
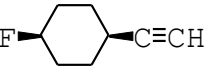
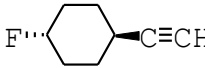


Answers to Puzzles of Chapter 9
Alkynes

9.1 (a) 2-butyne (b) 5-bromo-6-methyl-3-butyne (c) 3-phenyl-1-propyne
(d) 3-propyl-1-heptyne (e) 2-hexen-4-yn-1-ol (f) 1,4-pentadiyne

9.2 (a) $\text{HC}\equiv\text{CCH}_2\text{Cl}$ (b) - $\text{CH}_2\text{C}\equiv\text{CCH}_3$ (c) $\text{CH}_3\text{CH}=\text{CHC}\equiv\text{CCH}=\text{CHCH}_3$

(d) $\text{HC}\equiv\text{C}\overset{\text{OH}}{\underset{|}{\text{C}}}\text{HClI}_2\text{CH}_3$

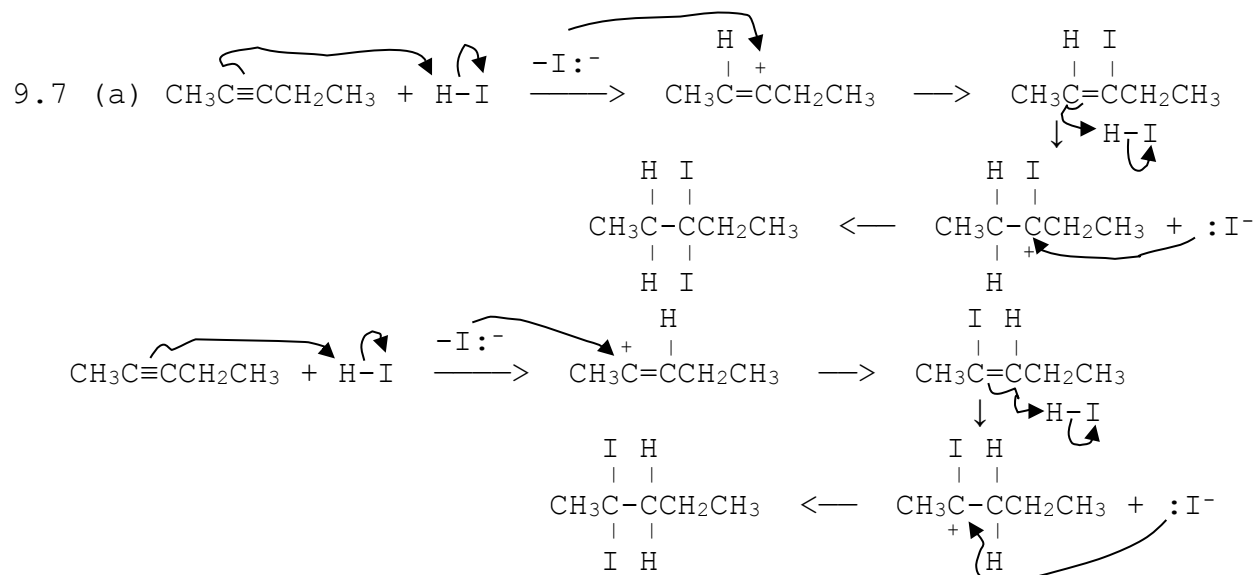
9.3 (a) e.g.,  (b) 
trans 1-ethynyl-4-fluorocyclohexane

9.4 (a) each C is *sp* (b) fully linear

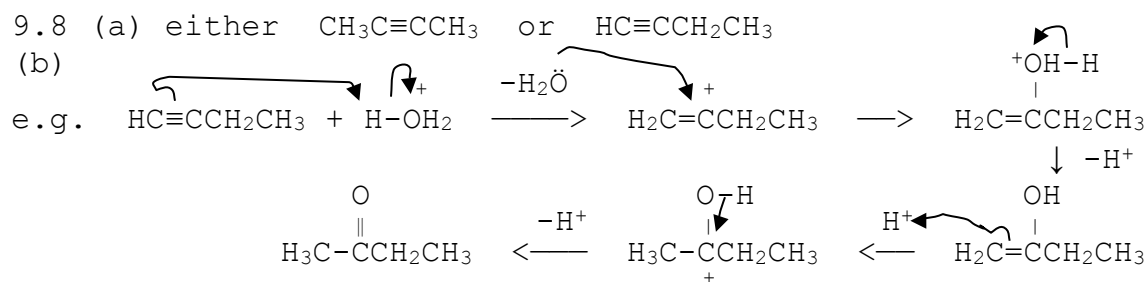
9.5 by bp: 1-butanol > 1-pentyne > 1-butyne

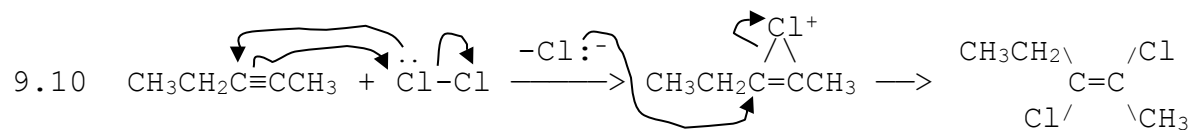
With greater size and dispersion forces, 1-pentyne has a higher bp than 1-butyne. With hydrogen "bonds" and dipole-dipole forces, 1-butanol has a higher bp than 1-pentyne.

9.6 a nonpolar solvent; e.g., hexane

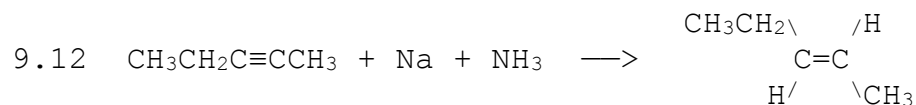


(b) *sp*





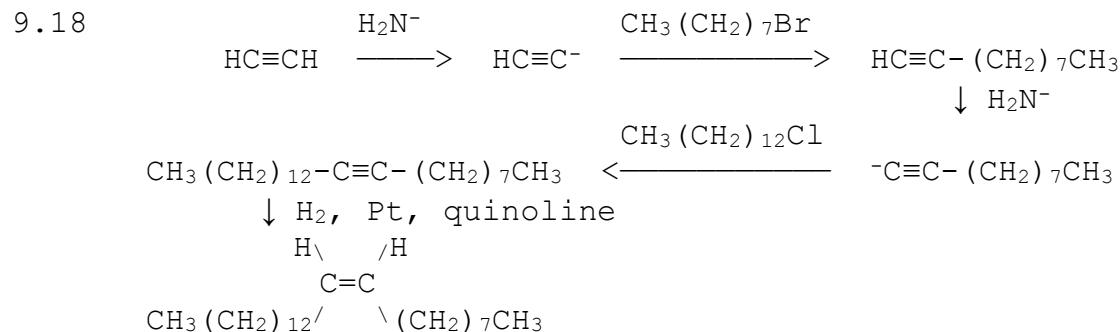
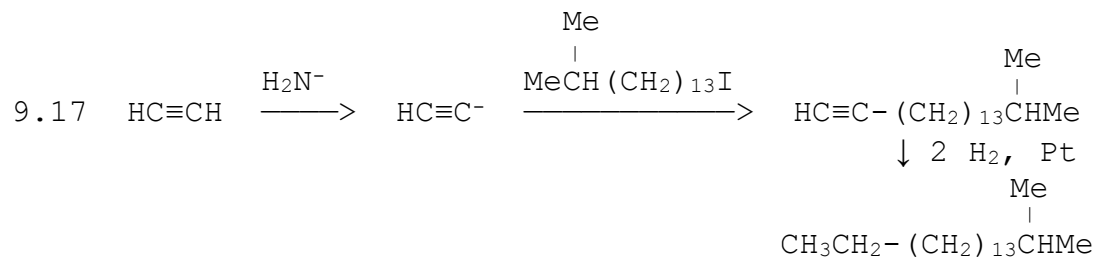
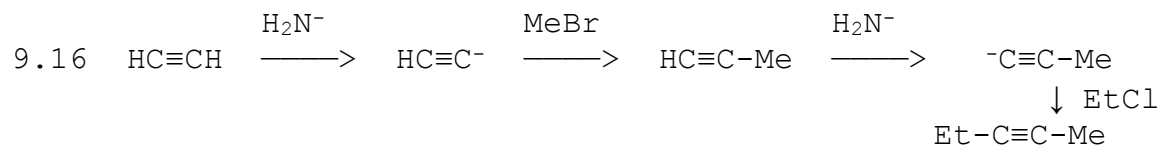
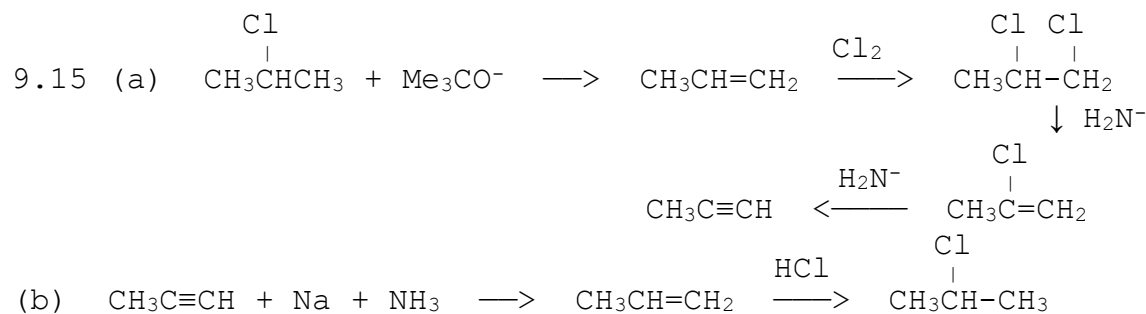
9.11 (a) Adding bromine turns the solution brown, but the color fades during reaction.
 (b) There is at least one π bond to react with bromine.



9.13 Ethyne's π bonds are inherently less stable, more energetic, and more reactive than the alternative σ bonds of ethene and ethane.

9.14 The stronger acid has a less basic conjugate base:

in basicity: $\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_3 < \text{CH}_3\text{OH}$
 because fewer (2) e^- pairs on the sp^2 O repel & destabilize its base e's less.



9.19 (a) 1,1-dichloro-2-pentyne (b) 5,5-dichloro-2-pentyne (c) 4-hexen-1-yne
 (d) 1-hexen-4-yne (e) 2,4-heptadiyn-1-ol (f) 3,5-heptadiyn-1-ol

9.20 (a) 1-butyne: $\text{HC}\equiv\text{CCH}_2\text{CH}_3$ (b) 1-hexyne: $\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

(c) e.g. 3-methyl-1-pentyne: $\text{HC}\equiv\text{CCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$

(d) 4-methyl-2-pentyne: $\text{CH}_3\text{C}\equiv\text{CCH}(\text{CH}_3)_2$ (e) 1-hexen-4-yne: $\text{CH}_2=\text{CHCH}_2\text{C}\equiv\text{CCH}_3$

(f) 4-hexen-1-yne: $\text{HC}\equiv\text{CCH}_2\text{CH}=\text{CHCH}_3$ (g) 3-butyne-2-ol: $\text{HC}\equiv\text{CCH}(\text{OH})\text{CH}_3$

9.21 (a) 2 C,C π bonds & 2 H,H σ bonds broken; 4 C,H σ bonds made

(b) $\Delta H = \text{energies of bonds broken} - \text{energies of bonds made}$

$$\cong (962 - 368) + 2(436) - 4(410) = -174 \text{ kJ/mol}$$

(c) negative ΔH is favorable

9.22 2-butyne is linear, longer, and has more dispersion forces than 1-butyne, whose C skeleton is bent: $\text{HC}\equiv\text{C}-\text{CH}_2$

$\backslash\text{CH}_3$

9.23 $\text{H}_3\text{C}\backslash\text{Cl}$

(a) $\text{C}=\text{C}$ (b) $\text{CH}_3-\text{CCl}_2-\text{CHCl}_2$ (c) $\text{CH}_3-\text{CBr}=\text{CH}_2$
 Cl/H

(d) $\text{CH}_3-\text{CBr}_2-\text{CH}_3$ (e) $\text{CH}_3-\text{CH}=\text{CH}_2$ (f) $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$

(g) no reaction (2 nucs) (h) $\text{CH}_3-\text{C}\equiv\text{C}^-$ (i) $\text{CH}_3-\text{CH}=\text{CH}_2$

(j) $\text{CH}_3-\text{CH}_2-\text{CH}_3$ (k) $\text{CH}_3-\text{C}\equiv\text{C}^- + \text{CH}_4$ (l) no reaction (2 nucs)

9.24 $\text{Me}\backslash\text{Cl}$

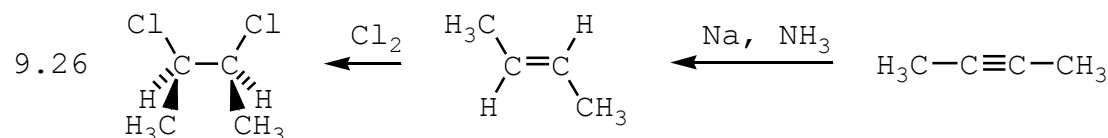
(a) $\text{C}=\text{C}$ (b) $\text{Me}-\text{CCl}_2-\text{CCl}_2-\text{Me}$ (c) $\text{Me}-\text{CBr}=\text{CH}-\text{Me}$
 Cl/Me

(d) $\text{Me}-\text{CBr}_2-\text{CH}_2-\text{Me}$ (e) $\text{Me}\backslash\text{H}$ (f) $\text{Me}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{Me}$
 $\text{C}=\text{C}$
 H/Me

(g) no rx. (2 nucs) (h) no rx. (2 nucs) (i) $\text{H}\backslash\text{H}$
 $\text{C}=\text{C}$

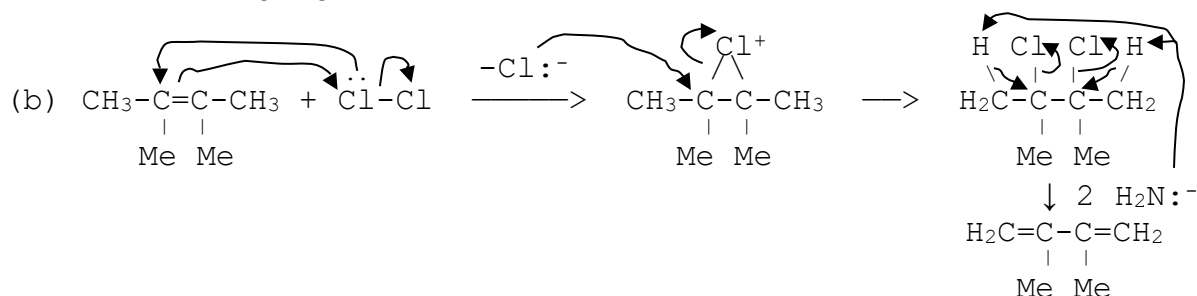
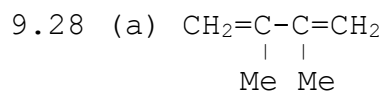
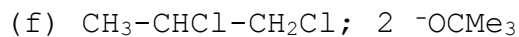
(j) $\text{Me}-\text{CH}_2-\text{CH}_2-\text{Me}$ (k) no rx. (2 nucs) (l) no rx. (2 nucs)
 Me/Me

9.25 $\text{HC}\equiv\text{CH} \longrightarrow \text{O}=\text{CH}-\text{CH}_3$

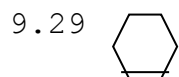


9.27 (a) $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$ (b) aq. $\text{H}_2\text{SO}_4 + \text{Hg}^{2+}$ (c) $\text{CH}_3-\text{CH}_2-\text{CBrI}-\text{CH}_2-\text{CH}_3$

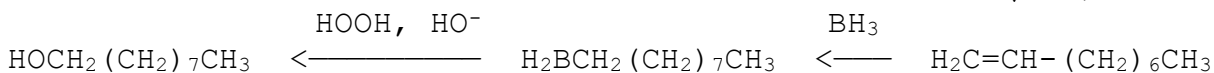
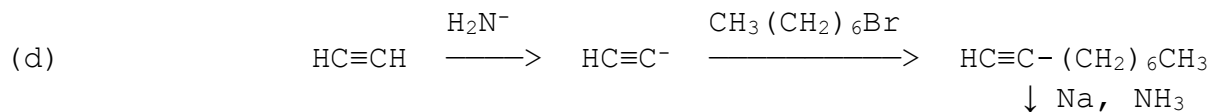
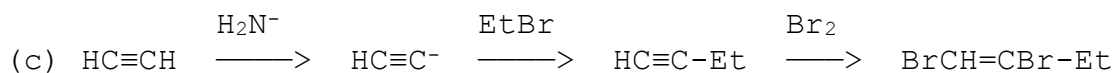
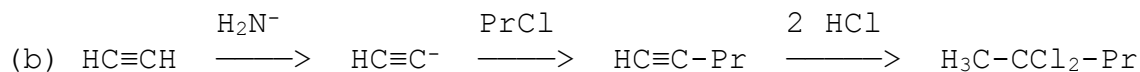
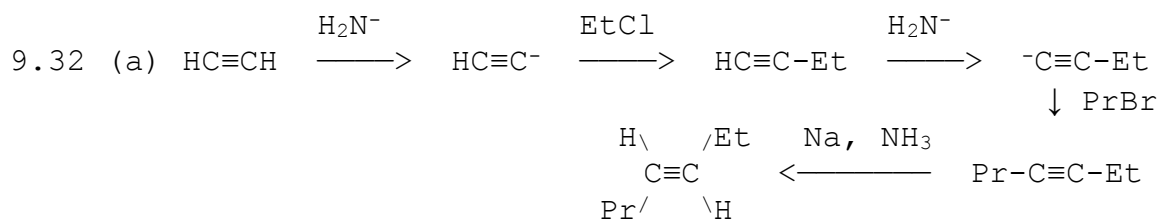
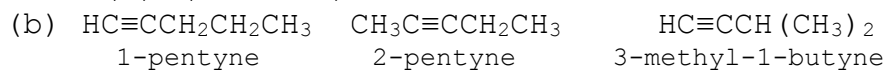
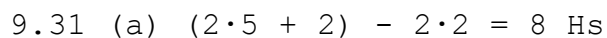
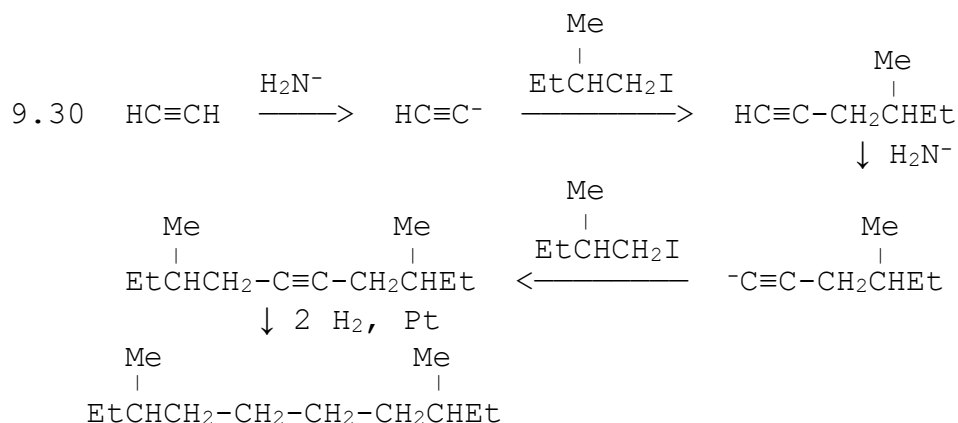
(d) $\text{Na} + \text{NH}_3$ (e) $^-\text{C}\equiv\text{C}-\text{CH}_3$; $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_3$; $\text{CH}_3\text{CH}_2\backslash\text{Br}$
 $\text{C}=\text{C}$
 Br/CH_3

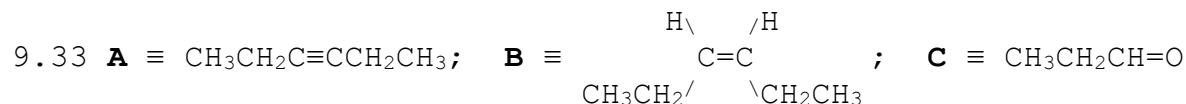
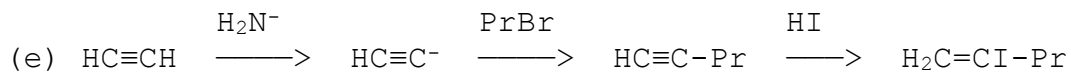


No alkyne because there are no β Hs on the Cs with the Cls

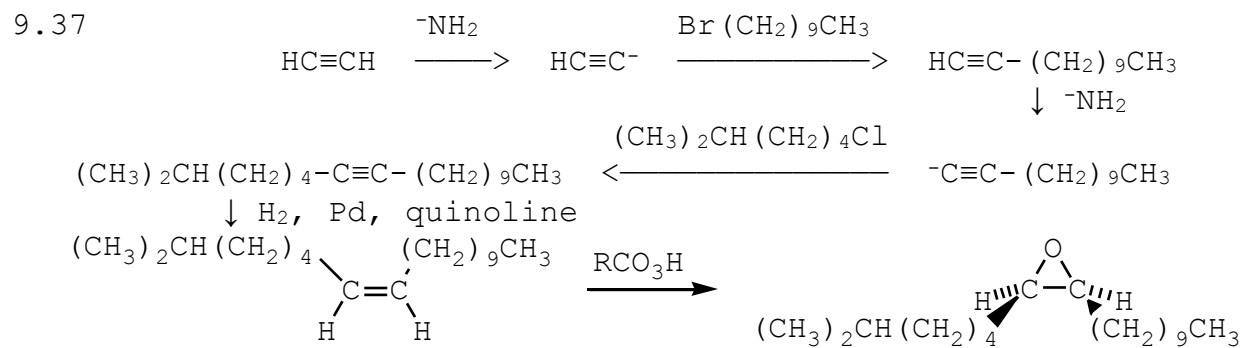
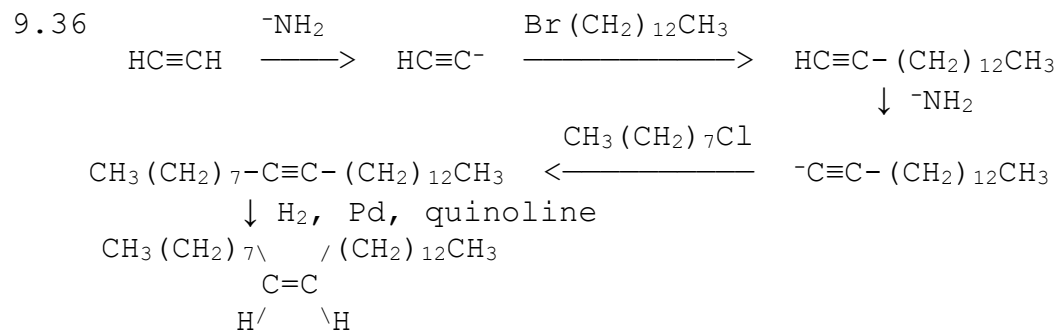
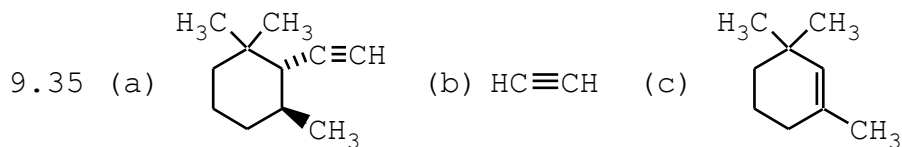


would have too much ring strain because the bonds at the $\text{C}\equiv\text{C}$ would try to be linear.





9.34 It is unstable because the linear geometry of the alkyne triple bond greatly strains the ring.



9.38 (a) no: the linear C≡C makes ring strain, released by reaction. (b) H₂, Pd, quinoline

12/06