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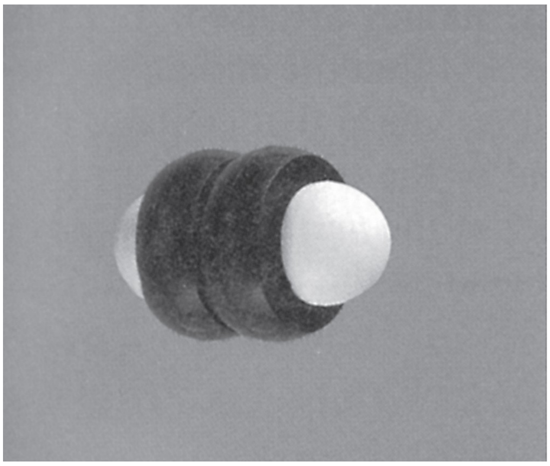


Alkynes

7.1 Introduction

So far we have discussed two kinds of carbon–carbon bonds: the single bond and the double bond. The carbon–carbon single bond is of low reactivity; its main function is to act as the principal cement holding most organic compounds together. The carbon–carbon double bond is unsaturated and hence highly reactive toward a wide variety of reagents; as a substituent it can exert remarkable effects on the rest of the molecule.

Now we come to the *carbon–carbon triple bond*, the functional group of the family called *alkynes*. Like the double bond it is unsaturated and highly reactive: toward the reagents that double bonds react with, and toward some others besides. It also can exert remarkable effects on the rest of the molecule, and in its own particular way. Through a combination of its characteristic properties, the carbon–carbon triple bond plays a special role—one of increasing importance—in organic synthesis.

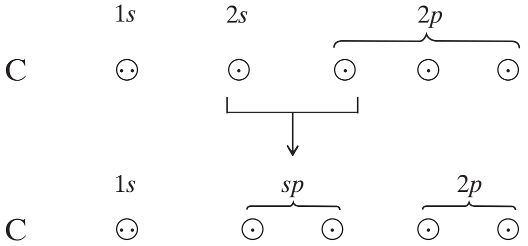
7.2 Structure of acetylene. The carbon–carbon triple bond

The simplest member of the alkyne family is **acetylene**, C_2H_2. Using the methods we applied to the structure of ethylene, we arrive at a structure in which the carbon atoms share *three* pairs of electrons, that is, are joined by a *triple bond. The* **carbon–carbon triple bond** *is the distinguishing feature of the alkyne structure.*

$$\mathrm{H{:}C{:}{:}{:}C{:}H} \qquad \mathrm{H{-}C{\equiv}C{-}H}$$

Acetylene

Again, quantum mechanics tells us a good deal more about acetylene, and about the carbon–carbon triple bond. To form bonds with two other atoms, carbon makes use of two equivalent hybrid orbitals: *sp* orbitals, formed by the mixing of *one s* and *one p* orbital. These *sp* orbitals lie along a straight line that passes through the carbon nucleus; the angle between the two orbitals is thus 180°. This **linear** arrangement permits the hybrid orbitals to be as far apart as possible. Just as mutual repulsion among orbitals gives four tetrahedral bonds or three trigonal bonds, so it gives two linear bonds.



***sp* Hybridization**

If we arrange the two carbons and the two hydrogens of acetylene to permit maximum overlap of orbitals, we obtain the structure shown in Fig. 7.1.

Figure 7.1 Acetylene molecule: only σ bonds shown.

$$\mathrm{H{-\!\!-}C\overset{\sigma}{-\!\!-}C\overset{\sigma}{-\!\!-}H}$$

Acetylene is a *linear molecule*, all four atoms lying along a single straight line. Both carbon–hydrogen and carbon–carbon bonds are cylindrically symmetrical about a line joining the nuclei, and are therefore σ bonds.

The molecule is not yet complete, however. In forming the *sp* orbitals already described, each carbon atom has used only one of its three *p* orbitals; it has two remaining *p* orbitals. Each of these consists of two equal lobes, whose axis lies at right angles both to the axis of the other *p* orbital and to the line of the *sp* orbitals; each *p* orbital is occupied by a single electron. But the sum of two perpendicular *p* orbitals is not four spherical lobes, but a single doughnut-shaped cloud (Fig. 7.2).

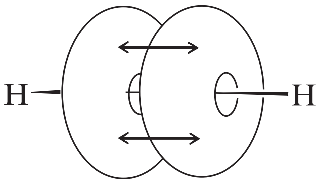


Figure 7.2 Acetylene molecule: two *p* orbitals on one carbon (doughnut-shaped cloud) can overlap two *p* orbitals on the other carbon.

Overlap of the *p* orbitals on one carbon with the *p* orbitals on the other carbon permits pairing of electrons. Two π bonds are formed, which together make a single cylindrical sheath about the line joining the nuclei (Fig. 7.3).

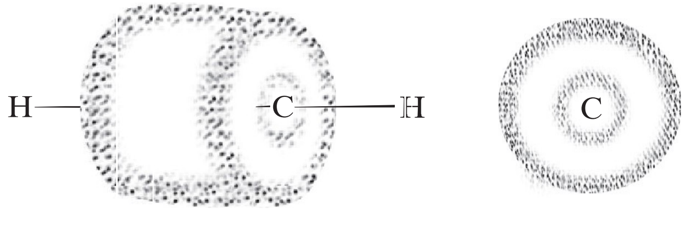
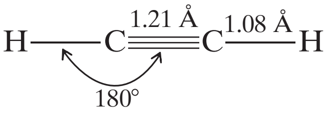


Figure 7.3 Acetylene molecule: carbon–carbon triple bond. The π cloud forms a cylindrical sheath.

The carbon–carbon "triple bond" is thus made up of one strong σ bond and two weaker π bonds; it has a total strength of 198 kcal. It is stronger than the carbon–carbon double bond of ethylene (163 kcal) or the carbon–carbon single bond of ethane (88 kcal), and therefore is shorter than either.



$$\mathrm{H{-}C\overset{1.21\ \text{Å}}{\equiv}C\overset{1.08\ \text{Å}}{-}H}$$

Figure 7.4 Acetylene molecule: shape and size.

Again, the quantum mechanical structure is verified by direct evidence. Electron diffraction, X-ray diffraction, and spectroscopy show acetylene (Fig. 7.4) to be a linear molecule. The C—C distance is 1.21 Å, as compared with 1.34 Å in ethylene and 1.53 Å in ethane. Figure 7.5 shows a model of the acetylene molecule.

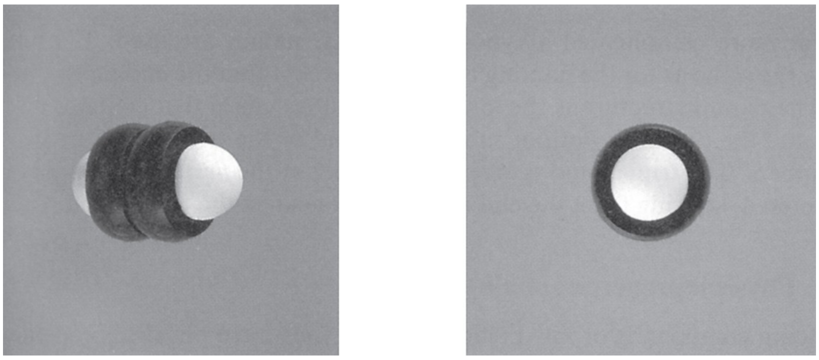


Figure 7.5 Electronic configuration and molecular shape. Model of the acetylene molecule : two views.

As in the case of the double bond, the structure of the triple bond is verified—although this time in a negative way—by the evidence of isomer number. As we can readily see from models, the linearity of the bonding should not permit geometric isomerism; no such isomers have ever been found.

The C—H distance in acetylene is 1.08 Å, even shorter than in ethylene (1.103 Å); because of their greater *s* character, *sp* orbitals are smaller than sp^2 orbitals, and *sp*-hybridized carbon forms shorter bonds than sp^2-hybridized carbon. The C—H bond dissociation energy in acetylene is not known, but we would expect it to be even greater than in ethylene. Oddly enough, the same *sp* hybridization that almost certainly makes cleavage of the C—H bond to form free radicals (*homolysis*) more difficult makes cleavage to form ions (*heterolysis*) easier.

$$\mathrm{HC{\equiv}C{:}H} \longrightarrow \mathrm{HC{\equiv}C\cdot + H\cdot}$$

Homolysis: *on electron to each fragment*

$$\mathrm{HC{\equiv}C{:}H} \longrightarrow \mathrm{HC{\equiv}C{:}^- + H^+}$$

Heterolysis: *both electrons to one fragment*

Problem 7.1 Compare the electronic configurations of CO_2, which is a linear molecule, and H_2O, which has a bond angle of 105°.

7.3 Higher alkynes. Nomenclature

Like the alkanes and alkenes, the alkynes form a homologous series, the increment again being CH_2.

The alkynes are named according to two systems. In one, they are considered to be derived from acetylene by replacement of one or both hydrogen atoms by alkyl groups.

$H—C{\equiv}C—C_2H_5$	$CH_3—C{\equiv}C—CH_3$	$CH_3—C{\equiv}C—CH(CH_3)_2$
Ethylacetylene	Dimethylacetylene	Isopropylmethylacetylene
1-Butyne	2-Butyne	4-Methyl-2-pentyne

For more complicated alkynes the **IUPAC** names are used. The rules are exactly the same as for the naming of alkenes, except that the ending **-yne** replaces *-ene*. The parent structure is the longest continuous chain that contains the triple bond, and the positions both of substituents and of the triple bond are indicated by numbers. The triple bond is given the number of the *first* triply bonded carbon encountered, starting from the end of the chain nearest the triple bond.

7.4 Physical properties of alkynes

Being compounds of low polarity, the alkynes have physical properties that are essentially the same as those of the alkanes and alkenes. They are insoluble in water but quite soluble in the usual organic solvents of low polarity: ligroin, ether, benzene, carbon tetrachloride. They are less dense than water. Their boiling points (Table 7.1) show the usual increase with increasing carbon number, and the usual effects of chain-branching; they are very nearly the same as the boiling points of alkanes or alkenes with the same carbon skeletons.

Table 5F.1 ALKYNES

Name	Formula	M.p., °C	B.p., °C	Relative density (at 20 °C)
Acetylene	$HC{\equiv}CH$	−82	−75	
Propyne	$HC{\equiv}CCH_3$	−101.5	−23	
1-Butyne	$HC{\equiv}CCH_2CH_3$	−122	9	
1-Pentyne	$HC{\equiv}C(CH_2)_2CH_3$	−98	40	0.695
1-Hexyne	$HC{\equiv}C(CH_2)_3CH_3$	−124	72	0.719
1-Heptyne	$HC{\equiv}C(CH_2)_4CH_3$	−80	100	0.733
1-Octyne	$HC{\equiv}C(CH_2)_5CH_3$	−70	126	0.747
1-Nonyne	$HC{\equiv}C(CH_2)_6CH_3$	−65	151	0.763
1-Decyne	$HC{\equiv}C(CH_2)_7CH_3$	−36	182	0.770
2-Butyne	$CH_3C{\equiv}CCH_3$	−24	27	0.694
2-Pentyne	$CH_3C{\equiv}CCH_2CH_3$	−101	55	0.714
3-Methyl-1-butyne	$HC{\equiv}CCH(CH_3)_2$		29	0.665
2-Hexyne	$CH_3C{\equiv}(CH_2)_2CH_3$	−92	84	0.730
3-Hexyne	$CH_3CH_2C{\equiv}CCH_2CH_3$	−51	81	0.725
3,3-Dimethyl-1-butyne	$HC{\equiv}CC(CH_3)_3$	−81	38	0.669
4-Octyne	$CH_3(CH_2)_2C{\equiv}C(CH_2)_2CH_3$		131	0.748
5-Decyne	$CH_3(CH_2)_3C{\equiv}C(CH_2)_3CH_3$		175	0.769

7.5 Industrial source of acetylene

The alkyne of chief industrial importance is the simplest member of the family, **acetylene**. It is made by the controlled, high-temperature partial oxidation of methane.

$$6CH_4 + O_2 \xrightarrow{1500\,°C} 2HC\equiv CH + 2CO + 10H_2$$

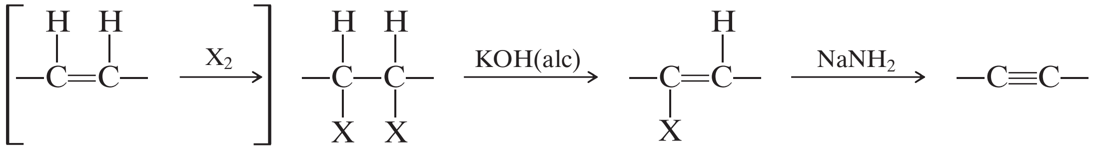
Because of the high cost of acetylene, its formerly huge market has dwindled, and most of the chemicals once made from it are now made from ethylene. It is still the source, however, of a number of compounds used to make polymers.

7.6 Preparation of alkynes

Making alkynes can involve either of two processes: generating a carbon–carbon triple bond, or increasing the size of a molecule that already contains a triple bond.

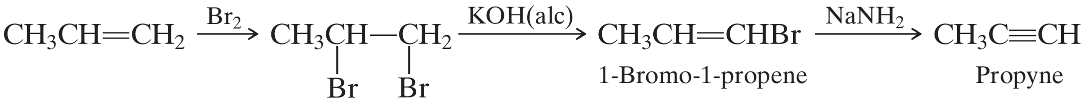
PREPARATION OF ALKYNES

1. Dehydrohalogenation of alkyl dihalides.



$$\left[-\overset{H}{C}=\overset{H}{C}- \xrightarrow{X_2} \right] -\underset{X}{\overset{H}{C}}-\underset{X}{\overset{H}{C}}- \xrightarrow{\text{KOH(alc)}} -\underset{X}{C}=\overset{H}{C}- \xrightarrow{NaNH_2} -C\equiv C-$$

Example:



$$CH_3CH=CH_2 \xrightarrow{Br_2} CH_3\underset{Br}{CH}-\underset{Br}{CH_2} \xrightarrow{\text{KOH(alc)}} CH_3CH=CHBr \xrightarrow{NaNH_2} CH_3C\equiv CH$$

1,2-Dibromopropane (Propylene bromide) — 1-Bromo-1-propene — Propyne

2. Reaction of metal acetylides with primary alkyl halides.

$$\left[-C\equiv C-H \xrightarrow{LiNH_2}\right] -C\equiv C{:}^-Li^+ + RX \longrightarrow -C\equiv C-R + LiX$$

R *must be* 1°

Examples:

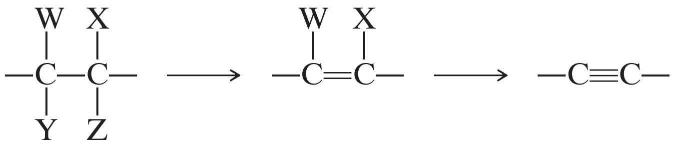
$$HC\equiv C{:}^-Li^+ + CH_3CH_2CH_2CH_2Br \longrightarrow HC\equiv C-CH_2CH_2CH_2CH_3$$

Lithium acetylide — *n*-Butyl bromide — 1-Hexyne (*n*-Butylacetylene)

$$CH_3(CH_2)_4C\equiv C{:}^-Li^+ + CH_3(CH_2)_3CH_2Cl \longrightarrow CH_3(CH_2)_4C\equiv C-CH_2(CH_2)_3CH_3$$

Lithium *n*-pentylacetylide — *n*-Pentyl chloride — 6-Dodecyne ■

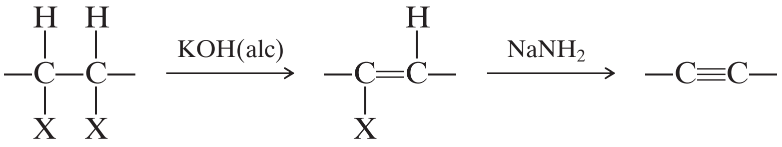
A carbon–carbon triple bond is formed in the same way as a double bond: elimination of atoms or groups from two adjacent carbons. The groups eliminated and the reagents used are essentially the same as in the preparation of alkenes.



$$-\underset{\underset{Y}{|}}{\overset{\overset{W}{|}}{C}}-\underset{\underset{Z}{|}}{\overset{\overset{X}{|}}{C}}- \longrightarrow -\overset{\overset{W}{|}}{C}{=}\overset{\overset{X}{|}}{C}- \longrightarrow -C{\equiv}C-$$

Dehydrohalogenation of vicinal dihalides is particularly useful since the dihalides themselves are readily obtained from the corresponding alkenes by addition of halogen.This amounts to conversion—by several steps—of a double bond into a triple bond.

Dehydrohalogenation can generally be carried out in two stages as shown.



$$-\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}- \xrightarrow{\text{KOH(alc)}} -\underset{\underset{X}{|}}{C}{=}\overset{\overset{H}{|}}{C}- \xrightarrow{\text{NaNH}_2} -C{\equiv}C-$$

A vinylic halide
Very unreactive

Carried through only the first stage, it is a valuable method for preparing unsaturated halides. The halides thus obtained, with halogen attached directly to double-bonded carbon, we recognize as vinylic halides; as we know, they are very unreactive. Under mild conditions, therefore, dehydrohalogenation stops at the vinylic halide stage; more vigorous conditions—use of a stronger base—are required for alkyne formation.

Conversion of smaller alkynes into larger ones is done by use of **metal acetylides**. These are particularly easy to generate because of a special property of certain alkynes and, once made, are highly versatile reagents.

7.7 Reactions of alkynes

Just as alkene chemistry is the chemistry of the carbon–carbon double bond, so alkyne chemistry is the chemistry of the carbon–carbon triple bond. Like alkenes, alkynes undergo electrophilic addition, and for the same reason: availability of the loosely held π electrons.

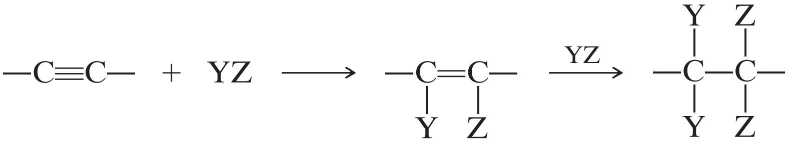
Addition of hydrogen, halogens, and hydrogen halides to alkynes is very much like addition to alkenes, except that here *two* molecules of reagent can be consumed for each triple bond. As shown, it is generally possible, by proper selection of conditions, to limit reaction to the first stage of addition, formation of alkenes. In some cases at least, this is made simpler because of the way that the substituents introduced in the first stage affect the second stage.

Besides addition, alkynes undergo certain reactions that are due to the acidity of a hydrogen atom held by triply bonded carbon.

Problem 7.2 (a) Write the equation for the two-stage addition of bromine to 2-butyne. (b) How will the first two bromine atoms affect the reactivity of the double bond? (c) How will this influence the competition for halogen between 2-butyne and 2,3-dibromo-2-butene?(d) In what proportions would you mix the reagents to help limit reaction to the first stage? (e) Would you bubble 2-butyne into a solution of Br_2 in CCl_4, or drip the bromine solution into a solution of 2-butyne?

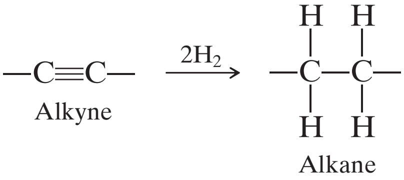
REACTIONS OF ALKYNES

Addition Reactions

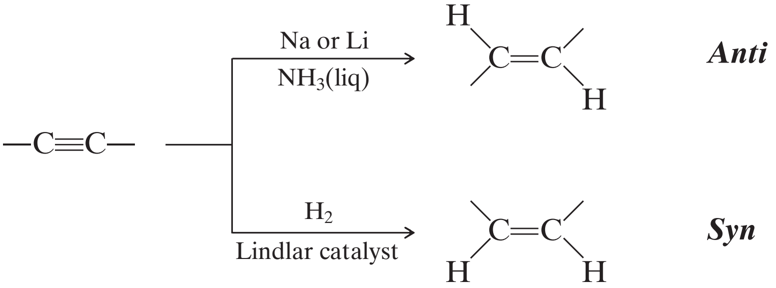


$$-C\equiv C- \;+\; YZ \longrightarrow -\underset{Y}{C}{=}\underset{Z}{C}- \xrightarrow{YZ} -\overset{Y}{\underset{Y}{C}}-\overset{Z}{\underset{Z}{C}}-$$

1. Addition of hydrogen.

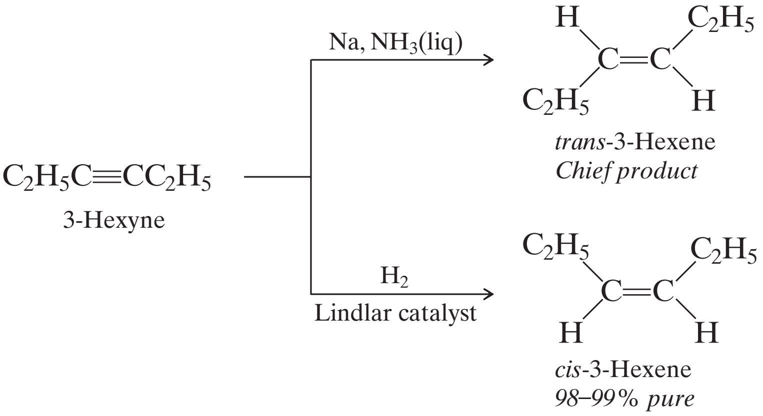


$$\underset{\text{Alkyne}}{-C\equiv C-} \xrightarrow{2H_2} \underset{\text{Alkane}}{-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-}$$



Examples:

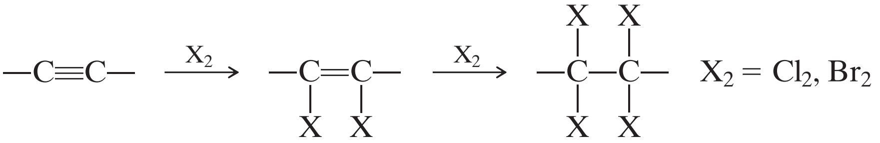
$$\underset{\text{2-Butyne}}{CH_3-C\equiv C-CH_3} \xrightarrow{2H_2,\ Ni} \underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3}$$



trans-3-Hexene
Chief product

cis-3-Hexene
98–99% pure

2. Addition of halogens.

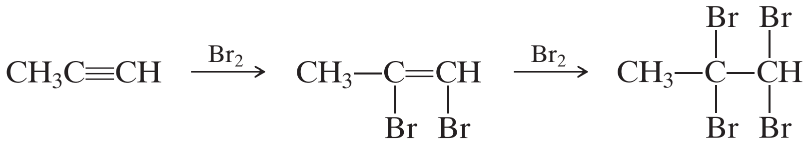


$$-C\equiv C- \xrightarrow{X_2} -\underset{X}{C}{=}\underset{X}{C}- \xrightarrow{X_2} -\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}- \quad X_2 = Cl_2, Br_2$$

CONTINUED

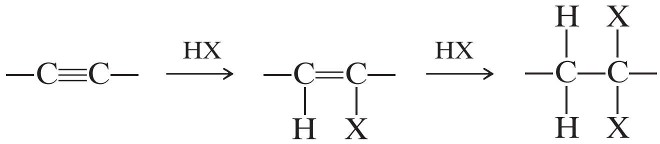
CONTINUED

Example:



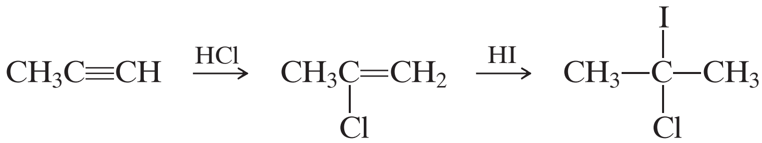
$$CH_3C{\equiv}CH \xrightarrow{Br_2} CH_3{-}\underset{Br}{C}{=}\underset{Br}{CH} \xrightarrow{Br_2} CH_3{-}\overset{Br}{\underset{Br}{C}}{-}\overset{Br}{\underset{Br}{CH}}$$

3. Addition of hydrogen halides.



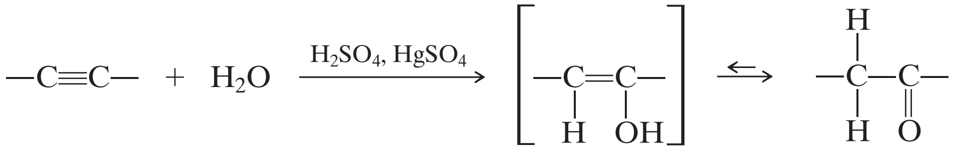
$$-C{\equiv}C- \xrightarrow{HX} -\underset{H}{C}{=}\underset{X}{C}- \xrightarrow{HX} -\overset{H}{\underset{H}{C}}-\overset{X}{\underset{X}{C}}- \qquad HX = HCl, HBr, HI$$

Example:



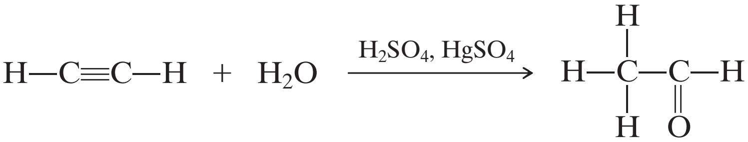
$$CH_3C{\equiv}CH \xrightarrow{HCl} CH_3\underset{Cl}{C}{=}CH_2 \xrightarrow{HI} CH_3{-}\overset{I}{\underset{Cl}{C}}{-}CH_3$$

4. Addition of water. Hydration.



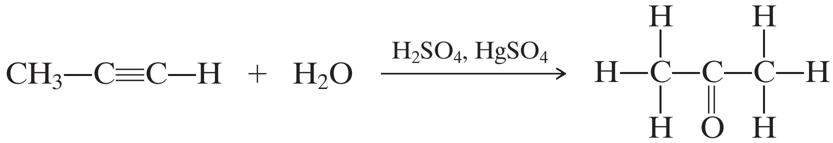
$$-C{\equiv}C- \;+\; H_2O \xrightarrow{H_2SO_4,\ HgSO_4} \left[-\underset{H}{C}{=}\underset{OH}{C}-\right] \leftrightarrows -\overset{H}{\underset{H}{C}}-\underset{\overset{\|}{O}}{C}-$$

Examples:



$$H{-}C{\equiv}C{-}H \;+\; H_2O \xrightarrow{H_2SO_4,\ HgSO_4} H{-}\overset{H}{\underset{H}{C}}{-}\underset{\overset{\|}{O}}{C}{-}H$$

Acetaldehyde



$$CH_3{-}C{\equiv}C{-}H \;+\; H_2O \xrightarrow{H_2SO_4,\ HgSO_4} H{-}\overset{H}{\underset{H}{C}}{-}\underset{\overset{\|}{O}}{C}{-}\overset{H}{\underset{H}{C}}{-}H$$

Acetone

Reactions as Acids

$$-C{\equiv}C{-}H + \text{base} \longrightarrow -C{\equiv}C{:}^-$$

5. Formation of metal acetylides.

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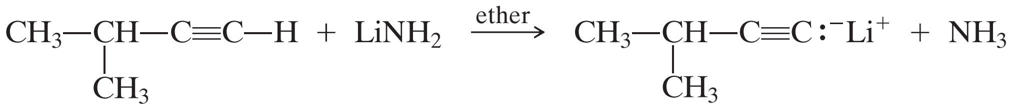
Examples:



$$CH_3-\underset{\substack{|\\ CH_3}}{CH}-C\equiv C-H + LiNH_2 \xrightarrow{\text{ether}} CH_3-\underset{\substack{|\\ CH_3}}{CH}-C\equiv C{:}^-Li^+ + NH_3$$

Lithium isopropylacetylide

$$CH_3-C\equiv C-H + n\text{-}BuLi \longrightarrow CH_3C\equiv C^-Li^+ + n\text{-}BuH$$

Lithium methylacetylide

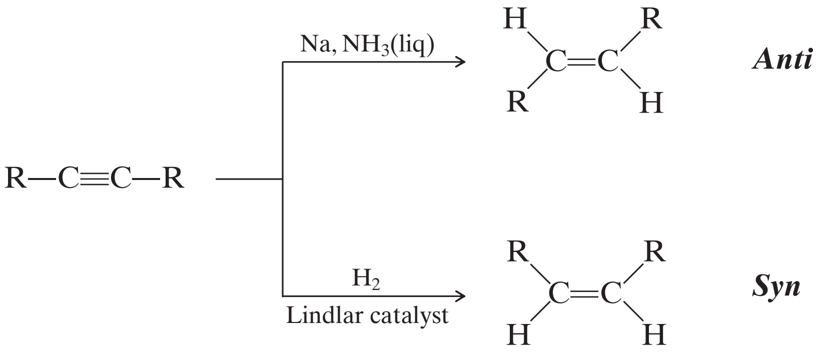
$$HC\equiv CH + C_2H_5MgBr \longrightarrow HC\equiv CMgBr + C_2H_6$$

Ethynylmagnesium bromide

7.8 Reduction to alkenes

Reduction of an alkyne to the double-bond stage can—unless the triple bond is at the end of a chain—yield either a *cis* alkene or a *trans* alkene. Just which isomer predominates depends upon the choice of reducing agent.

Predominantly *trans* alkene is obtained by reduction of alkynes with sodium or lithium in liquid ammonia. Almost entirely *cis* alkene (as high as 98%) is obtained by hydrogenation of alkynes with several different catalysts: a specially prepared palladium called the *Lindlar catalyst*, for example.



Each of these reactions is, then, highly stereoselective. The stereoselectivity in the *syn*-reduction of alkynes is attributed, in a general way, to the attachment of two hydrogens to the same side of an alkyne sitting on the catalyst surface; presumably this same stereochemistry holds for the hydrogenation of terminal alkynes, $RC\equiv CH$, which cannot yield *cis* and *trans* alkenes.

The mechanism that gives rise to *anti*-reduction will not be taken up here.

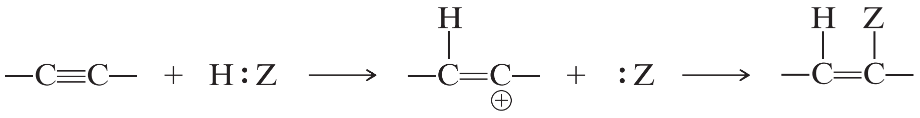
We have discussed many times the stereospecificity of biological systems. Where alkenes are concerned, this takes the form of diastereospecificity: organisms discriminating between geometric isomers. We saw a number of examples of this in the response of insects toward pheromones. For synthetic materials to be effective in a living organism, we said, the stereospecificity of biological action demands an equal stereoselectivity in the synthesis of these materials. Many new methods have been developed to generate double bonds stereoselectively; but the simplest and the one most often turned to is the hydrogenation of alkynes.

The matter goes much further than this. These alkenes may be the final products desired, as with some pheromones. But more often they are simply an intermediate stage. Alkenes undergo a variety of reactions, many of them diastereoselective and even enantioselective; if the stereoselectivity of these reactions is to be utilized fully, one must start with a stereochemically pure alkene.

Problem 7.3 Most methods of making alkenes yield predominantly the more stable isomer, usually the *trans*. Outline all steps in the conversion of a mixture of 75% *trans*-2-pentene and 25% *cis*-2-pentene into essentially pure *cis*-2-pentene.

7.9 Mechanism of electrophilic addition to alkynes

Addition of acids like the hydrogen halides is electrophilic addition, and it appears to follow the same mechanism with alkynes as with alkenes: via an intermediate carbocation. The difference is that here the intermediate is a *vinylic cation*.



$$-C\equiv C- \ + \ H:Z \longrightarrow -\overset{H}{\overset{|}{C}}=\underset{\oplus}{C}- \ + \ :Z \longrightarrow -\overset{H}{\overset{|}{C}}=\overset{Z}{\overset{|}{C}}-$$

A vinylic cation

We have learned that—relative to the substrates for heterolysis—vinyl cations are even less stable than primary alkyl cations; and we saw that, by heterolysis, they are formed comparatively slowly and can be generated only by the departure of "super" leaving groups.

Now, in electrophilic addition to alkenes, reactivity depends upon the stability of the intermediate carbocation: the more stable the carbocation, the faster it is formed. Does this mean, then, that addition to alkynes will be a great deal slower than to alkenes?

The fact is, it is *not* very much slower: addition of protic acids to alkynes takes place at very much the same rate as to alkenes. The explanation is found in our definition of stability of a carbocation: *relative to the substrate from which it is generated*. Relative to substrates for heterolysis, vinylic cations *are* unstable, and we have attributed this to the unusually strong bond holding the leaving group in vinylic substrates—not to any inherent instability in the cations themselves. And by het-erolysis vinylic cations are slow to form. But in addition reactions the substrates are alkenes and alkynes, and these compounds must be the standards for comparison of carbocation stabilities: an alkene for a saturated carbocation, and an alkyne for a vinylic cation. Relative to the substrate from which each is generated *in an addition reaction*, the two are of about the same stability. The energy climb from alkyne to a vinylic cation is about the same as the climb from an alkene to a saturated cation.

Toward the addition of halogens, alkynes are considerably less reactive than alkenes. For alkenes, as we have seen, this reaction involves the initial formation of a cyclic halonium ion. The lower reactivity of alkynes has been attributed to the greater difficulty of forming such cyclic intermediates.

Problem 7.4 The addition of HCl to 3,3-dimethyl-1-butyne gives the following products: 2,2-dichloro-3,3-dimethylbutane (44%), 2,3-dichloro-2,3-dimethylbutane (18%), 1,3-dichloro-2,3-dimethylbutane (34%). Account in detail for the formation of each of these products.

Problem 7.5 Hydration of propyne yields the ketone *acetone*, CH_3COCH_3, rather than the aldehyde CH_3CH_2CHO. What does this suggest about the orientation of the initial addition?

7.10 Acidity of alkynes. Very weak acids

In our earlier consideration of acids (in the Lowry-Brønsted sense), we took *acidity* to be a measure of the tendency of a compound to lose a hydrogen ion. Appreciable acidity is generally shown by compounds in which hydrogen is attached to a rather electronegative atom (for example, N, O, S, X). The bond holding the hydrogen is polar, and the relatively positive hydrogen can separate as the positive ion; considered from another viewpoint, an electronegative element can better accommodate the pair of electrons left behind. In view of the electronegativity series, F > O > N > C, it is not surprising to find that HF is a fairly strong acid, H_2O a comparatively weak one, NH_3 still weaker, and CH_4 so weak that we would not ordinarily consider it an acid at all.

In organic chemistry we are frequently concerned with the acidities of compounds that do not turn litmus red or neutralize aqueous bases, yet have a tendency—even though small—to lose a hydrogen ion.

A triply bonded carbon acts as though it were an entirely different element—a more electronegative one—from a carbon having only single or double bonds. As a result, hydrogen attached to triply bonded carbon, as in acetylene or any alkyne with the triple bond at the end of the chain ($RC\equiv C—H$), shows appreciable acidity. For example, sodium reacts with acetylene to liberate hydrogen gas and form the compound *sodium acetylide*.

$$HC\equiv C—H \;+\; Na \longrightarrow \underset{\text{Sodium acetylide}}{HC\equiv C{:}^{-}Na^{+}} \;+\; \tfrac{1}{2}H_2$$

Now, just how strong an acid is acetylene? Using the method of displacement, let us compare it with a number of familiar compounds, inorganic and organic.

Lithium metal reacts with ammonia to form lithium amide, $LiNH_2$, which is the salt of the weak acid, $H—NH_2$.

$$NH_3 \;+\; Li \longrightarrow \underset{\substack{\text{Lithium}\\ \text{amide}}}{Li^{+}NH_2^{-}} \;+\; \tfrac{1}{2}H_2$$

Addition of acetylene to lithium amide dissolved in ether gives ammonia and lithium acetylide.

$$\underset{\substack{\text{Stronger}\\ \text{acid}}}{HC\equiv C—H} \;+\; \underset{\substack{\text{Stronger}\\ \text{base}}}{Li^{+}NH_2^{-}} \;\rightleftarrows\; \underset{\substack{\text{Weaker}\\ \text{acid}}}{H—NH_2} \;+\; \underset{\substack{\text{Weaker}\\ \text{base}}}{HC\equiv C^{-}Li^{+}}$$

The weaker acid, $H—NH_2$, is displaced from its salt by the stronger acid, $HC\equiv C—H$. In other language, the strong base, NH_2^{-}, pulls the proton away from the weaker base, $HC{\equiv}C^-$; if NH_2^- holds the proton more tightly than $HC{\equiv}C^-$, then $H{-}NH_2$ must necessarily be a weaker acid than $HC{\equiv}C{-}H$.

Acetylene is a weaker acid than water. When water is added to an acetylide, hydroxide ion is formed and acetylene is liberated. In a similar way, acetylene can be shown to be a weaker acid than alcohols, too.

$$\underset{\substack{\text{Stronger}\\ \text{acid}}}{\mathrm{H{-}OH}} + \underset{\substack{\text{Stronger}\\ \text{base}}}{\mathrm{HC{\equiv}C^-Li^+}} \rightleftharpoons \underset{\substack{\text{Weaker}\\ \text{acid}}}{\mathrm{HC{\equiv}C{-}H}} + \underset{\substack{\text{Weaker}\\ \text{base}}}{\mathrm{Li^+OH^-}}$$

We can now insert acetylene into our sequences of relative acidity and basicity. Other alkynes that contain a hydrogen attached to triply bonded carbon—that is, *terminal alkynes*—show comparable acidity.

Relative acidities $H_2O > ROH > HC{\equiv}CH > NH_3 > RH$

Relative basicities $OH^- < OR^- < HC{\equiv}C^- < NH_2^- < R^-$

According to our sequence, acetylene should be a stronger acid than an alkane, RH. This is quite true, and the difference in acidity is of considerable use in synthesis.

If a terminal acetylene is treated with an alkylmagnesium halide or an alkyllithium, the alkane is displaced from its "salt", and the metal acetylide is obtained. For example:

$$\underset{\text{Propyne}}{\mathrm{CH_3C{\equiv}C{-}H}} + \mathrm{C_2H_5MgBr} \longrightarrow \mathrm{C_2H_6} + \underset{\substack{\text{Propyn-1-ylmagnesium}\\ \text{bromide}}}{\mathrm{CH_3C{\equiv}C{-}MgBr}}$$

$$\underset{\text{Propyne}}{\mathrm{CH_3C{\equiv}C{-}H}} + \mathrm{CH_3CH_2CH_2CH_2Li} \longrightarrow \mathrm{CH_3CH_2CH_2CH_3} + \underset{\text{Propyn-1-yllithium}}{\mathrm{CH_3C{\equiv}C{-}Li}}$$

Such reactions provide the best route to these important organometallic compounds.

How can we account for the fact that hydrogen attached to triply bonded carbon is especially acidic? How can we account for the fact that acetylene is a stronger acid than, say, ethane? A possible explanation can be found in the electronic configurations of the anions.

If acetylene is a stronger acid than ethane, then the acetylide ion must be a weaker base than the ethide ion, $C_2H_5^-$. In the acetylide anion the unshared pair

$$\underset{\substack{\text{Acetylene}\\ \textit{stronger}\\ \textit{acid}}}{\mathrm{HC{\equiv}CH{:}H}} \rightleftharpoons \mathrm{H^+} + \underset{\substack{\text{Acetylide ion}\\ \textit{Weaker}\\ \textit{base}}}{\mathrm{HC{\equiv}C{:}^-}}$$

$$\underset{\substack{\text{Ethane}\\ \textit{Weaker}\\ \textit{acid}}}{\mathrm{CH_3CH_2{:}H}} \longleftarrow \mathrm{H^+} + \underset{\substack{\text{Ethide ion}\\ \textit{Stronger}\\ \textit{base}}}{\mathrm{CH_3CH_2{:}^-}}$$

of electrons occupies an *sp* orbital; in the ethide anion the unshared pair of electrons occupies an sp^3 orbital. The availability of this pair for sharing with acids determines the basicity of the anion. Now, compared with an sp^3 orbital, an *sp* orbital has less *p* character and more *s* character. An electron in a *p* orbital is at some distance from the nucleus and is held relatively loosely; an electron in an *s* orbital, on the other hand, is close to the nucleus and is held more tightly. The acetylide ion is the weaker base since its pair of electrons is held more tightly, in an *sp* orbital.

Problem 7.6 The traditional method of making acetylene—with uses ranging from miners' lamps and bicycle lights to large-scale industrial production—involved the action of water on *calcium carbide*, CaC_2. (a) What do you suppose the structure of calcium carbide is? Can you suggest another name for it? (b) What is the nature of its reaction with water?

7.11 Reactions of metal acetylides. Synthesis of alkynes

We have described metal acetylides as important organometallic compounds. Now, why is this? Because *they enable us to convert little alkynes into big ones*.

Like lithium dialkylcoppers, lithium or sodium acetylides can react with primary alkyl halides.

$$\mathrm{RC{\equiv}C{-}Li} + \underset{\text{A 1° alkyl halide}}{\mathrm{R'X}} \longrightarrow \mathrm{RC{\equiv}C{-}R'} + \mathrm{LiX}$$

The alkyl group becomes attached to the triply bonded carbon, and a new, larger alkyne has been generated. For example:

$$\underset{\text{Ethynyllithium}}{\mathrm{HC{\equiv}C{-}Li}} + \mathrm{CH_3CH_2Br} \longrightarrow \underset{\text{1-Butyne}}{\mathrm{HC{\equiv}C{-}CH_2CH_3}} + \mathrm{LiBr}$$

$$\underset{\text{1-Butyn-1-yllithium}}{\mathrm{CH_3CH_2C{\equiv}C{-}Li}} + \mathrm{CH_3Br} \longrightarrow \underset{\text{2-Pentyne}}{\mathrm{CH_3CH_2C{\equiv}C{-}CH_3}} + \mathrm{LiBr}$$

This reaction gives acceptable yields only with primary alkyl halides, and for a familiar reason: acetylide ions are strong bases, and with secondary or tertiary alkyl halides, elimination is the predominant reaction.

As we shall find, complicated alcohols can be readily synthesized by use of Grignard reagents and organolithium compounds. These syntheses can involve not only alkyl organometallics but their alkynyl counterparts as well, and thus yield molecules that contain two highly reactive groups, the carbon-carbon triple bond and—OH.

7.12 Analysis of alkynes

In their response to characterization tests, alkynes resemble alkenes: they decolorize bromine in carbon tetrachloride without evolution of hydrogen bromide, and they decolorize cold, neutral, dilute permanganate; they are not oxidized by chromic anhydride. Like dienes, however, they are more unsaturated than alkenes. This property can be detected by determination of their molecular formulas (C_nH_{2n-2}) and by a quantitative hydrogenation (two moles of hydrogen are taken up per mole of hydrocarbon).

Proof of structure is best accomplished by the same degradative methods that are used in studying alkenes. Upon ozonolysis alkynes yield carboxylic acids, whereas alkenes yield aldehydes and ketones. For example:

$$\underset{\text{2-Pentyne}}{CH_3CH_2C\equiv CCH_3} \xrightarrow{O_3} \xrightarrow{H_2O} \underset{\text{Carboxylic acids}}{CH_3CH_2COOH \quad + \quad HOOCCH_3}$$

Acidic alkynes react with certain heavy metal ions, chiefly Ag^+ and Cu^+, to form insoluble acetylides. Formation of a precipitate upon addition of an alkyne to a solution of $AgNO_3$ in alcohol, for example, is an indication of hydrogen attached to triply bonded carbon. This reaction can be used to differentiate *terminal* alkynes (those with the triple bond at the *end* of the chain) from *non-terminal* alkynes.

$$\underset{\substack{\text{1-Butyne}\\ \textit{A terminal alkyne}}}{CH_3CH_2C\equiv C—H} \xrightarrow{Ag^+} \underset{\text{Precipitate}}{CH_3CH_2C\equiv C—Ag} \left[\xrightarrow{HNO_3} \underset{\text{1-Butyne}}{CH_3CH_2C\equiv C—H} + Ag^+\right]$$

$$\underset{\substack{\text{2-Butyne}\\ \textit{A non-terminal alkyne}}}{CH_3—C\equiv C—CH_3} \xrightarrow{Ag^+} \text{no reaction}$$

If allowed to dry, these heavy metal acetylides are likely to explode. They should be destroyed while still wet by warming with nitric acid; the strong mineral acid regenerates the weak acid, acetylene.

Problem 7.7 Contrast the ozonolysis products of the following isomers: (a) 1-pentyne, (b) 2-pentyne, (c) 3-methyl-1-butyne, (d) 1,3-pentadiene, (e) 1,4-pentadiene.

EXERCISE

1. (a) Draw structures of the seven isomeric alkynes of formula C_6H_{10}. (b) Give the IUPAC and derived name of each. (c) Indicate which ones will react with Ag^+ or $Cu(NH_3)_2{}^+$. (d) Draw structures of the ozonolysis products expected from each.

2. Outline all steps in the synthesis of propyne from each of the following compounds, using any needed organic or inorganic reagents.

(a) 1,2-dibromopropane
(b) propylene
(c) isopropyl bromide
(d) *n*-propyl alcohol
(e) 1,1-dichloropropane
(f) acetylene

3. Outline all steps in the synthesis from acetylene of each of the following compounds, using any needed organic or inorganic reagents.

(a) ethylene
(b) ethane
(c) 1,1-dibromoethane
(d) vinyl chloride
(h) 1-butyne
(i) 2-butyne
(j) *cis*-2-butene
(k) *trans*-2-butene

(e) 1,2-dichloroethane
(f) acetaldehyde
(g) propyne
(l) 1-pentyne
(m) 2-pentyne
(n) 3-hexyne

4. Give structures and names of the organic products expected from the reaction (if any) of 1-butyne with:

(a) 1 mol H_2, Ni
(b) 2 mol H_2, Ni
(c) 1 mol Br_2
(d) 2 mol Br_2
(e) 1 mol HCl
(f) 2 mol HCl
(g) H_2O, H^+,Hg^{2+}
(h) Ag^+
(i) product (h) + HNO_3
(j) $LiNH_2$
(k) product (j) + C_2H_5Br
(l) product (j) + *tert*-butyl chloride
(m) C_2H_5MgBr
(n) product (m) + H_2O
(o) O_3, then H_2O
(p) hot $KMnO_4$

5. Outline all steps in the synthesis from 2-butyne of each of the following compounds, using any needed organic or inorganic reagents.

(a) *cis*-2-butene
(b) *trans*-2-butene
(c) *meso*-2,3-dibromobutane
(d) racemic *threo*-3-chloro-2-butanol
(e) *meso*-2,3-butanediol
(f) racemic 2,3-butanediol
(g) 2-butanone, $CH_3CH_2COCH_3$

6. Outline all steps in a possible laboratory synthesis of each of the following, using acetylene and alcohols of four carbons or fewer as your only organic source, and any necessary inorganic reagents. (*Remember*: Work backwards.)

(a) *meso*-3,4-dibromohexane
(b) racemic (2*R*,3*R*;2*S*,3*S*)-2,3-heptanediol

7. Describe chemical methods (simple tests where possible) that would distinguish between:

(a) 2-pentyne and *n*-pentane
(b) 1-pentyne and 1-pentene
(c) 2-pentyne and 2-pentene
(d) 1-pentyne and 2-pentyne
(e) 1,3-pentadiene and *n*-pentane
(f) 1,3-pentadiene and 1-pentyne
(g) 1,4-pentadiene and 2-pentyne
(h) 2-hexyne and isopropyl alcohol

Tell exactly what you would *do* and *see*.

8. On the basis of physical properties, an unknown compound is believed to be one of the following:

diethyl ether (b.p. 35 °C)
n-pentane (b.p. 36 °C)
2-pentene (b.p. 36 °C)
1-chloropropene (b.p. 37 °C)
trimethylethylene(b.p. 39 °C)
1-pentyne (b.p. 40 °C)
methylene chloride (b.p. 40 °C)
3,3-dimethyl-1-butene (b.p. 41 °C)
1,3-pentadiene (b.p. 42 °C)

Describe how you would go about finding out which of the possibilities the unknown actually is. Where possible, use simple chemical tests; where necessary, use more elaborate chemical methods like quantitative hydrogenation and cleavage. Tell exactly what you would *do* and *see*.

9. *Muscalure* is the sex pheromone of the common house fly. On the basis of the following synthesis, give the structure of muscalure (and, of course, of the intermediates A and B).

$$\begin{aligned} n\text{-}C_{13}H_{27}C{\equiv}CH \;+\; n\text{-BuLi} &\longrightarrow \text{A } (C_{15}H_{27}Li) \\ \text{A} \;+\; n\text{-}C_8H_{17}Br &\longrightarrow \text{B } (C_{23}H_{44}) \\ \text{B} \;+\; H_2\text{, Lindlar catalyst} &\longrightarrow \textit{muscalure } (C_{23}H_{46}) \end{aligned}$$