, 9.4

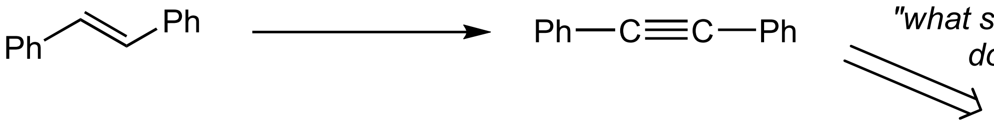
V. Alkyne Synthesis

A. By Dehydrohalogenation (9.4)

FYI: a terminal alkyne product will be deprotonated in strongly basic conditions, so aqueous workup is required to neutralize.

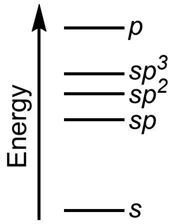


Practice: Provide reagents to achieve the following transformation.

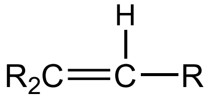


retrosynthesis asks *"what starting material do I need?"*

B. Alkyne Synthesis using $RC{\equiv}\ddot{C}^{\ominus}$ $(RC{\equiv}CNa)$



Acidity of Alkynes (9.3)

	$R-C\equiv C-H$	 $R_2C=\overset{H}{C}-R$	R_3C-H
	alkyne	alkene	alkane
pK_a	26	36	49

Why? Look at conjugate bases!

$R-C\equiv\ddot{C}^{\ominus}$ $R_2C=\ddot{C}^{\ominus}-R$ $R_3C\colon^{\ominus}$

SkillBuilder 9.2

Preparation of Acetylide/Alkynide Anions

Need a VERY STRONG base to deprotonate $RC\equiv CH$

$$RC\equiv CH \quad + \quad NaNH_2 \quad \rightleftharpoons$$

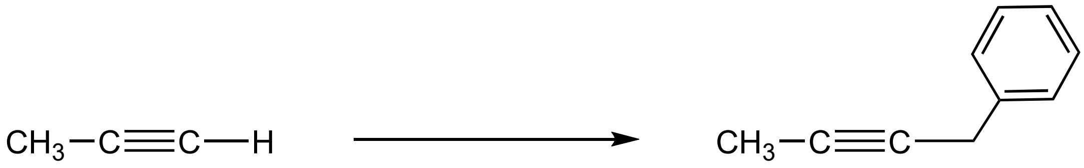
pK_a 26

Synthesis Using Acetylide/Alkynide Anions: 1) Deprotonation; 2) Alkylation

$$CH_3C\equiv C-H \xrightarrow[NH_3]{NaNH_2} \qquad \xrightarrow{CH_3CH_2-Br}$$

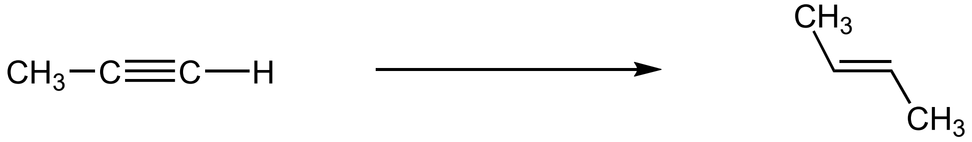
terminal alkyne

Practice: Provide reagents to achieve the following transformation.

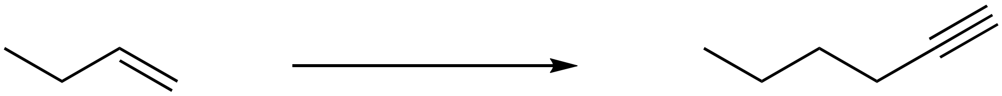


SkillBuilder 9.5

Provide reagents to achieve the following transformation.



Provide reagents to achieve the following transformation.



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Chapter 9 (Klein) Summary: Reactions of Alkynes

I. Structure, Properties and Nomenclature of Alkynes (9.1, 9.2) SkillBuilder 9.1

II. Reductions of alkynes (9.5)
  i) H_2/catalyst (e.g., Pd, Ni, Pt, $RhCl[PR_3]_3$) adds 2 equiv. to give an alkane
  ii) H_2/poisoned cat. (Lindlar's catalyst) adds 1 equiv. to give a cis alkene
  iii) Na/NH_3 (dissolving metal reduction) converts internal alkyne to a trans alkene

III. Ozonolysis of alkynes (9.9)
  i) cleave C≡C triple bond to give 2 carboxylic acids

IV. Addition reactions
  i) Br_2 (adds 2 equivalents) (9.8)
  ii) HBr (adds 2 equivalents, both Markovnikov) (9.6)
  iii) Hydration of alkynes (9.7) ***SkillBuilders 9.3, 9.4***
    A) Markovnikov addition of -H and -OH (one equivalent) to give enol
    B) tautomerization of enol to ketone/ald. (1st step protonate; 2nd step deprotonate)

V. Alkyne preparation by double E2/dehydrohalogenation
  i) loss of HX twice with strong base and heat (9.4)

VI. Alkyne synthesis by alkylation reaction (9.10)
  i) deprotonation of alkynes (9.3)
    A) acidity of alkynes ($RC{\equiv}CH + NaNH_2 \rightarrow RC{\equiv}CNa$) ***SkillBuilder 9.2***
    B) RC≡CNa can be a nucleophile (S_N2 on MeI or primary R'X) ***SkillBuilder 9.5***

VII. Synthesis strategies (9.11) ***SkillBuilder 9.6***
  i) Are there any changes to the carbon skeleton? (use RC≡CNa nucleophile + R'X)
  ii) Are there any changes to the identity/position of functional group?
  iii) Make logical disconnections to develop a retrosynthetic plan.

Suggested textbook problems 1–66 (skip 44a).

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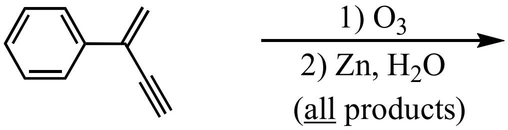
Alkene/Alkyne Predict the Products Homework, Part II

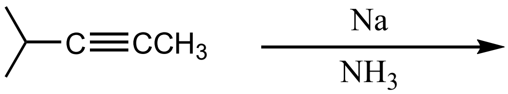
Name:______________________________________

Predict the major product(s) expected for each of the following reactions. **Remember to indicate stereochemistry, when appropriate**. If no reaction is expected, write NR.

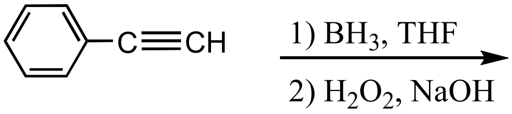
A)



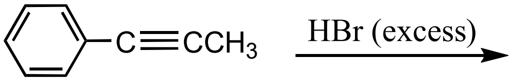
B)



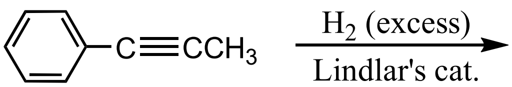
C)



D)



E)



F)

$$CH_3CH_2C\equiv CH \xrightarrow[2)\ CH_3I]{1)\ NaNH_2}$$

For each of the following reactions, predict the major product(s) and describe the product(s) as either a, b, c, d or e.

- **a)** a single product with no chiral centers
- **b)** a single meso product
- **c)** a 1:1 mixture of enantiomers (racemate)
- **d)** a mixture of diastereomers
- **e)** a single enantiomer