vinylic radical is present in much higher concentration, the ultimate product of the reaction, the trans alkene, is derived from this radical.

The anion formed in Eq. 14.18d is also more basic than the amide anion and readily removes a proton from ammonia to complete the addition.

\[ \text{Na}^+ + \text{R} = \text{C} - \text{H} \rightarrow \text{R} = \text{C} - \text{H} + \text{NH}_2 \text{Na}^+ \tag{14.18e} \]

Because ordinary alkenes do not react with the solvated electron (the initial equilibrium analogous to Eq. 14.18a is too unfavorable), the reaction stops at the trans alkene stage.

The Na/NH\textsubscript{3} reduction of alkynes does not work well on 1-alkynes unless certain modifications are made in the reaction conditions. (This is explored in Problem 14.39.) However, this is not a serious limitation for the reaction, because the reduction of 1-alkynes to 1-alkenes is easily accomplished by catalytic hydrogenation (Sec. 14.6A).

**PROBLEM 14.14** What product is obtained in each case when 3-hexyne is treated in each of the following ways? (Hint: The products of the two reactions are stereoisomers.)

(a) with sodium in liquid ammonia and the product of that reaction with D\textsubscript{2} over Pd/C

(b) with H\textsubscript{2} over Pd/C and quinoline and the product of that reaction with D\textsubscript{2} over Pd/C

---

### 14.7 ACIDITY OF 1-ALKYNES

**A. Acetylenic Anions**

Most hydrocarbons do not react as Brønsted acids. Nevertheless, let’s imagine such a reaction in which a proton is removed from a hydrocarbon by a very strong base $\text{B}^{−}$.

\[ \text{C} - \text{H} + \text{B}^{−} \rightleftharpoons \text{C}^{−} + \text{B} - \text{H} \tag{14.19} \]

In this equation, the conjugate base of the hydrocarbon is a carbon anion, or *carbanion*. Recall from Sec. 8.8B that a carbanion is a species with an unshared electron pair and a negative charge on carbon.

The conjugate base of an alkane, called generally an *alkyl anion*, has an electron pair in an $sp^3$ orbital. An example of such an ion is the 2-propanide anion:

[Diagram of 2-propanide anion]
The conjugate base of an alkene, called generally a \textit{vinylic anion}, has an electron pair in an \textit{sp} \textsuperscript{2} orbital. An example of this type of carbanion is the 1-propenide anion:

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{C} = \text{C} \\
\text{H} \\
\end{array} \quad \text{sp}^2 \text{ orbital}
\]

\textbf{1-propenide anion}  \\
(a \textit{vinylic anion})

The anion derived from the ionization of a 1-alkyne, generally called an \textit{acetylenic anion}, has an electron pair in an \textit{sp} orbital. An example of this type of anion is the 1-propynide anion:

\[
\begin{array}{c}
\text{CH}_3 \equiv \text{C} \\
\text{sp} \text{ orbital}
\end{array}
\]

\textbf{1-propynide anion}  \\
(an \textit{acetylenic anion})

The approximate acidities of the different types of aliphatic hydrocarbons have been measured or estimated:

\[
\begin{array}{cccc}
\text{R}_3\text{C} \equiv \text{H} & \text{R}_2\text{C} \equiv \text{C} & \text{R} \text{C} \equiv \text{C} \equiv \text{H} \\
\text{alkane} & \text{alkene} & \text{alkyne} \\
\text{approximate } pK_a & \geq 55 & 42 & 25
\end{array}
\] (14.20)

These data show, first, that carbanions are extremely strong bases (that is, hydrocarbons are very weak acids); and second, that alkynes are the most acidic of the aliphatic hydrocarbons.

Alkyl anions and vinylic anions are seldom if ever formed by proton removal from the corresponding hydrocarbons; the hydrocarbons are simply not acidic enough. However, alkynes are sufficiently acidic that their conjugate-base acetylenic anions can be formed with strong bases. One base commonly used for this purpose is sodium amide, or sodamide, $\text{Na}^+ \cdot \cdot \cdot \text{NH}_2$, dissolved in its conjugate acid, liquid ammonia. The amide ion, $\cdot \cdot \cdot \text{NH}_2$, is the conjugate base of ammonia, which, as an \textit{acid}, has a $pK_a$ of about 35.

\[
\begin{array}{c}
\text{H} \\
\end{array} \quad \text{alkyne} \quad \text{amide ion}
\]

Because the amide ion is a much stronger base than an acetylenic anion, the equilibrium for removal of the acetylenic proton by amide ion is very favorable:

\[
\begin{array}{c}
\text{R} \equiv \text{C} \equiv \text{C} \equiv \text{H} \quad \text{R} \equiv \text{C} \equiv \text{C} \equiv \text{H} \\
\text{Na}^+ \quad \cdot \cdot \cdot \text{NH}_2 \quad \cdot \cdot \cdot \text{NH}_2 \quad \cdot \cdot \cdot \text{NH}_2
\end{array} \quad \text{pK}_a = 35 \quad \text{(14.21)}
\]

In fact, the sodium salt of an alkyne can be formed from a 1-alkyne quantitatively with NaNH$_2$. Because the amide ion is a much \textit{weaker} base than either a vinylic anion or an alkyl anion, these ions \textit{cannot} be prepared using sodium amide (Problem 14.17).

The relative acidity of alkynes plays a role in the method usually used to prepare \textit{acetylenic Grignard reagents}, which are reagents with the general structure $\text{R} \equiv \text{C} \equiv \text{C} \equiv \text{MgBr}$. Recall from Sec. 8.8A that Grignard reagents are generally prepared by the reactions of alkyl halides with magnesium.
with magnesium. The “alkyl halide” starting material for the preparation of an acetylenic Grignard reagent by this method would be a 1-bromoalkyne—that is, $R\text{C}≡\text{C}−\text{Br}$. Such compounds are not generally available commercially and are difficult to prepare and store. Fortunately, acetylenic Grignard reagents are accessible by the acid–base reaction between a 1-alkyne and another Grignard reagent. Methylmagnesium bromide or ethylmagnesium bromide are often used for this purpose.

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}≡\text{C}−\text{H} + \text{CH}_3\text{CH}_2\text{MgBr} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{C}≡\text{C}−\text{MgBr} + \text{CH}_3\text{CH}_3$$

(14.23)

ethane (a gas)

$$\text{H}−\text{C}≡\text{C}−\text{H} + \text{CH}_3\text{CH}_2−\text{MgBr} \rightarrow \text{H}−\text{C}≡\text{C}−\text{MgBr} + \text{CH}_3\text{CH}_3$$

(14.24)

ethynylmagnesium bromide

This reaction is extremely rapid and is driven to completion by the formation of ethane gas (when $\text{CH}_3\text{CH}_2\text{MgBr}$ is used as the Grignard reagent). This reaction is an example of a transmetallation: a reaction in which a metal is transferred from one carbon to another. However, it is really just another Brønsted acid–base reaction:

$$\text{BrMg}^+ + \text{CH}_2\text{CH}_3\text{H}−\text{C}≡\text{C}−\text{R} \rightarrow \text{H}−\text{CH}_3\text{CH}_2\text{Mg}^+ + \text{BrMg}^+:\text{C}≡\text{C}−\text{R}$$

(14.25)

Although Grignard reagents are covalent compounds, the two Grignard reagents in this equation are represented as ionic compounds to stress the acid–base character of the equilibrium. This reaction is similar in principle to the reaction of a Grignard reagent with water or alcohols (Eq. 8.27, p. 363). Like all Brønsted acid–base equilibria, this one favors formation of the weaker base, which, in this case, is the acetylenic Grignard reagent. The release of ethane gas in the reaction with ethylmagnesium bromide makes the reaction irreversible and at one time was also a useful test for 1-alkynes. Alkynes with an internal triple bond do not react because they lack an acidic acetylenic hydrogen.

What is the reason for the relative acidities of the hydrocarbons? Sec. 3.6A discussed two important factors that affect the acidity of an acid $A−\text{H}$: the $A−\text{H}$ bond strength and the electronegativity of the group $A$. Bond dissociation energies show that acetylenic $C−\text{H}$ bonds are the strongest of all the $C−\text{H}$ bonds in the aliphatic hydrocarbons:

$$R \text{C}≡\text{C}−\text{H} > R_2\text{C}≡\text{C}−\text{H} > R_3\text{C}−\text{H}$$

(14.26)

<table>
<thead>
<tr>
<th></th>
<th>Acetylenic C−H</th>
<th>Vinylic C−H</th>
<th>Alkyl C−H</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A−\text{H}$</td>
<td>(548 kJ mol$^{-1}$, 131 kcal mol$^{-1}$)</td>
<td>(460 kJ mol$^{-1}$, 110 kcal mol$^{-1}$)</td>
<td>(402–418 kJ mol$^{-1}$, 96–100 kcal mol$^{-1}$)</td>
</tr>
</tbody>
</table>

If bond strength were the major factor controlling hydrocarbon acidity, then alkynes would be the least acidic hydrocarbons. Because they are in fact the most acidic hydrocarbons, the electronegativities of the carbons themselves must govern acidity. Thus, the relative electronegativities of carbon atoms increase in the order $sp^3 < sp^2 < sp$, and the electronegativity differences on acidity must outweigh the effects of bond strength.
This trend in electronegativity with hybridization can be explained in the following way. The electrons in \( sp\)-hybridized orbitals are closer to the nucleus, on the average, than \( sp^2\) electrons, which in turn are closer than \( sp^3\) electrons (Sec. 14.2). In other words, electrons in orbitals with larger amounts of \( s\) character are drawn closer to the nucleus. This is a stabilizing effect because the interaction energy between particles of opposite charge (electrons and nuclei) becomes more strongly negative (that is, favorable) as the distance between them decreases (the electrostatic law; Eq. 3.40, p. 113). Thus, the stabilization of unshared electron pairs is in the order \( sp^3 < sp^2 < sp\). In other words, \textit{unshared electron pairs have lower energy when they are in orbitals with greater }s\textit{ character.}

**PROBLEMS**

14.15 Each of the following compounds protonates on nitrogen. Draw the conjugate acid of each. Which compound is more basic? Explain.

\[
\begin{align*}
\text{H}_3\text{C} & \text{CH} = \text{NH} \quad \text{H}_3\text{C} & \text{C} = \text{N} : \\
\text{A} & \quad \text{B}
\end{align*}
\]

14.16 (a) Ion A is more acidic than ion B in the gas phase. Is this the acidity order predicted by hybridization arguments? Explain.

\[
\begin{align*}
\text{H}_3\text{C} & \text{CH} = \text{O} : \text{H} \\
\text{A} & \quad \text{B}
\end{align*}
\]

(b) Ion B is less acidic because it is stabilized by resonance, whereas ion A is not. Show the resonance structure for ion B, and, with the aid of an energy diagram, show why stabilization of ion B should reduce its acidity.

(c) In aqueous solution, ion A is less acidic than ion B. Explain.

14.17 (a) Using the \( pK_a\) values of the hydrocarbons and ammonia, estimate the equilibrium constant for (1) the reaction in Eq. 14.22 and (2) the analogous reaction of an alkane with amide ion. (Hint: See Study Problem 3.6, p. 91)

(b) Use your calculation to explain why sodium amide cannot be used to form alkyl anions from alkanes.

**B. Acetylenic Anions as Nucleophiles**

Although acetylenic anions are the weakest bases of the simple hydrocarbon anions, they are nevertheless strong bases—much stronger, for example, than hydroxide or alkoxides. They undergo many of the characteristic reactions of strong bases, such as \( S_{N2}\) reactions with alkyl halides or alkyl sulfonates (Secs. 9.4, 10.3A). Thus, acetylenic anions can be used as nucleophiles in \( S_{N2}\) reactions to prepare other alkynes.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{Na}^+ : \text{C} = \text{CH} \quad \xrightarrow{\text{NH}_3 (\text{liq})} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C} = \text{CH} + \text{Na}^+ : \text{Br}^- \quad (14.27)
\]

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C} = \text{C} : \text{Na}^+ + \text{H}_3\text{C} \quad \xrightarrow{\text{Br}^-} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C} = \text{C} = \text{CH}_3 + \text{Na}^+ : \text{Br}^- \quad (14.28)
\]

The acetylenic anions in these reactions are formed by the reactions of the appropriate 1-alkynes with NaNH\(_3\) in liquid ammonia (Sec. 14.7A). The alkyl halides and sulfonates, as in most other \( S_{N2}\) reactions, must be unhindered primary compounds. (Why? See Secs. 9.4D, 9.5G.)
The reaction of acetylenic anions with alkyl halides or sulfonates is important because *it is another method of carbon–carbon bond formation*. Let’s review the methods covered so far:

1. cyclopropane formation by the addition of carbenes to alkenes (Sec. 9.8)
2. reaction of Grignard reagents with ethylene oxide and lithium organocuprate reagents with epoxides (Sec. 11.4C)
3. reaction of acetylenic anions with alkyl halides or sulfonates (this section)

**PROBLEMS**

14.18 Give the structures of the products in each of the following reactions.

(a) \( \text{CH}_3\text{C}≡\text{C}:\text{Na}^+ + \text{CH}_3\text{CH}_2\text{I} \rightarrow \) 
(b) butyl tosylate + Ph\text{C}≡\text{C}:\text{Na}^+ \rightarrow 
(c) \( \text{CH}_3\text{C}≡\text{C}:\text{MgBr} + \text{ethylene oxide} \rightarrow \text{H}_2\text{O}^+ \)
(d) Br(CH\(_2\))\(_5\)Br + H\text{C}≡\text{C}:\text{Na}^+ (excess) \rightarrow 

14.19 Explain why graduate student Choke Fumely, in attempting to synthesize 4,4-dimethyl-2-pentyne using the reaction of H\(_3\)C\(-\text{C}≡\text{C}:\text{Na}^+\) with tert-butyl bromide, obtained none of the desired product.

14.20 Propose a synthesis of 4,4-dimethyl-2-pentyne (the compound in Problem 14.19) from an alkyl halide and an alkyne.

14.21 Outline two different preparations of 2-pentyne that involve an alkyne and an alkyl halide.

14.22 Propose another pair of reactants that could be used to prepare 2-heptyne (the product in Eq. 14.28).

**14.8 ORGANIC SYNTHESIS USING ALKYNES**

Let’s tie together what we’ve learned about alkyne reactions and organic synthesis. The solution to Study Problem 14.2 requires all of the fundamental operations of organic synthesis: the formation of carbon–carbon bonds, the transformation of functional groups, and the establishment of stereochemistry (Sec. 11.9).

Notice that this problem stipulates the use of starting materials containing five or fewer carbons. This stipulation is made because such compounds are readily available from commercial sources and are relatively inexpensive.

**Study Problem 14.2**

Outline a synthesis of the following compound from acetylene and any other compounds containing no more than five carbons:

\[
\text{cis-2-methyl-5-tridecene}
\]

**Solution** As usual, we start with the target molecule and work backward. First, notice the stereochemistry of the target molecule: it is a cis alkene. We’ve covered only one method of preparing cis alkenes free of their trans isomers: the hydrogenation of alkynes (Sec. 14.6A). This reaction, then, is used in the last step of the synthesis: