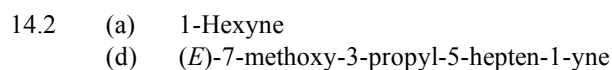
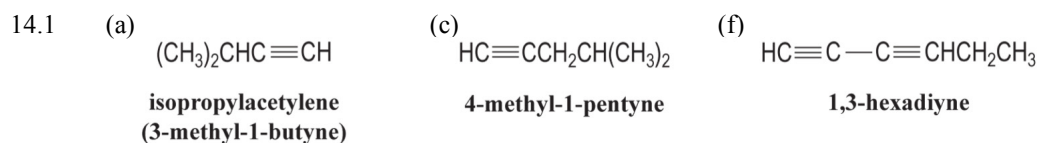


Chapter 14

The Chemistry of Alkynes

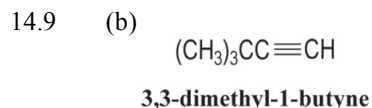
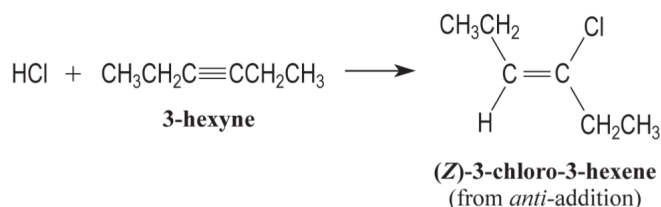
Solutions to In-Text Problems



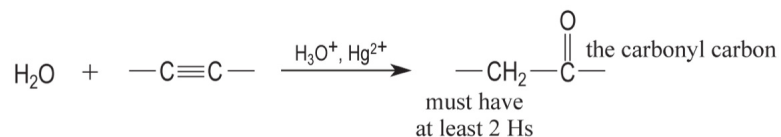
14.3 (b) Cyclodecyne is much more stable than cyclohexyne (and in fact can be isolated), because the distance of 4.1 Å referred to in part (a) can be bridged by six carbons with reasonable bond lengths and bond angles.

14.6 The proton NMR spectrum of propyne should consist of two resonances. Evidently, the two happen to have the same chemical shift of δ 1.8, which is in fact a reasonable chemical shift for both acetylenic and propargylic protons.

14.8 The product is (*Z*)-3-chloro-3-hexene:

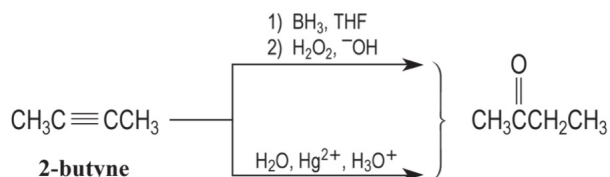


14.10 (b) Hydration can only be used to prepare ketones that have at least two hydrogens on the carbon α (that is, adjacent) to the carbonyl carbon:

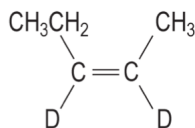


The ketone shown does not fulfill this requirement.

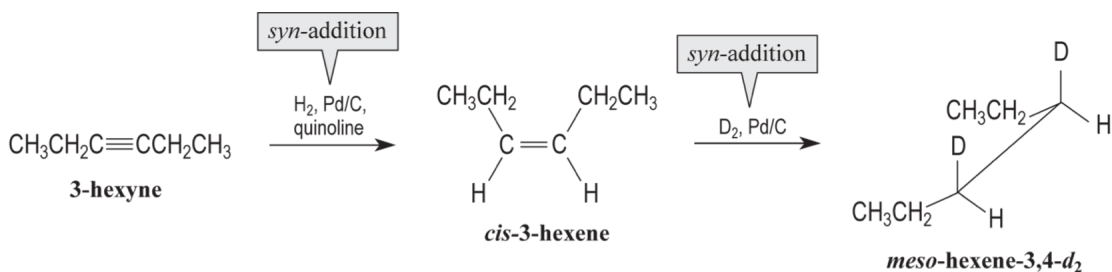
14.12 (b) Because it is symmetrical, 2-butyne gives the same product in the two reactions:



- 14.13 (b) The product is the alkane octane, $\text{CH}_3(\text{CH}_2)_6\text{CH}_3$.
 (d) The product is the alkene that results from *syn*-addition of D_2 :

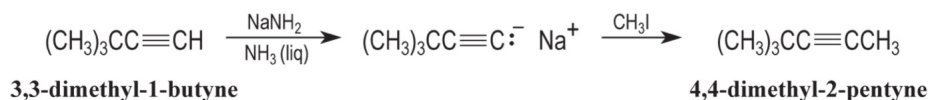


- 14.14 (b) The first reaction is a *syn*-addition that gives *cis*-3-hexene; the second is another *syn*-addition that gives *meso*-hexane-3,4- d_2 .

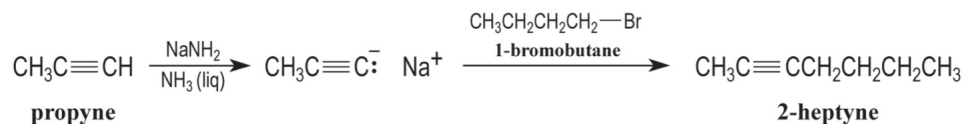


- 14.17 (a) The $\text{p}K_a$ of ammonia is about 35 (which indicates the basicity of the amide ion), and that of an alkyne acetylenic hydrogen is about 25 (Eq. 14.20, text p. 663). Use the method described in Eq. 3.25b, text p. 104, to find that the K_{eq} for Eq. 14.22 is about 10^{+10} . With the $\text{p}K_a$ of an alkane taken as 55, the K_{eq} for the reaction of the amide base with an alkane is about 10^{-20} .
 (b) As the calculation in part (a) shows, the reaction of sodium amide with an alkane is quite unfavorable. For that reason, this base cannot be used to form the conjugate-base anions of alkanes.
- 14.18 (a) This is an $\text{S}_{\text{N}}2$ reaction of the anion with ethyl iodide to give 2-pentyne, $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_3$, plus sodium iodide, $\text{Na}^+ \text{I}^-$.
 (d) Sodium acetylide reacts with both alkyl halide groups to give a 1,8-nonadiyne, $\text{HC}\equiv\text{C}(\text{CH}_2)_5\text{C}\equiv\text{CH}$, plus two equivalents of sodium bromide, $\text{Na}^+ \text{Br}^-$.

- 14.20 The preparation involves the reaction of 3,3-dimethyl-1-butyne with sodium amide, then with methyl iodide.

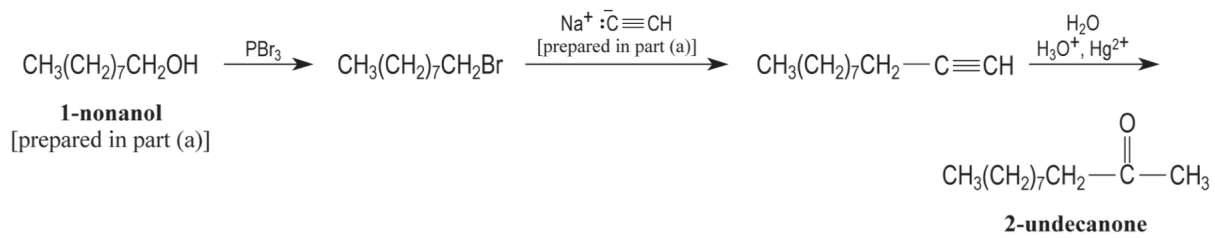


- 14.22 As in the solution to Problem 14.21, either alkyl group can be introduced by the reaction with an alkyl halide. The alternative to Eq. 14.28 is to use the acetylenic anion derived from propyne followed by alkylation with 1-bromobutane.



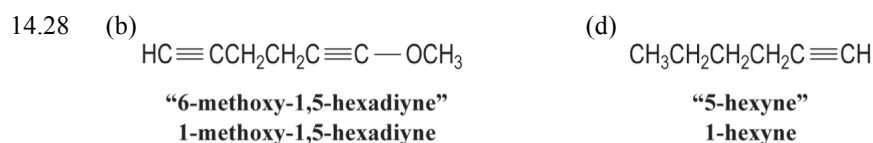
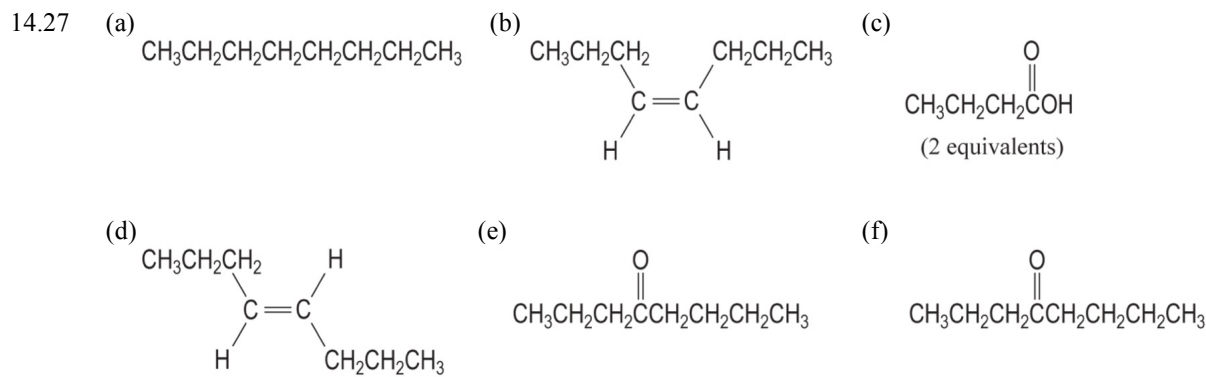
However, the reaction shown in Eq. 14.28 is probably superior because CH_3Br is the more reactive alkyl halide.

- 14.23 (b) A synthesis of 2-undecanone from compounds containing five or fewer carbons:

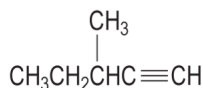


- 14.25 Catalytic hydrogenation with a Lindlar catalyst should bring about hydrogenation of the alkyne to a cis-alkene group without affecting the existing alkene.

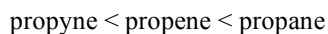
Solutions to Additional Problems



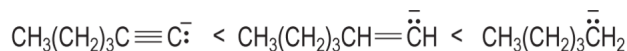
14.29 (b) Either the cis or the trans isomer of the cyclopropane derivative in part (d) is a satisfactory answer. Another is



14.30 (b) Hybridization affects the lengths of C—C bonds in the same way that it affects the lengths of C—H bonds. Therefore, the lengths of C—C bonds increase in the following order:



14.31 (b) Because alkynes are more acidic than alkenes, which are more acidic than alkanes, the acetylenic anion is less basic than the vinylic anion, which is less basic than the alkyl anion. Thus, the basicity order is

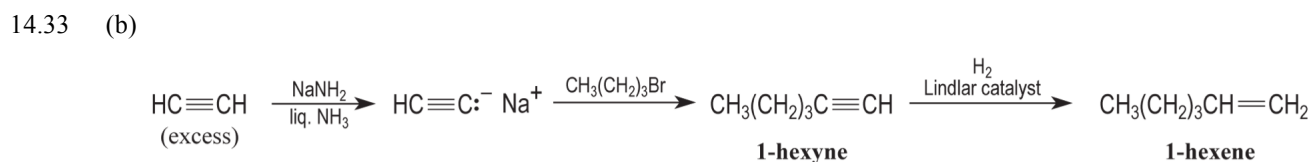


14.32 (b) Only the 1-alkyne should react with $\text{C}_2\text{H}_5\text{MgBr}$ to release a gas (ethane).

(d) Forget about chemical tests; propyne is a gas and 1-decyne is a liquid at room temperature.

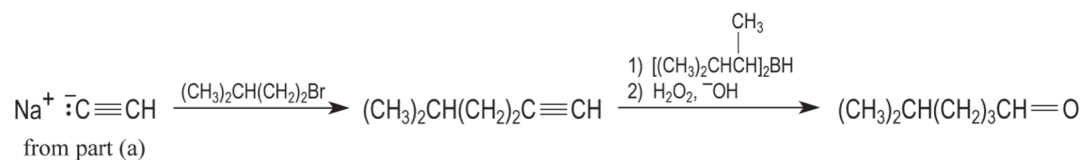


How would you know this? You know that *propane* is a gas, right? (It is used instead of natural gas in rural areas for heating or in barbecue grills as a fuel for cooking.) You also know that the presence of a double or triple bond has little effect on the physical properties of hydrocarbons. Thus, propyne is a gas also.

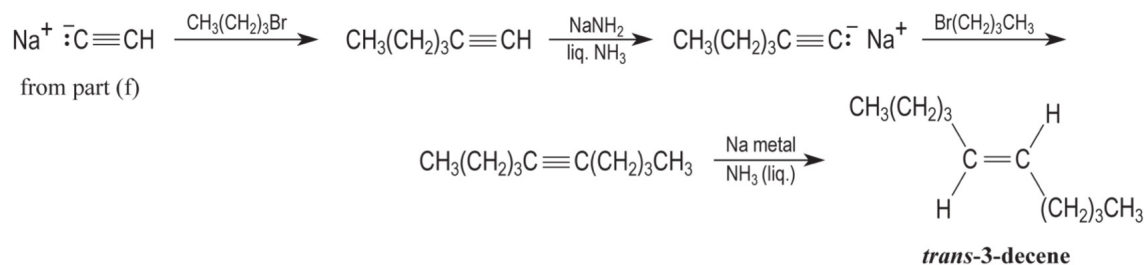


(d) 1-Hexyne was prepared in part (b).

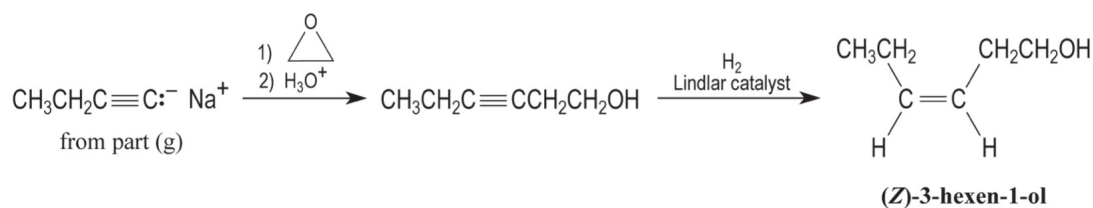
(f)



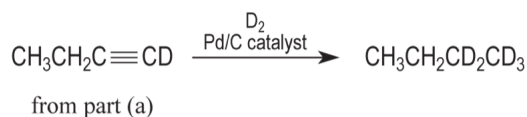
(h)



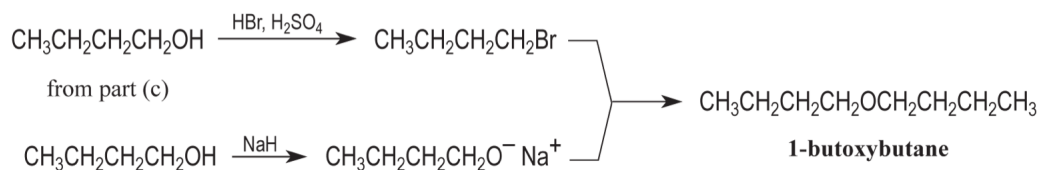
(j)



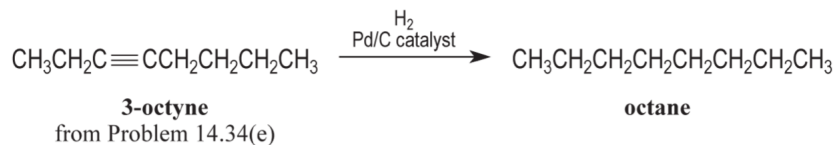
14.34 (b)



(d)

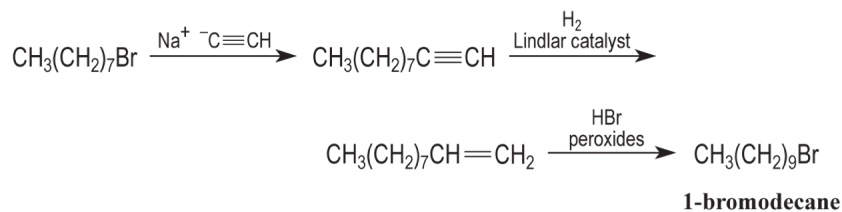


(f)

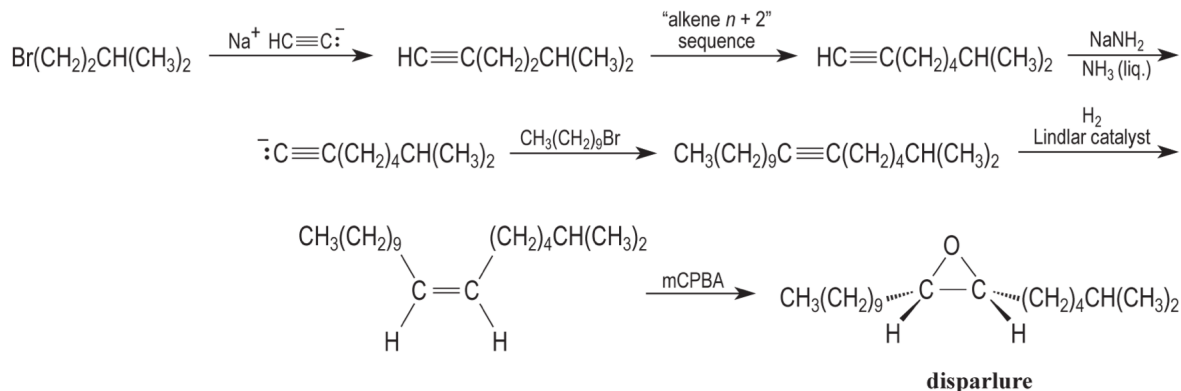


14.37 This problem is similar to the previous one. Disparlure is a *cis*-epoxide, which can be prepared by epoxidation of a *cis*-alkene. (Recall that this reaction proceeds with retention of stereochemistry; Sec. 11.2A.) The *cis*-alkene can be prepared by hydrogenation of an alkyne.

First prepare 1-bromodecane from 1-bromo-octane, which was prepared in the solution to Problem 14.36.



Next, alkylate sodium acetylide with 1-bromo-3-methylbutane (isoamyl bromide). Apply the alkyne $n + 2$ sequence described in the previous solution, alkylate the conjugate base of the resulting alkyne with 1-bromodecane, hydrogenate, and form the epoxide to complete the synthesis.

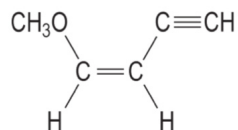


- 14.38 (b) The "anionic carbon" of one Grignard reagent acts as a base toward the C—H bond of the other.



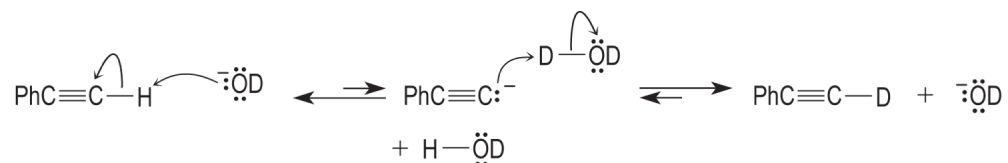
An excess of acetylene, by Le Châtelier's principle, drives the equilibrium to the left.

- 14.40 (b) The IR data suggest a 1-alkyne, and this diagnosis is confirmed by the formation of a gas (ethane) when the compound is treated with $\text{C}_2\text{H}_5\text{MgBr}$. The three-proton δ 3.41 singlet suggests a methoxy group. The structure is 3-methoxypropyne, $\text{HC}\equiv\text{CCH}_2\text{OCH}_3$.
- (d) The IR data suggest a 1-alkyne. The presence of a methoxy group is indicated by the three-proton singlet at δ 3.79. There is one additional degree of unsaturation; because three carbons are already accounted for, the unsaturation must be in the remaining two. Consequently, there is a double bond. Cis stereochemistry is suggested by the small 6-Hz coupling constant between the vinylic protons. (See Table 13.3 on text p. 614.) The splitting suggests that one of the vinylic protons (δ 4.52) is also coupled to an acetylenic proton. The chemical shift of the other vinylic proton (δ 6.38) suggests that it is α to the methoxy oxygen. All of these data conspire to give the following structure:



(Z)-1-methoxy-1-buten-3-yne

- 14.41 (b) Assuming that all resonances for chemically nonequivalent carbons are separately observable, 1-hexyne, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$, should have a CMR spectrum consisting of six resonances; 4-methyl-2-pentyne, $(\text{CH}_3)_2\text{CHC}\equiv\text{CCH}_3$, should have a CMR spectrum consisting of five, because two of the methyl groups are chemically equivalent.
- 14.42 (b) This mechanism consists of two successive Brønsted acid–base reactions.



14.43 The ozonolysis results define compound *B* as 1,5-hexadiene. $\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}_2$. Because compound *B* is produced by hydrogenation of compound *A*, and because *two equivalents* of H_2 must be added to compound *A* (C_6H_6) to give compound *B* (C_6H_{10}), compound *A* must be 1,5-hexadiyne, $\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{C}\equiv\text{CH}$.

14.45 (a) The Grignard reagent converts 1-hexyne into the acetylenic Grignard reagent; see Eq. 14.23 on text p. 664. Protonolysis of the Grignard reagent by D_2O gives $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CD}$ as the final product.

(c) 1-Octyne is converted into its conjugate-base acetylide ion with NaNH_2 . This ion is alkylated by diethyl sulfate to give 3-undecyne.

