Chapter 3: Alkenes and Alkynes





lycopene

(alternating double boods)

Hydrogenation of Alkenes and Alkynes

Hydrocarbons that have carbon-carbon double bond are called alkenes; those with a carbon-carbon triple bond are alkynes



Compounds with more than one double or triple bonds exist. Multiple double bonds may lead to dienes, trienes, tetraenes and polyenes. β-carotene and lycopene are examples of polyenes



When two or more multiple bonds re present in a molecule, they can be classified depending on the relative positions of the bonds $\mathcal{L}^{\mathfrak{sp}^3}$ set





C = C - C - C = CC = C - C - C = Cnonconjugated (isolated)

Which of the following compounds have conjugated multiple bonds?



Nomenclature

The ending <u>ene</u> is used to designate carbon-carbon double bond. When more than one double bond is present, the ending is <u>diene</u>, triene, tetraene and so on. The ending <u>yne</u> is used for triple carbon-carbon bond.

Select the longest chain that includes both carbons of the double bond or triple bond.



named as a butene, not as a pentene

Number the chain from the end nearest the multiple bond so that the carbon atoms in that bond have the lowest possible numbers.

$$\overset{1}{C} = \overset{2}{C} = \overset{3}{C} = \overset{4}{C} = \overset{5}{C} = \overset{6}{C} = \overset{6}{C} = \overset{6}{C} = \overset{6}{C} = \overset{1}{C} = \overset{6}{C} = \overset{1}{C} = \overset{1}$$

If the multiple bond is equidistant from both ends of the chain, number the chain from the end nearest the first branch point.

Indicate the position of the multiple bond using the lower numbered carbon atom of that bond.

$$^{1}_{CH_{2}} \stackrel{2}{=} \stackrel{3}{CHCH_{2}} \stackrel{4}{CH_{3}}$$
 1-butene, *not* 2-butene

If more than one multiple bond is present, number the chain from the end nearest the first multiple bond.

If the double bond and the triple bond are equidistant from the end of the chain, the double bond receives the lowest number.



The root name is from the longest carbon chain containing the multiple bond

CH ₃ CH ₃	CH ₂ =CH ₂	HC≡CH	
ethane	ethene ✓	ethyne ✓	
CH ₃ CH ₂ CH ₃ propane	CH ₂ =CHCH ₃ propene ✓	HC=CCH ₃	
CH3CH2CH2CH3	$CH_2 = CH - H_2 CH_3$	2-butane so are	n J
	$CH_3 - CH = CH - CH_3$	2-butane z-butan	e





The numbering rules applied

 $CH = CH - CH - CH_3$

⊁

4-methyl-2-pentene (*Not* 2-methyl-3-pentene; the chain is numbered so that the double bond gets the lower number.)

CH₃-

 $\begin{array}{c}
1 \\
CH_2 \\
\hline
CH_2CH_3 \\
\hline
CH_2CH_3 \\
\hline
CH_2CH_3 \\
\hline
CH_2CH_3 \\
\hline
Named this way
\end{array}$

(Named this way, even though there is a five-carbon chain present, because that chain does not include both carbons of the double bond.)

$$^{1}_{CH_{2}} = ^{2}_{CH} - ^{3}_{CH} = ^{4}_{CH_{2}}$$

1,3-butadiene (Note the *a* inserted in the name, to help in pronunciation.)



1-penten-4-yne



1-penten-4-yne



4-hepten-1-yne

With the cyclic hydrocarbons, we start numbering the ring with the carbons of the multiple bond.



cyclopentene (No number is necessary, because there is only one possible structure.)



names.)

CH₃

3





1,3-cyclohexadiene

1,4-cyclohexadiene



2-bromo-1,3-pentadiene

Some Common names

 $CH_3CH = CH_2$ $CH_2 = CH_2$ HC≡CH acetylene (ethene) A <u>acetylene</u> comment varme (ethyne) ethylene propylene (propene)_ یار تی ایک مالی می برد نابی می این نابی می دارد نابی می دارد











Some Facts about Double Bonds

رائی ملک حکیا حکی ایجاد اکان کل رل bond حوں الک یوے بکرے aging Spr Squee clill Fetra hydra 1 1915-21 12 Sp2 tryand planer $C = \frac{\pi}{c} C$ 1200 = END = 0

TABLE 3.1 — Comparison of C—C and C—C Bor	Ids
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Property	C—C	C==C
 Number of atoms attached to a carbon 	4 (tetrahedral)	3 (trigonal)
2. Rotation	relatively free	restricted
3. Geometry	many conformations are possible; staggered is preferred	planar
4. Bond angle	109.5°	120°
5. Bond length	1.54 Å	1.34 Å

The Orbital Model of a Double Bond; the pi Bond



Atomic orbitals of carbon

The 2*s* and two 2*p* orbitals are combined to form three hybrid sp^2 orbitals, leaving one electron still in a *p* orbital.













Cis-Trans Isomerism in Alkenes





trans-1,2-dichloroethene bp 47°C, mp −50°C T V wot polar The Chemistry of Vision





Are cis-trans isomers possible for 1-butene and 2-butene?



Geometric isomers of alkenes can be interconverted if sufficient energy is supplied to break the pi bond and allow rotation about the remaining sigma Prans Jois aspectosis par de bond. i asel gla طلع کا رازوریت کاکل محومت مما الحصو علم مسلم Rohan با مرک الوابعة روسا محمو علم مسلم Rohan

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reformation of

the IT-bord

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ركاكه'

حيك بدي احد دالا, لوب ،

atomic number) ----

چان الم بیل

N Co

المعا (م) الموار

دطلع عادو ومدة مرتبطة مرابرا بطة 0 المتعلية عادة عاد الالية كانزر ر مرد مين يعهم ين جمع كات وحدة N ور مدر) نیفتار)

مل ادل. Syster deal stor 「野野」炎」 やまた | 町田 三田 日日 日日日日 , (c r لاترا الكريونة المعى متعل C 23/61 ab M صاحاتم CL 000 aromatic 5 s, ćis لم ل الم الم H₃C 2 trans-6.20 (²) cis-3-methyl-2-pentene العدر الذري ٢ y 1920 cg atomic number philip of the synthese synthese states and the second states and the second sec 02. 50 d نا ر 0'N المها دفرية د*د*′ σU ادائه برجری دیدی ادل ایک برجری دیدی ادل ایک کاری بعدیت 010 بعريب ک يسب ک المرابط في کر کر المرابط ميک Wans Cis Louis K Ъ 1/3/5nerrarriene

Addition and Substitution Reactions Compared



Addition of halogens X2 (\mathbb{B}_{2} , \mathcal{O}_{2} , \mathcal{O}_{2} , \mathcal{O}_{2} , \mathcal{O}_{2})

 $\begin{array}{c} \text{CH}_{3}\text{CH} = \text{CHCH}_{3} + \underbrace{\text{Cl}}_{2} \longrightarrow & \text{CH}_{3}\text{CH} - \text{CHCH}_{3} \\ & & | & | \\ \text{Sembervical} & & | & | \\ \text{Cl} & \text{Cl} & \text{Cl} \\ \text{allheve} & & \text{Cl} & \text{Cl} \\ \text{2,3-dichlorobutane} \\ & \text{bp } 1-4^{\circ}\text{C} & & \text{bp } 117-\frac{1}{6}19^{\circ}\text{C} \end{array}$







Browine added

Subvrated

- END

BN

Bonz 6 unsahrshal Hydran alkene allyne c = c' + Br - c - c'

0



Acids that add this way are the hydrogen halides (H-F, H-Cl, H-Br, H-I) and sulfuric acid (H-OSO3H)

$$CH_{2} = CH_{2} + H - Cl \longrightarrow CH_{2} - CH_{2} \quad (or CH_{3}CH_{2}Cl)$$

$$H \quad Cl$$

$$H \quad Cl$$

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$$Cl$$

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$$Cl$$

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$$Cl$$

$$CH_{3} = CH_{2} + H - Cl$$

$$H \quad Cl$$

$$Cl$$

$$CH_{3} = CH_{2} + H - Cl$$

$$Cl$$

$$CH_{3} = CH_{3} + CH_{3} + Cl$$

$$CH_{3} = CH_{3} + C$$



Write the equation for each of the following reactions

a)2-butene + HCl

b)3-Hexene + HI

c)4-methylcyclopentene + HBr

Table 3.2Classification of Reagents and Alkenes bySymmetry with Regard to Addition Reactions

	Symmetric	Unsymmetric
Reagents	Br – Br	H + Br
	Cl — Cl	н—он
	н+н	H – OSO ₃ H
Alkenes	$CH_2 = CH_2$	$CH_{3}CH = CH_{2}$
		CH ₃
	mirror plane	not a mirror plane




Addition of Unsymmetric Reagents to Unsymmetric Alkenes; Markovnikov's Rule



















Markovnokov's Rule Explained













Reaction coordinate

Energy









transition state for hydroboration

0

$$3 \text{ CH}_{3}\text{CH}=\text{CH}_{2} + \text{BH}_{3} \longrightarrow \text{CH}_{3}\text{CH}_{2}\text{CH}_{2} - \text{B}$$

$$\text{Propene} \quad \text{borane} \quad \text{tri-}n\text{-propylborane}$$

$$\mathcal{CH}_{2}\text{CH}_{2}\text{CH}_{3}$$

$$\mathcal{CH}_{2}\text{CH}_{2}\text{CH}_{3}$$

 $(CH_3CH_2CH_2)_3B + 3 H_2O_2 + 3 NaOH \longrightarrow$ tri-*n*-propylborane

 $3 \text{ CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{OH} + \text{Na}_{3}\text{BO}_{3} + 3 \text{ H}_{2}\text{O}$ *n*-propyl <u>alcohol</u> sodium borate



per,

 $CH_{3} \xrightarrow[]{} CH_{2} \xrightarrow[]{} BH_{3} \xrightarrow[]{} H_{2}O_{2} \xrightarrow[]{} OH^{-} \longrightarrow[]{} OH^{-} \xrightarrow[]{} OH^{-} \xrightarrow[]{}$





What alkene is needed to obtain he alcohol below via hydroboration-oxidation sequence, what product would this alkene give with acid-catalyzed hydration.



Addition of Hydrogen



0



~ per

Addition to Conjugated Systems











Cycloaddition to Conjugated Dienes: Diels-Alder Reaction












Free-Radical Additions; Polyethene





$$ROCH_2CH_2 \xrightarrow{CH_2=CH_2} ROCH_2CH_2CH_2CH_2CH_2$$

ROCH₂CH₂CH₂CH₂CH₂CH₂ and so on













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Other Alkene Oxidations







Atomic orbitals of carbon The 2*s* and one 2*p* orbital are combined to form two hybrid *sp* orbitals, leaving one electron in each of two *p* orbitals.



addition of halogen 7 2NSrz Br Br C = C $H-C\equiv C-H \xrightarrow{Br_2}$ $H - \dot{C} - \dot{C} - H$ manail cis for ethyng aibility 261 c.S. (rans-1,2-dibromoethene Br Br Br 1,1,2,2-tetrabromoethane مريق فري لاين تقرير properetes ---other computin as to legel a find a f > سرزار در العناما بزار محمد ذراح) وزارة العزام الجريكي ٣- كلاند م المتفرع تعل لرجة العلكان بالنبة الشاط الكميا في الكيني ولاركاني كانتظ مكالاكان الفرالا في معديث الحكانة درجة العامان وجس



Table 3.3 – Common Petroleum Fractions			
Boiling range, °C	Name	Range of carbon atoms per molecule	Use
<20	gases	C ₁ to C ₄	heating, cooking, petrochemical raw material
20–200	naphtha; straight-run gasoline	C_5 to C_{12}	fuel; lighter fractions (such as petroleum ether, bp 30°C–60°C) also used as laboratory solvents
200–300	kerosene	C ₁₂ to C ₁₅	fuel
300–400	fuel oil	C ₁₅ to C ₁₈	heating homes, diesel fuel
>400		over C ₁₈	lubricating oil, greases, paraffin waxes, asphalt







MSS

Bry Norden



2,2-dibromopropane





increasing acidity



در مای Membrial شیخه افتلای عدد ۸ میچ کیو کرامد وردا می کارد افتلای رامنیمی یکوی عذال ی کیوی





C C

REACTIONS SUMMARY







$$3 \text{ RCH}=CH_2 \xrightarrow{BH_3} (RCH_2CH_2)_3 \xrightarrow{B} \frac{H_2O_2}{HO^-} 3 \text{ RCH}_2CH_2OH$$









 $nH_2C = CH_2 \xrightarrow{\text{catalyst}} (-CH_2 - CH_2)_n$



 $C = C \left(\frac{1. O_3}{2. Zn, H^+} \right) C = O + O = C \left(\frac{1. O_3}{2. Zn, H^+} \right) C = O$









$R-C \equiv C-H + Na^+ NH_2^- \xrightarrow{NH_3} R-C \equiv C = Na^+ + NH_3$





allyl carbocation

$$C-C-C=C + E-C-C=C-C-Nu$$

$$| | |$$

$$E Nu$$

$$1,2-product$$

$$1,4-product$$


