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OpenCourseWare (2023)

CHEMISTRY II

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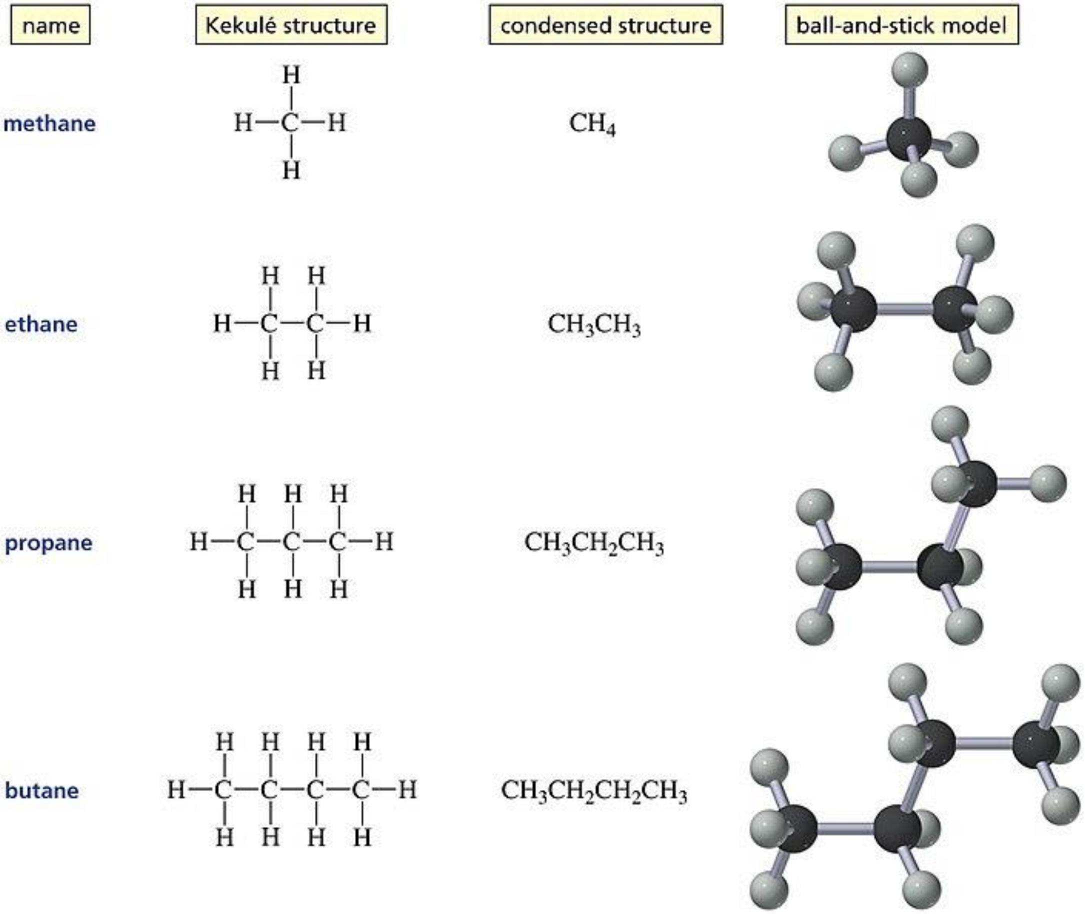
HYDROCARBON COMPOUNDS

Contents

Straight-Chain Alkanes

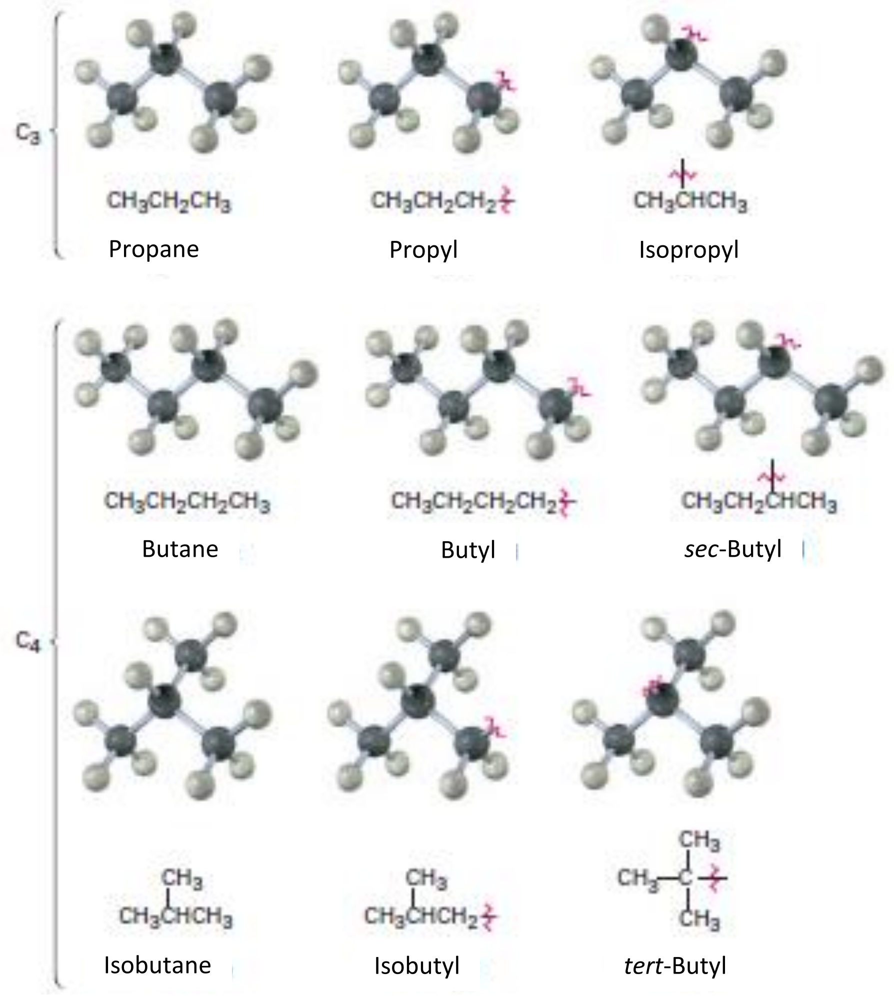
- Methane (CH_4) is the smallest member of a series of hycrocarbons known as alkanes.
- Alkanes are hydrocarbons that have only single bonds between atoms.



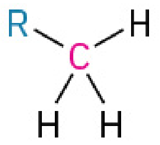
name	Kekulé structure	condensed structure	ball-and-stick model
methane		CH_4	
ethane		CH_3CH_3	
propane		$CH_3CH_2CH_3$	
butane		$CH_3CH_2CH_2CH_3$	

Number of carbons (n)	Name	Formula (C_nH_{2n+2})
1	Methane	CH_4
2	Ethane	C_2H_6
3	Propane	C_3H_8
4	Butane	C_4H_{10}
5	Pentane	C_5H_{12}
6	Hexane	C_6H_{14}
7	Heptane	C_7H_{16}
8	Octane	C_8H_{18}

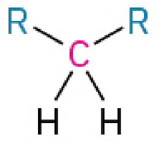
Branched-Chain Alkanes



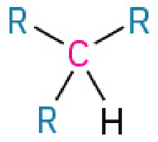
Primary carbon is bonded to one other carbon



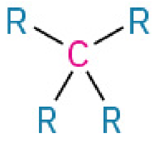
Secondary carbon is bonded to two other carbon



Tertiary carbon is bonded to three other carbon

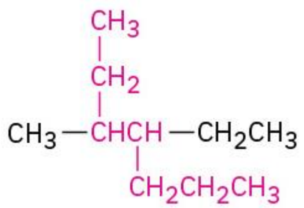


Quaternary carbon is bonded to four other carbon

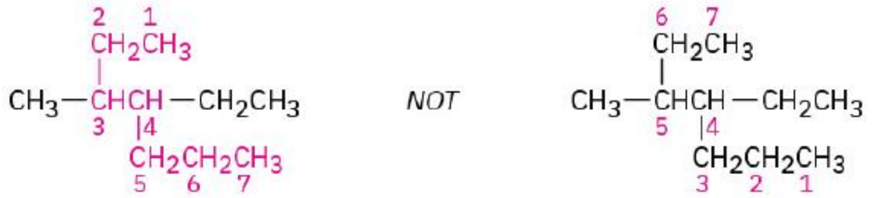


Naming branched-chain alkanes

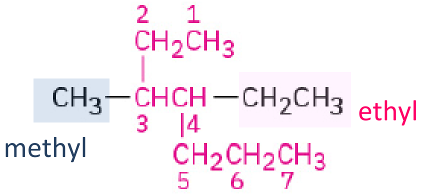
Step 1. Count the number of carbon atoms in the longest continuous chain.


$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{\overset{CH_2}{|}}{CH}CH-CH_2CH_3}$ with $\mathrm{CH_2CH_2CH_3}$ on the second CH

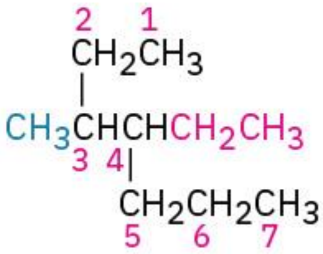
Step 2. Number each carbon in the parent chain.


$\mathrm{CH_3-\overset{CH_2CH_3}{CH}\underset{CH_2CH_2CH_3}{CH}-CH_2CH_3}$

Step 3. Name each alkyl group substituent.

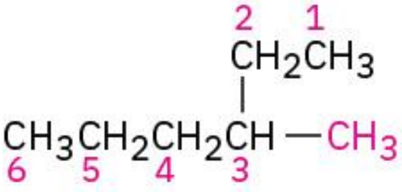

$\mathrm{CH_3-\overset{CH_2CH_3}{CH}\underset{CH_2CH_2CH_3}{CH}-CH_2CH_3}$

Step 4. Write the name as a single word. If the same alkyl group occurs more than once as a branch on the parent structure, use a prefix (di-, tri-, tetra-, and so on) before its name to indicate how many times it appears.


$\mathrm{CH_3\overset{CH_2CH_3}{CH}\underset{CH_2CH_2CH_3}{CH}CH_2CH_3}$

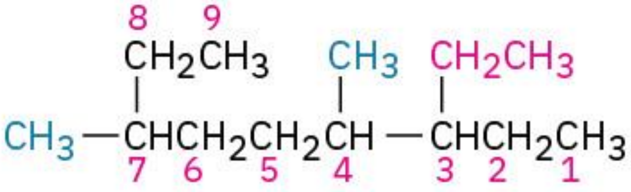
4-Ethyl-3-methylheptane

EXAMPLES



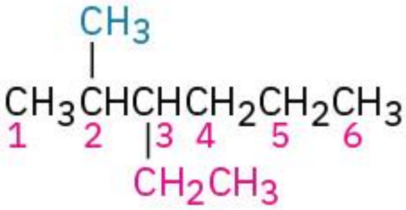
$CH_3CH_2CH_2\overset{CH_2CH_3}{\overset{|}{C}}H-CH_3$

3-Methylhexane



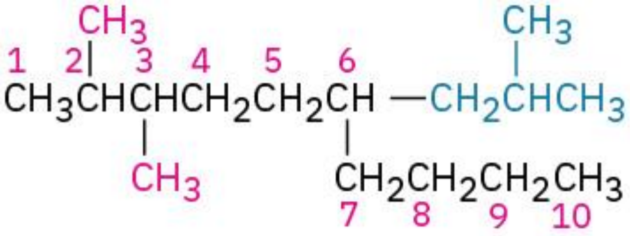
$CH_3-\overset{CH_2CH_3}{\overset{|}{C}}HCH_2CH_2\overset{CH_3}{\overset{|}{C}}H-\overset{CH_2CH_3}{\overset{|}{C}}HCH_2CH_3$

3-Ethyl-4,7-dimethylnonane



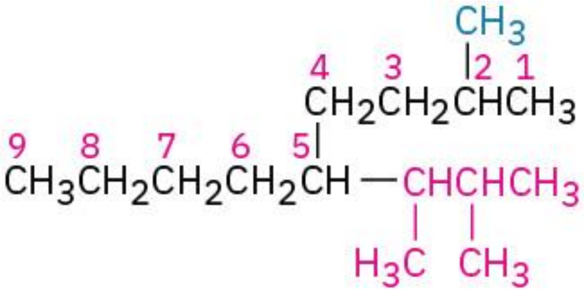
$CH_3\overset{CH_3}{\overset{|}{C}}H\underset{CH_2CH_3}{\underset{|}{C}}HCH_2CH_2CH_3$

3-Ethyl-2-methylhexane



$CH_3\overset{CH_3}{\overset{|}{C}}H\underset{CH_3}{\underset{|}{C}}HCH_2CH_2\underset{CH_2CH_2CH_2CH_3}{\underset{|}{C}}H-CH_2\overset{CH_3}{\overset{|}{C}}HCH_3$

2,3-Dimethyl-6-(2-methylpropyl)decane

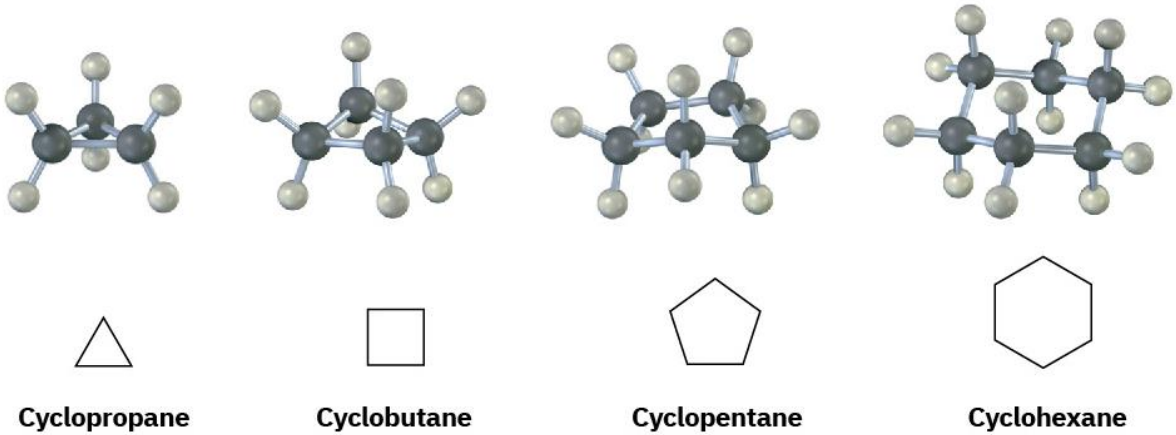


$CH_3CH_2CH_2CH_2\overset{CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_3}{\overset{|}{C}}H-\underset{H_3C}{\underset{|}{C}}H\underset{CH_3}{\underset{|}{C}}HCH_3$

5-(1,2-Dimethylpropyl)-2-methylnonane

CYCLOALKANES

An organic compound that contains a hydrocarbon ring is called a **cyclic hydrocarbon.** To indicate that a hydrocarbon has a ring structure, the prefix *cyclo-* is used with the hydrocarbon name. Thus, cyclic hydrocarbons that contain only single bonds are called **cycloalkanes.**



Naming substituted cycloalkanes

- With cycloalkanes, there is no need to find the longest chain because the ring is always considered to be the parent chain.
- Numbering is started on the carbon that is bonded to the substituent group.
- When there are two or more substituents, the carbons are numbered around the ring in a way that gives the lowest-possible set of numbers for the substituents.
- If only one group is attached to the ring, no number is necessary.

CYCLOALKANES

Step 1. Count the carbons in the ring, and use the name of the parent cyclic hydrocarbon.

Step 2. Number the ring, starting from one of the CH_3— branches. Find the numbering that gives the lowest possible set of numbers for the branches.

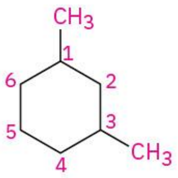
Step 3. Name the substituents.

Step 4. Add the prefix to show the number of groups present.

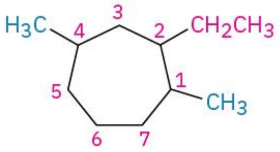
Step 5. Order the substituents alphabetically.

Step 6. Put the name together using the name of the parent cycloalkane. Use commas between separate numbers, and hyphens between numbers and words.

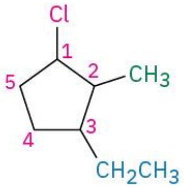
EXAMPLES



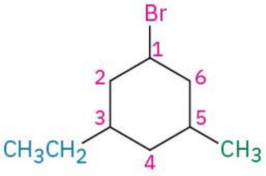
1,3-Dimethylcyclohexane



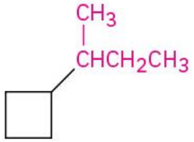
2-Ethyl-1,4-dimethylcycloheptane



1-Chloro-3-ethyl-2-methyl-cyclopentane



1-Bromo-3-ethyl-5-methyl-cyclohexane



(1-Methylpropyl)cyclobutane or *sec*-butylcyclobutane

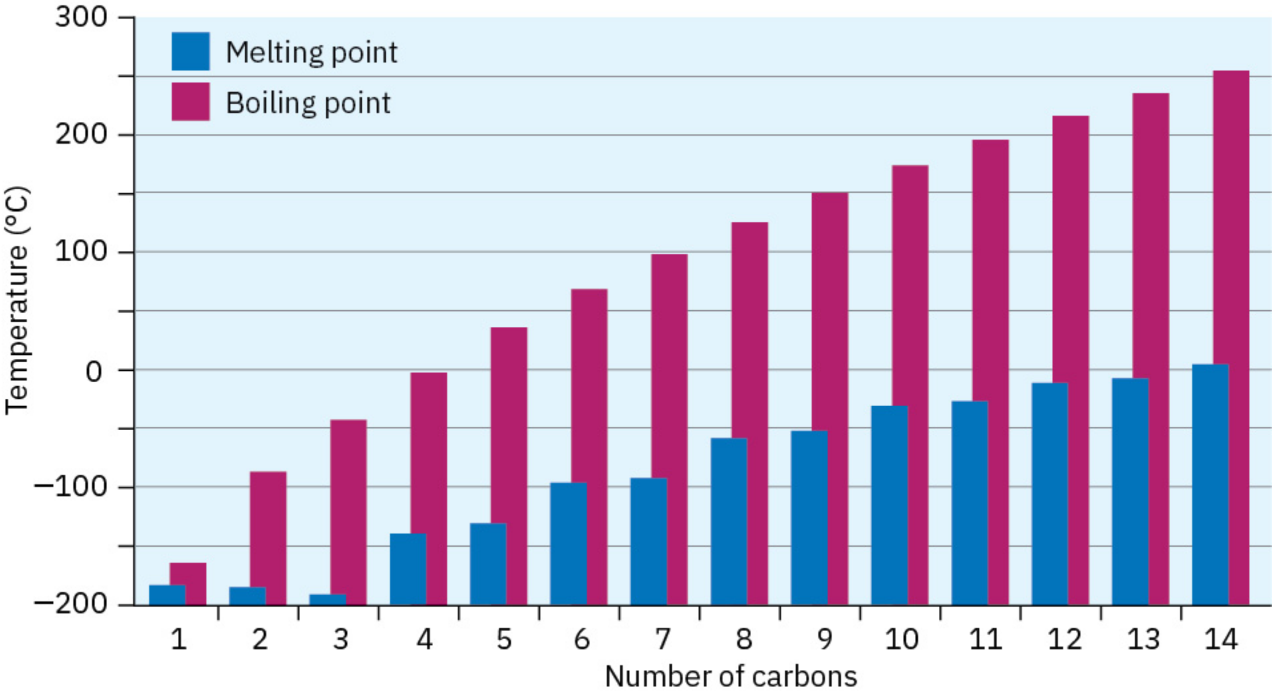
Physical properties of Alkanes

Polarity, melting, and boiling points

✓ *Nonpolar molecules:* Alkanes are composed of relatively nonpolar C—C bonds and C—H bonds.

✓ *Weak attractions:* Alkanes tend to have lower melting points and boiling points than other organic compounds of comparable molecular weights.

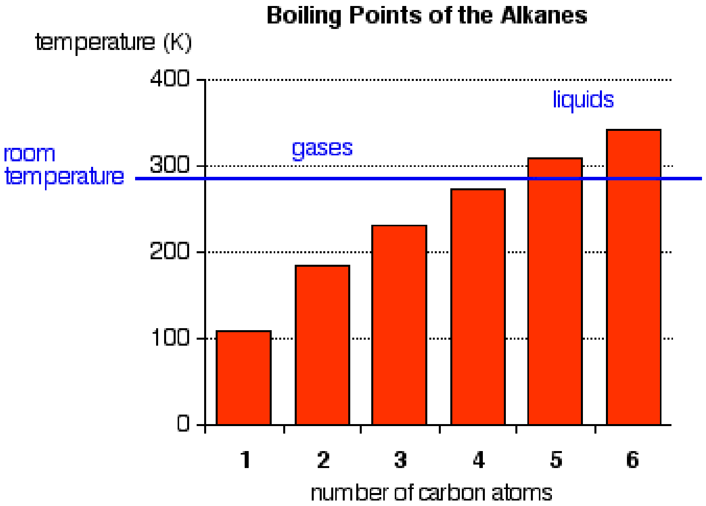
✓ *Branched alkanes:* Increased branching lowers an alkane's boiling point.



Physical properties of Alkanes

Polarity, melting, and boiling points

- ✓ The first four alkanes are gases at room temperature, and solids do not begin to appear until about $C_{17}H_{36}$, but this is imprecise because different isomers typically have different melting and boiling points.



Cycloalkanes have boiling points that are approximately 20 K higher than the corresponding straight chain alkane

Solubility

- ✓ Alkanes (nonpolar) are insoluble in water (polar), and since they are less dense than water, they float (e.g., oil slicks).
- ✓ Alkanes and other substances that do not dissolve in water are often referred to as being hydrophobic (“water fearing”).

Chemical properties of Alkanes (Paraffins)

- ✓ Alkanes are *not very reactive* because of its bonding:

Four covalent bonds ⇒ Four σ bonds ⇒ Higher stability

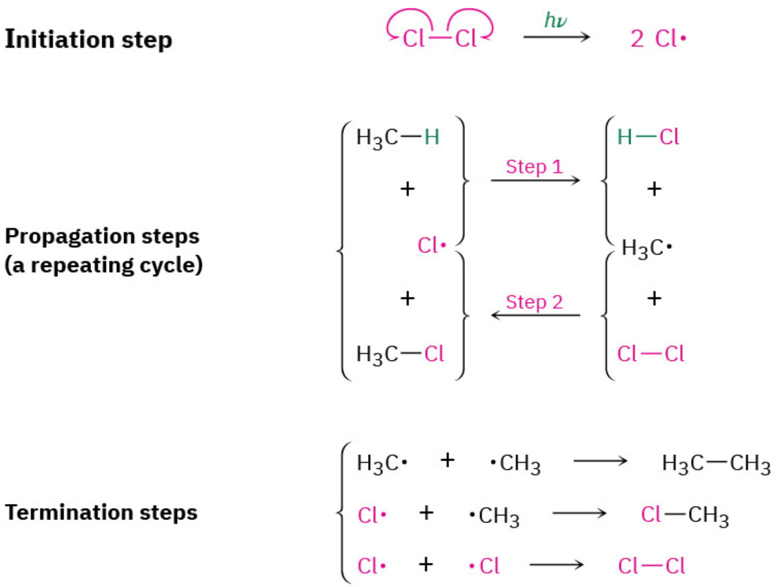
Examples of reactions with alkanes:

Combustion

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O \qquad \Delta H = -890 \text{ kJ/mol}$$

Chlorination of methane (radical reaction)

Overall reaction $CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$



Chemical properties of Alkanes (Paraffins)

- ✓ Alkanes are *not very reactive* because of its bonding:

  Four covalent bonds ⇒ Four σ bonds ⇒ Higher stability

- ✓ Alkanes are *less dense* than water.

- ✓ Alkanes are *non-polar solvents*

- ✓ Alkanes are *not miscible* in water:

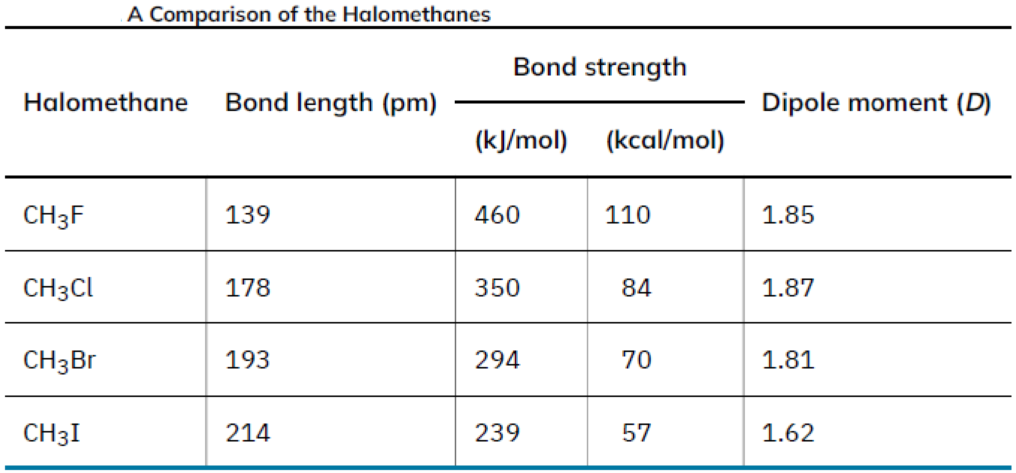
  Weak dipole-dipole bonds ⇒ They can not break the strong H-O bond in H_2O

- ✓ From Methane to Butane are *very flammable gases* at STP. Pentane is an *extremely flammable liquid*.

HALOALKANES

- ✓ Bond strength of C–X decreases as the size of X increases.

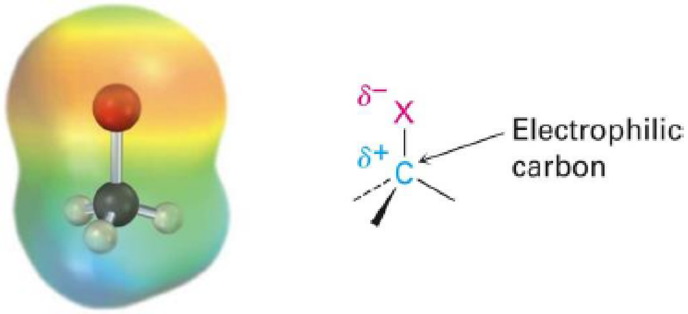
Short bonds are stronger than longer bonds



A Comparison of the Halomethanes

Halomethane	Bond length (pm)	Bond strength		Dipole moment (*D*)
		(kJ/mol)	(kcal/mol)	
CH_3F	139	460	110	1.85
CH_3Cl	178	350	84	1.87
CH_3Br	193	294	70	1.81
CH_3I	214	239	57	1.62

- ✓ C–X bond is polarized.



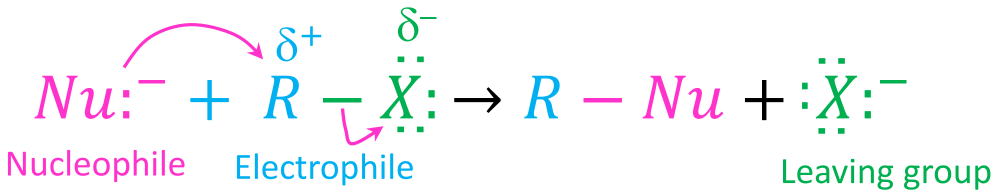
- ✓ Boiling points higher than the corresponding alkanes.
  - ✓ Coulombic attraction (dipole-dipole interaction)
  - ✓ Polarizability

HALOALKANES

Nucleophilic Substitution: two mechanisms

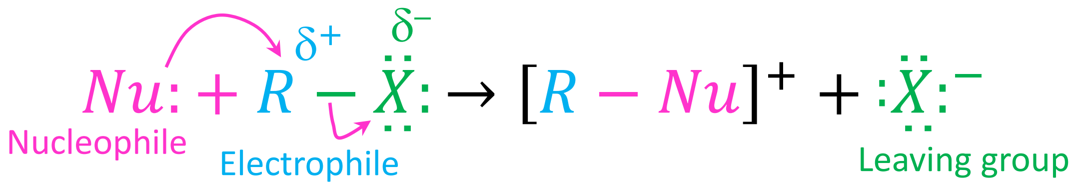
$$\boxed{R - X + Nu:^- \rightarrow R - Nu + X:^-}$$

Negative nucleophile gives neutral product



$$Nu:^- + \overset{\delta^+}{R} - \overset{\delta^-}{\ddot{\underset{..}{X}}}: \rightarrow R - Nu + :\ddot{\underset{..}{X}}:^-$$

Neutral nucleophile gives positively charged product (as a salt)

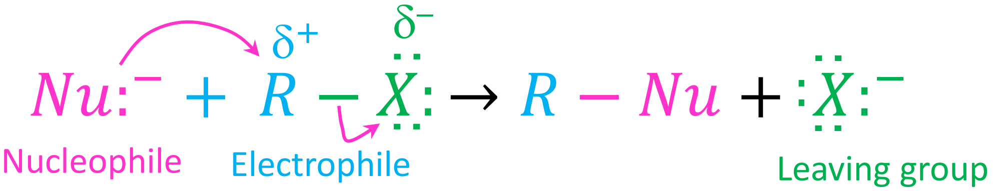


$$Nu: + \overset{\delta^+}{R} - \overset{\delta^-}{\ddot{\underset{..}{X}}}: \rightarrow [R - Nu]^+ + :\ddot{\underset{..}{X}}:^-$$

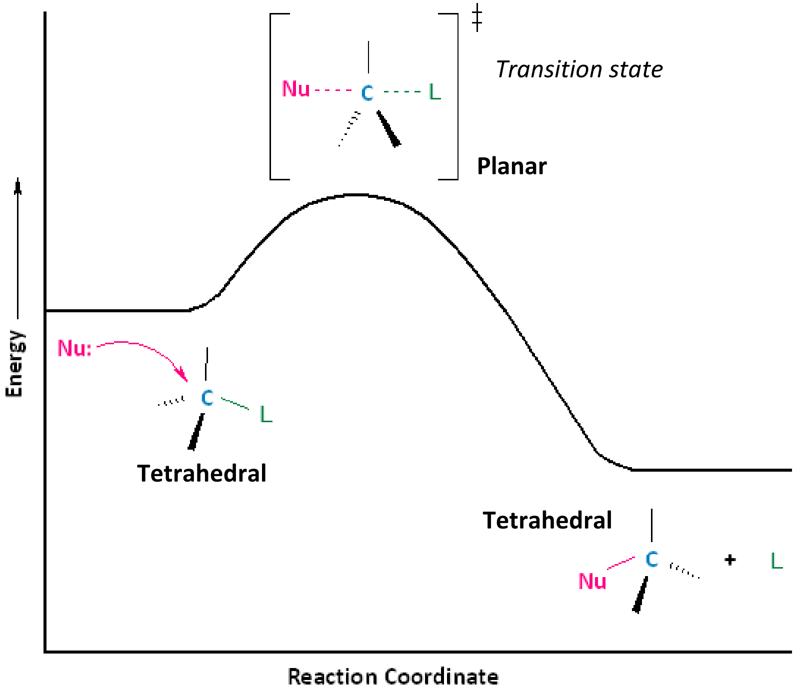
The S_N2 reaction

HALOALKANES

This mechanism is designated **S_N2**, where *S* stands for *S*ubstitution, *N* for *N*ucleophilic, and 2 for a ***bi*molecular reaction**



$$Nu:^- + \overset{\delta+}{R} - \overset{\delta-}{\ddot{\underset{..}{X}}}: \rightarrow R - Nu + :\ddot{\underset{..}{X}}:^-$$



Reaction rate = Rate of disappearance of reactant

$$\boxed{\text{Rate} = k\ [\text{haloalkane}]\ [\text{nucleophile}]}$$

HALOALKANES

S_N2: Inversion of the configuration

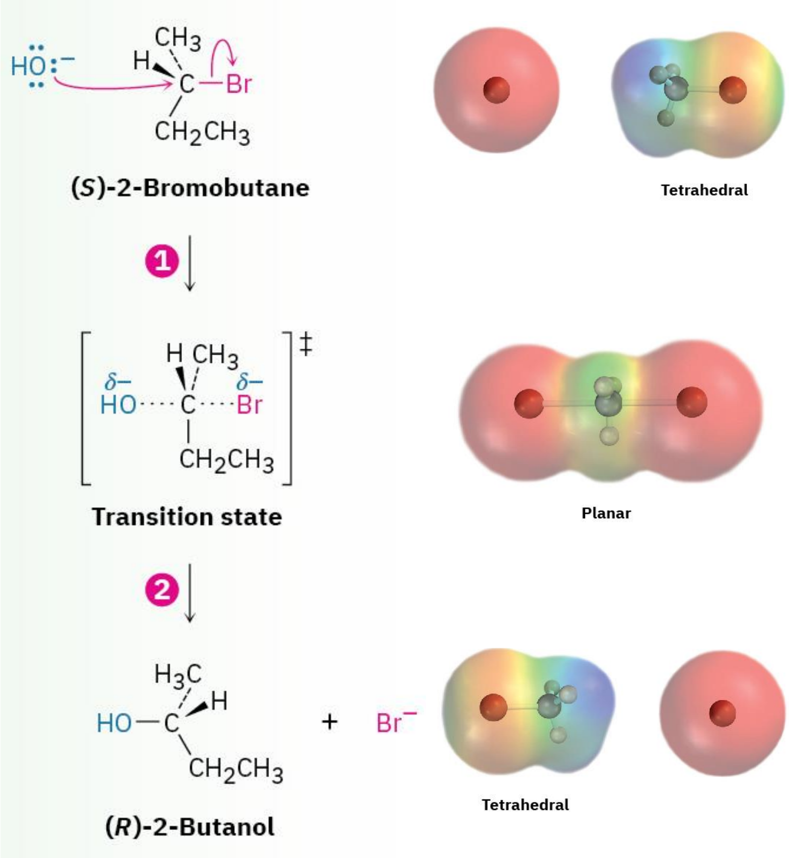
The reversal of the arrangement of atoms or groups of atoms about a reaction center in a S_N2 reaction.

Frontside or Backside attack?

Reaction: $CH(CH_3)(CH_2CH_3)Br + OH^- \rightarrow CH(CH_3)(CH_2CH_3)OH + Br^-$

Mechanism:

STEREOSPECIFIC REACTION



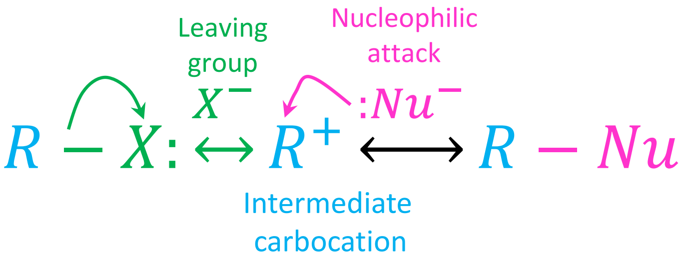
Nucleophile (OH^-) attacks the alkyl halide carbon through its lone-pair electrons, 180° away from the leaving group (Br). A transition state is generated with a partially formed C-OH bond and a partially broken C-Br bond.

TRANSITION STATE: Pentacoordinated carbon

Reaction takes place with an inversion of the configuration and the leaving group (Br^-) departs.

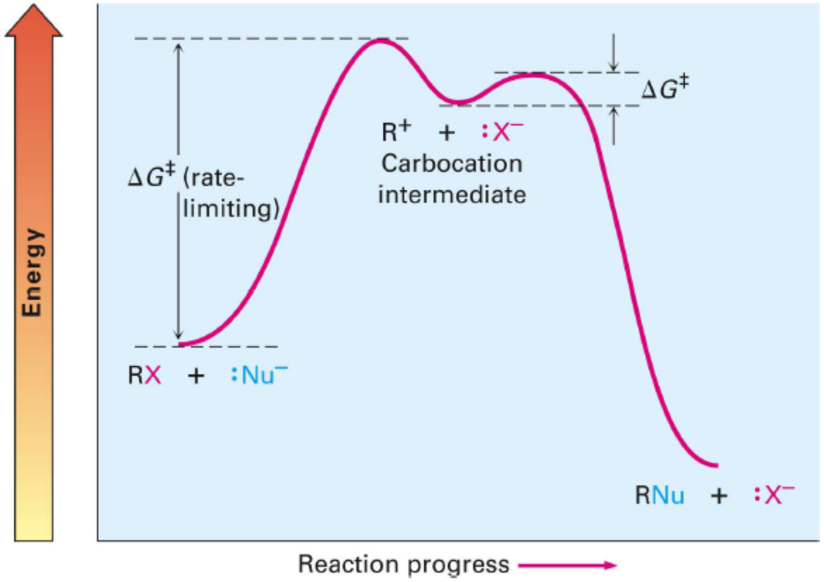
The S_N1 Reaction

This mechanism is designated **S_N1**, where *S* stands for *S*ubstitution, *N* for *N*ucleophilic, and 1 for an ***uni*molecular reaction**

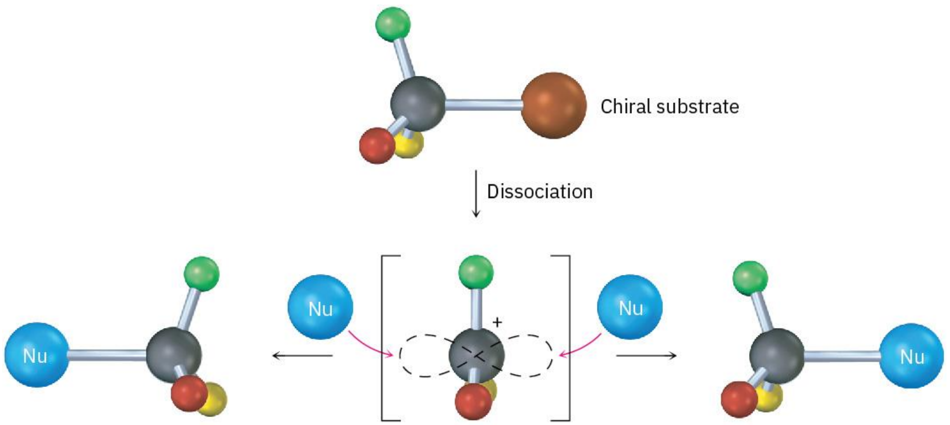


$$R - X: \leftrightarrow X^- \; R^+ \; :Nu^- \longleftrightarrow R - Nu$$

$$\boxed{\text{Rate} = k\,[\text{haloalkane}]}$$



STEREOCHEMISTRY OF THE S_N1 REACTION



50% inversion of configuration

Planar, achiral carbocation intermediate

50% retention of configuration

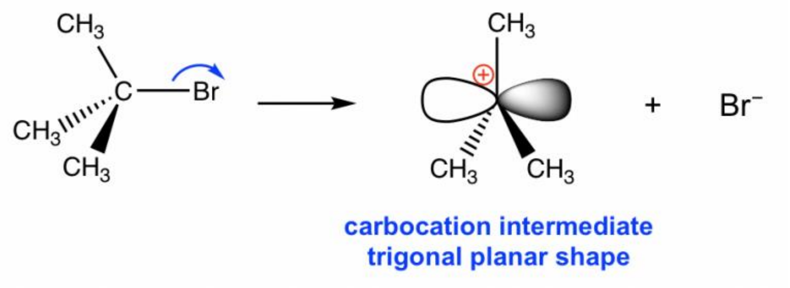
The S_N1 Reaction

HALOALKANES

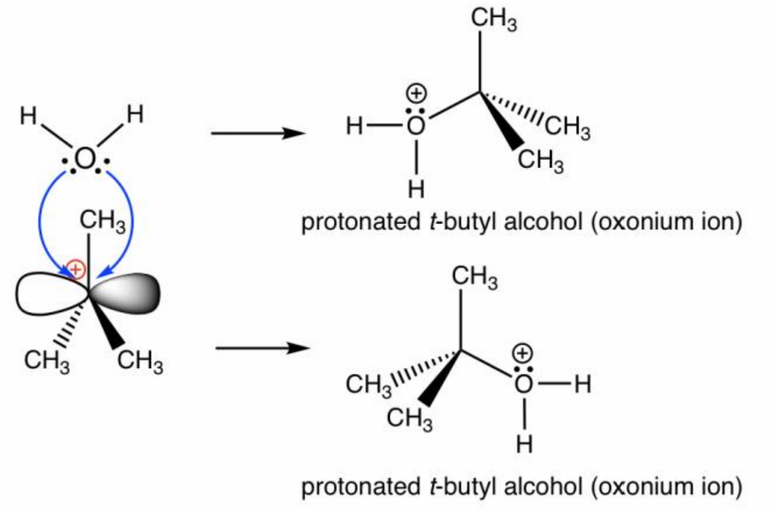
Mechanism

Reaction: $(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$

Step 1: The ionization of a C–X bond forms slowly a tertiary carbocation intermediate. Step 1 is the rate-determining step.



Step 2: Rapid reaction of a nucleophile and an electrophile to form a new covalent bond. H2O attacks from both sides of the planar tertiary carbocation.

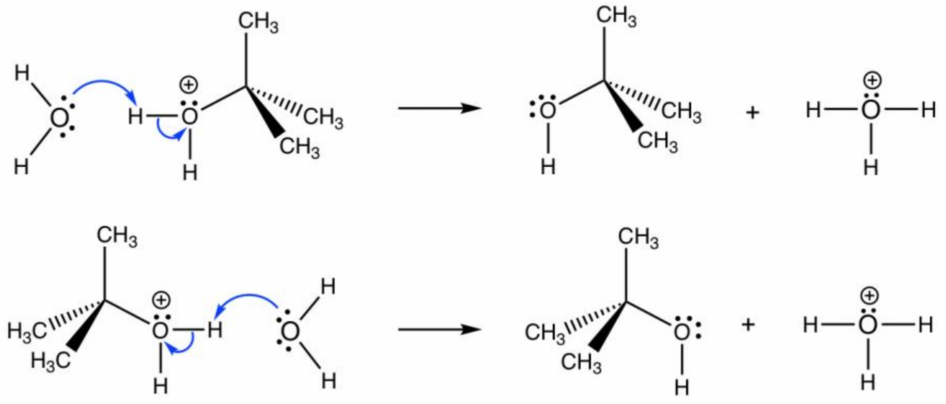


HALOALKANES

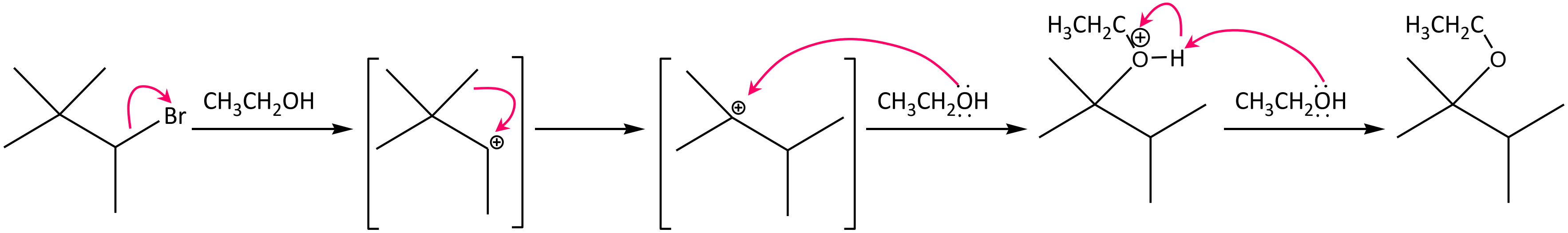
The S_N1 Reaction

Mechanism

Step 3: Take a proton away. Rapid deprotonation to produce a neutral final product.



Rearrangement to form a more stable carbocation:



HALOALKANES

What determines whether S_N1 or S_N2 predominates?

A. Structure of the Nucleophile

- The better the nucleophile ⇒ the more likely S_N2 reaction
- S_N1 reaction occur at approximately the same rate with any of the common nucleophiles, regardless of their relative nucleophilicities. The nucleophile can't affect the reaction rate.

Increasing nucleophilicity ↑

Effectiveness as a Nucleophile	Nucleophile
Good	Br^-, I^- CH_3S^-, RS^- OH^-, CH_3O^-, RO^-
Moderate	Cl^-, F^- CH_3COO^-, $RCOO^-$ CH_3SH, RSH, R_2S NH_3, RNH_2, R_2NH, R_3N
Poor	H_2O CH_3OH, ROH CH_3COOH, $RCOOH$

- ✓ Negatively charged species are better nucleophiles than neutral species.
- ✓ Nucleophilicity decreases across a period.
- ✓ Smaller group is better nucleophile than bulky group.

HALOALKANES

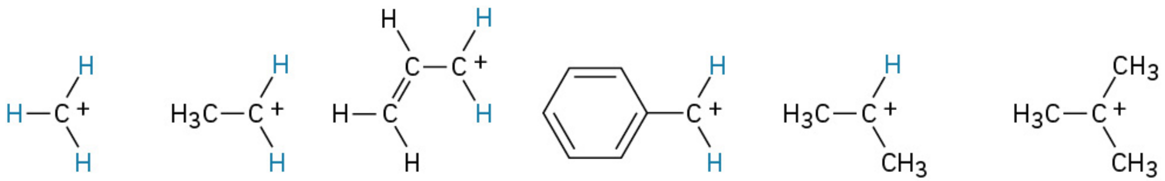
What determines whether S_N1 or S_N2 predominates?

B. Structure of the Haloalkane

S_N1 reactions ⇒ *electronic factors* ⇒ the relative stabilities of carbocation intermediates

S_N2 reactions ⇒ *steric factors*

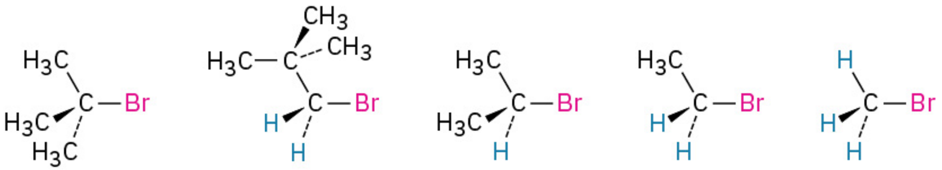
1. Relative stabilities of carbocations:



Methyl < **Primary** < **Allylic** ≈ **Benzylic** ≈ **Secondary** < **Tertiary**

Carbocation stability

2. Steric hindrance:



	Tertiary	**Neopentyl**	**Secondary**	**Primary**	**Methyl**
Relative reactivity	< 1	1	500	40,000	2,000,000

S_N2 reactivity

HALOALKANES

What determines whether S_N1 or S_N2 predominates?

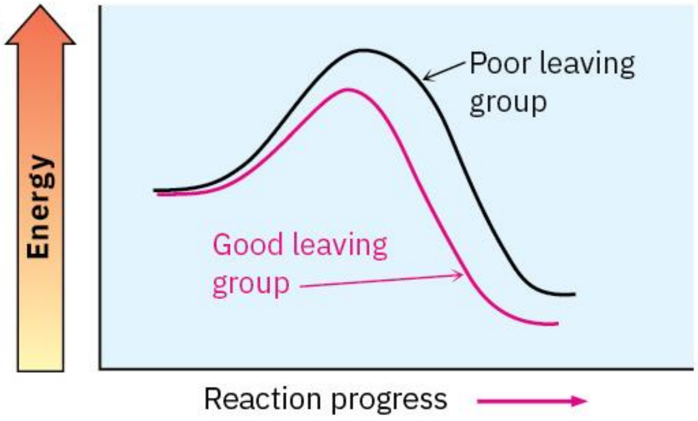
C. The leaving group

The halogens Cl^-, Br^-, and I^- make good leaving groups because their size and electronegativity help to stabilize the resulting negative charge.

	OH^-, NH_2^-, OR^-	F^-	Cl^-	Br^-	I^-	$TosO^-$
Relative reactivity	$<<1$	1	200	10,000	30,000	60,000

Leaving group reactivity →

In S_N2 reactions



HALOALKANES

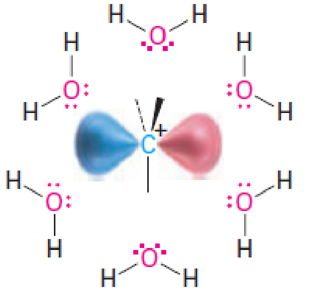
What determines whether S_N1 or S_N2 predominates?

C. The Solvent

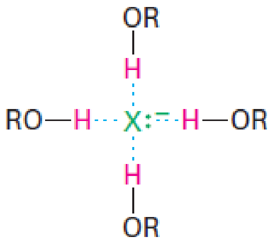
Protic solvents contain -OH groups and are hydrogen-bond donors. Good solvents in S_N1 reactions

	Ethanol	40% Water/ 60% Ethanol	80% Water/ 20% Ethanol	Water
Relative reactivity	1	100	14,000	100,000

Solvent reactivity →



S_N1 reaction:
Solvent stabilizes carbocation



S_N2 reaction:
Solvent reduces nucleophilicity due to enhanced ground-state stability

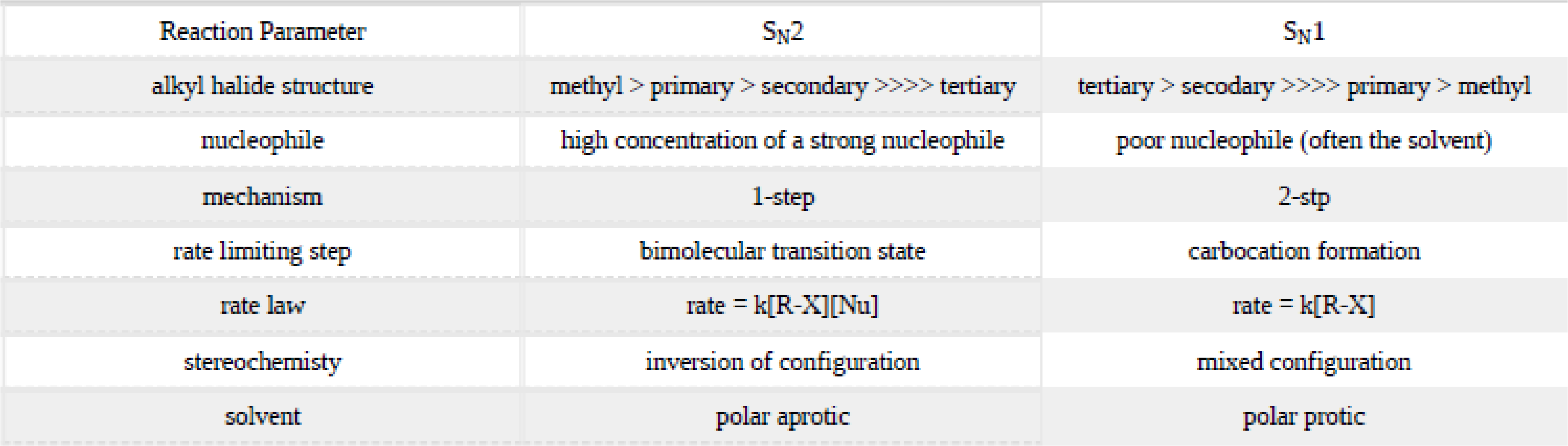
Aprotic solvents Good solvents for in S_N2 reactions and they cannot be used in S_N1 reactions.

Solvent	CH_3OH	H_2O	DMSO	DMF	CH_3CN	HMPA
Relative reactivity	1	7	1300	2800	5000	200,000

Solvent reactivity →

What determines whether S_N1 or S_N2 predominates?

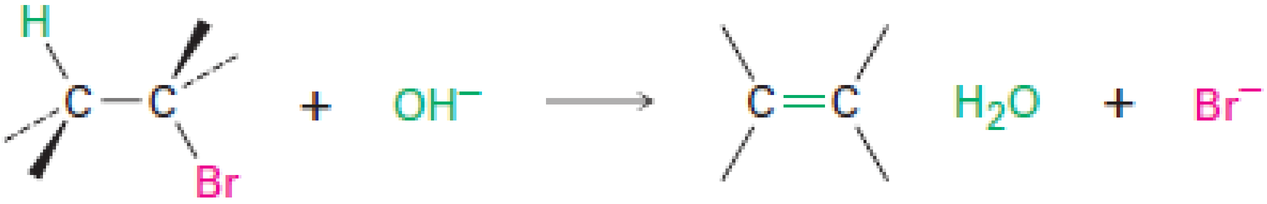
SUMMARY OF S_N1 *versus* S_N2 REACTION OF HALOALKANES



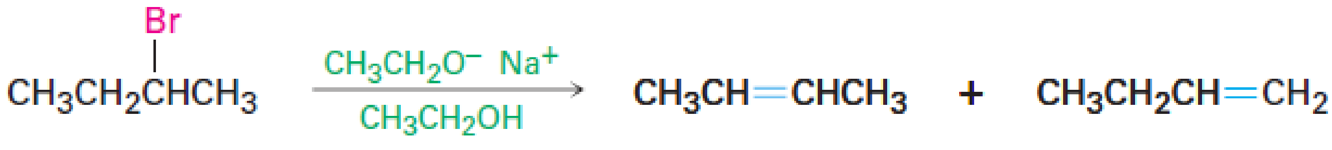
Reaction Parameter	S_N2	S_N1
alkyl halide structure	methyl > primary > secondary >>>> tertiary	tertiary > secodary >>>> primary > methyl
nucleophile	high concentration of a strong nucleophile	poor nucleophile (often the solvent)
mechanism	1-step	2-stp
rate limiting step	bimolecular transition state	carbocation formation
rate law	rate = k[R-X][Nu]	rate = k[R-X]
stereochemisty	inversion of configuration	mixed configuration
solvent	polar aprotic	polar protic

HALOALKANES

Elimination reactions



Regiochemistry: *Zaitsev's Rule.* The more highly substituted alkene product predominates.



$$CH_3CH_2\overset{\displaystyle Br}{\overset{|}{C}}HCH_3 \xrightarrow[CH_3CH_2OH]{CH_3CH_2O^- \; Na^+} CH_3CH{=}CHCH_3 + CH_3CH_2CH{=}CH_2$$

2-Bromobutane

2-Butene (81%)

1-Butene (19%)

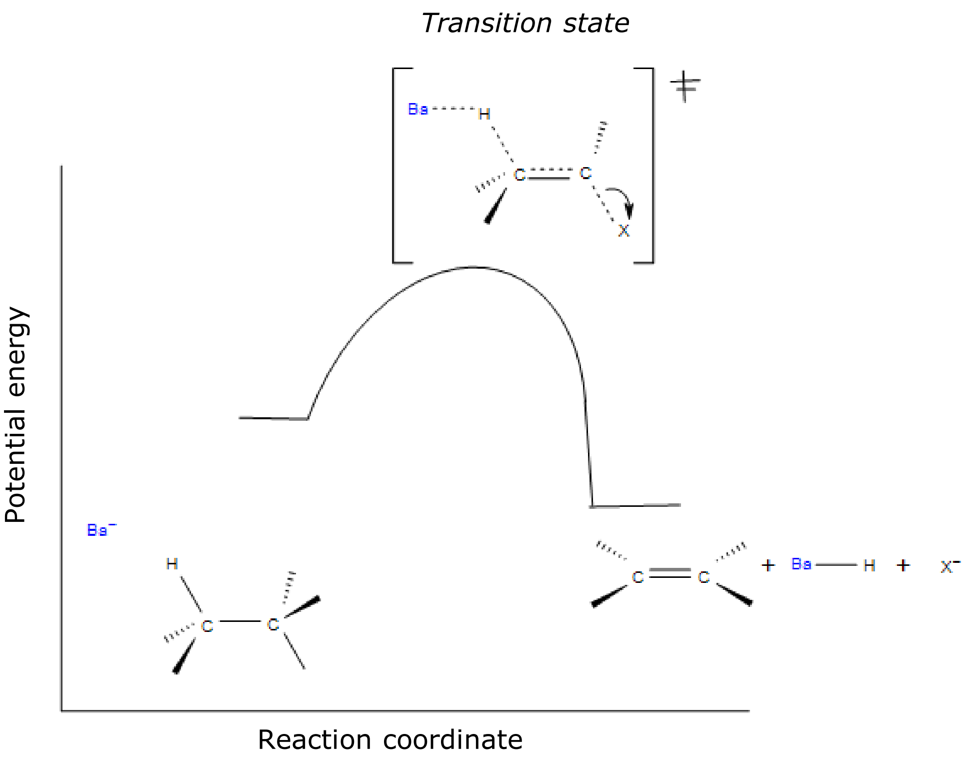
HALOALKANES

The E2 Mechanism

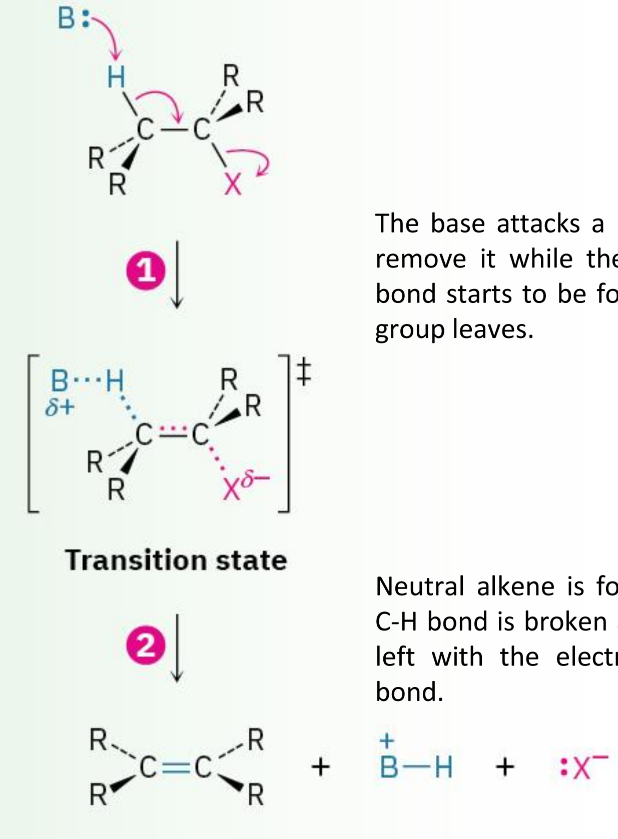
This mechanism is designated **E2**, where *E* stands for *Elimination* and 2 for a ***bi*molecular reaction**.

*Haloalkane is treated with a **strong base***

Rate = *k* [haloalkane] [Base]



C-H and C-X bonds break simultaneously, giving the alkene in a single step without intermediates.

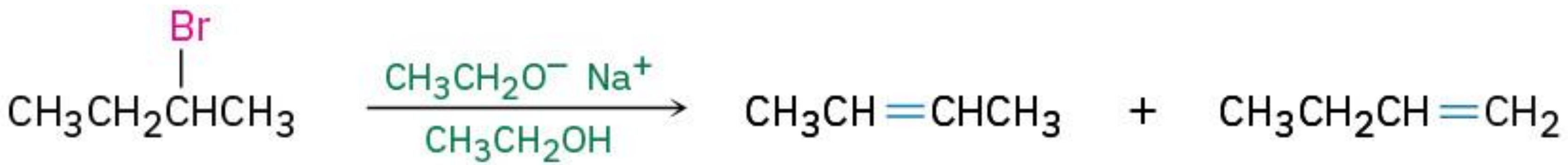


The base attacks a H and begins to remove it while the alkene double bond starts to be formed and the X group leaves.

Neutral alkene is formed when the C-H bond is broken and X group has left with the electron pair of the bond.

Regioselectivity of E2 – Zaitsev’s Rule

Examples:

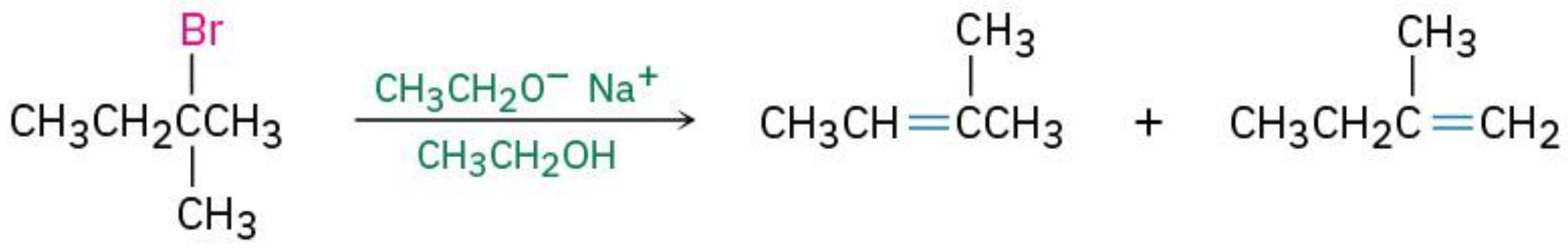


$$CH_3CH_2\overset{\overset{\large Br}{|}}{C}HCH_3 \xrightarrow[CH_3CH_2OH]{CH_3CH_2O^-\ Na^+} CH_3CH{=}CHCH_3 + CH_3CH_2CH{=}CH_2$$

2-Bromobutane

2-Butene (81%)

1-Butene (19%)



$$CH_3CH_2\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large Br}{|}}{C}}CH_3 \xrightarrow[CH_3CH_2OH]{CH_3CH_2O^-\ Na^+} CH_3CH{=}\overset{\overset{\large CH_3}{|}}{C}CH_3 + CH_3CH_2\overset{\overset{\large CH_3}{|}}{C}{=}CH_2$$

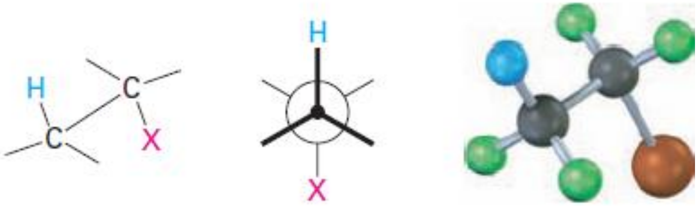
2-Bromo-2-methylbutane

2-Methyl-2-butene (70%)

2-Methyl-1-butene (30%)

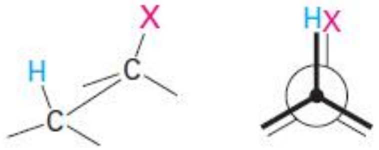
HALOALKANES

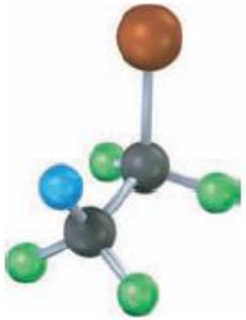
Stereoselectivity of E2



Anti periplanar geometry

(staggered, lower energy)

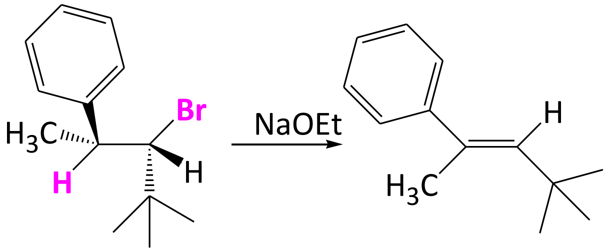


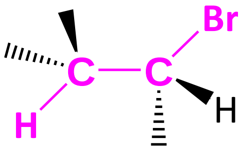


Syn periplanar geometry

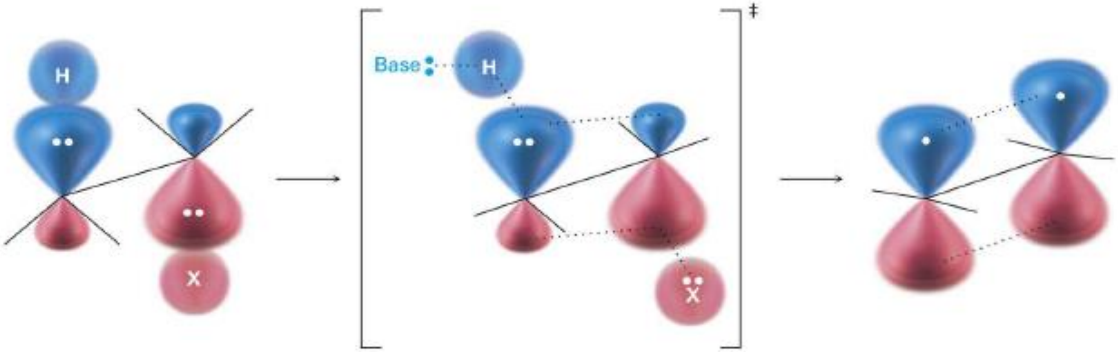
(eclipsed, higher energy)

Example:





These four atoms (H-C-C-Br) must all lie in the same plane



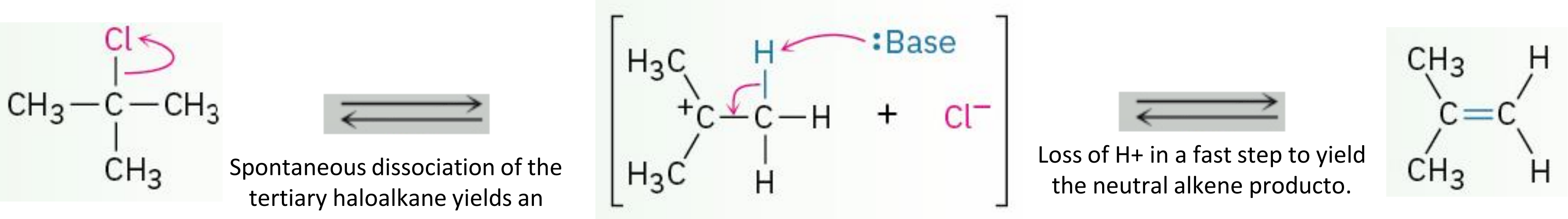
Anti periplanar reactant

Anti transition state

Alkene product

The E1 Mechanism

This mechanism is designated **E1**, where *E* stands for *Elimination* and 1 for an ***uni*molecular reaction**.

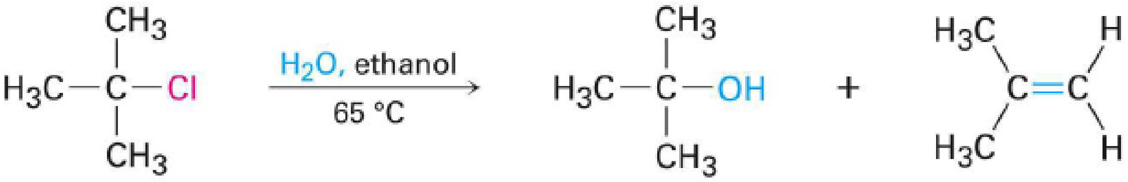


Spontaneous dissociation of the tertiary haloalkane yields an tertiary intermediate carbocation in a slow rate-limiting step.

Loss of H+ in a fast step to yield the neutral alkene producto.

- ❖ No stereoselectivity
- ❖ Regioselectivity: Zaitsev's Rule ⇒ the most stable product

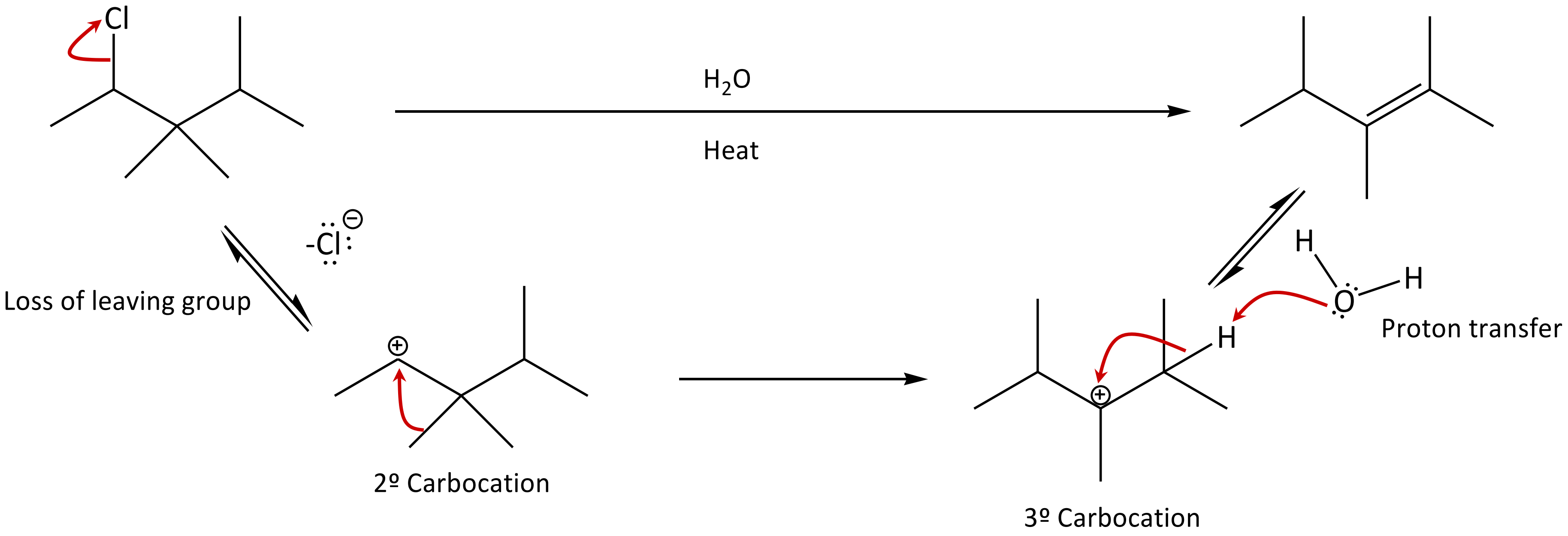
The best E1 substrates are also the best S_N1 substrates ⇒ Mixture of products



2-Chloro-2-methylpropane **2-Methyl-2-propanol (64%)** **2-Methylpropene (36%)**

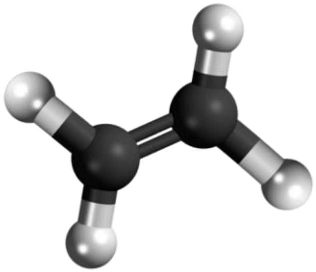
HALOALKANES

Carbocation Rearrangement during E1

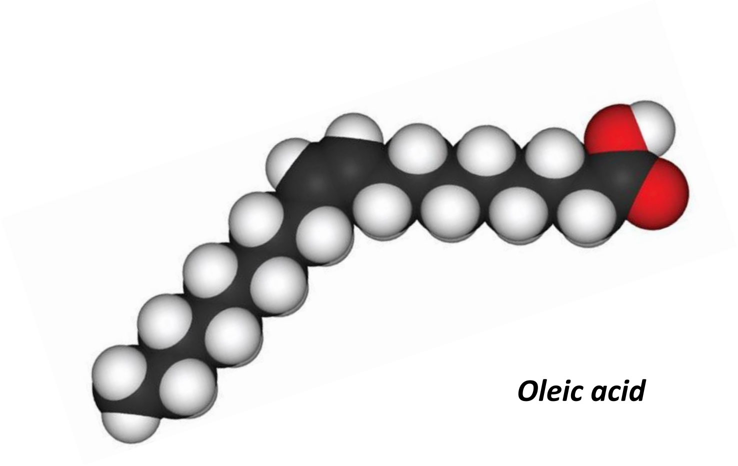


Introduction

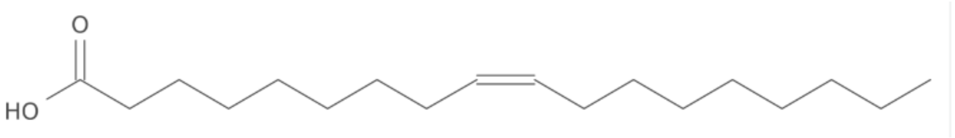
***Alkene**: hydrocarbon that contains a carbon-carbon double bond.*

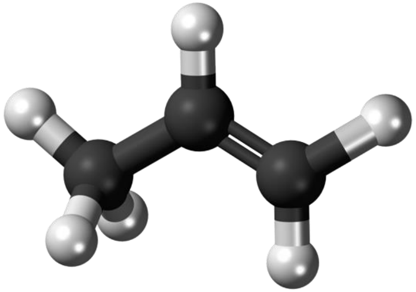


Ethylene



Oleic acid

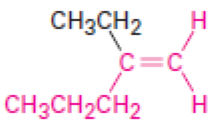


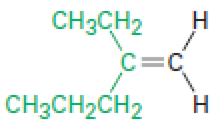


Propylene

Naming Alkenes

<u>Step 1</u>. Name the parent hydrocarbon. Find the longest carbon chain containing the double bond, and name the compound accordingly, using the suffix -ene:

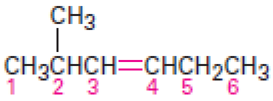




Named as a *pentene* *NOT* as a hexene, since the double bond is not contained in the six-carbon chain

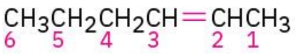
<u>Step 2</u>. Number the carbon atoms in the chain. Begin at the end nearer the double bond or, if the double bond is equidistant from the two ends, begin at the end nearer the first branch point. This rule ensures that the double bond carbons receive the lowest possible numbers

$\underset{6}{CH_3}\underset{5}{CH_2}\underset{4}{CH_2}\underset{3}{CH}{=}\underset{2}{CH}\underset{1}{CH_3}$



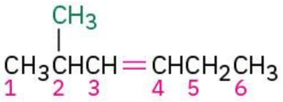
$\underset{1}{CH_3}\underset{2}{\overset{\overset{\large CH_3}{|}}{C}H}\underset{3}{CH}{=}\underset{4}{CH}\underset{5}{CH_2}\underset{6}{CH_3}$

<u>Step 3</u>. Write the full name.



$\underset{6}{CH_3}\underset{5}{CH_2}\underset{4}{CH_2}\underset{3}{CH}{=}\underset{2}{CH}\underset{1}{CH_3}$

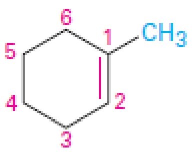
2-Hexene



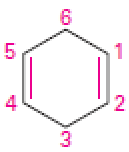
$\underset{1}{CH_3}\underset{2}{\overset{\overset{\large CH_3}{|}}{C}H}\underset{3}{CH}{=}\underset{4}{CH}\underset{5}{CH_2}\underset{6}{CH_3}$

2-Methyl-3-hexene

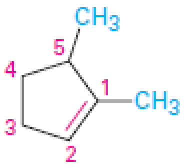
Cycloalkenes: *the double bond is between C1 and C2 and the first substituent has as low a number as possible. It's not necessary to indicate the position of the double bond in the name because it's always between C1 and C2.*



1-Methylcyclohexene



1,4-Cyclohexadiene
(New: Cyclohexa-1,4-diene)



1,5-Dimethylcyclopentene

Substituents:

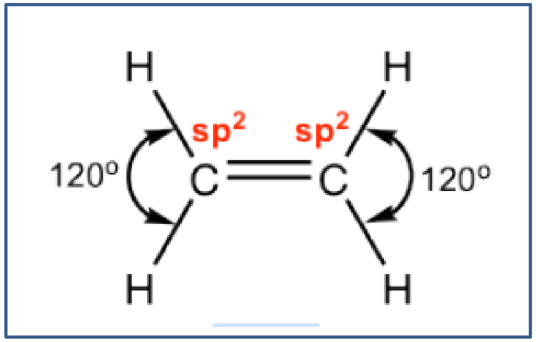
A methylene group

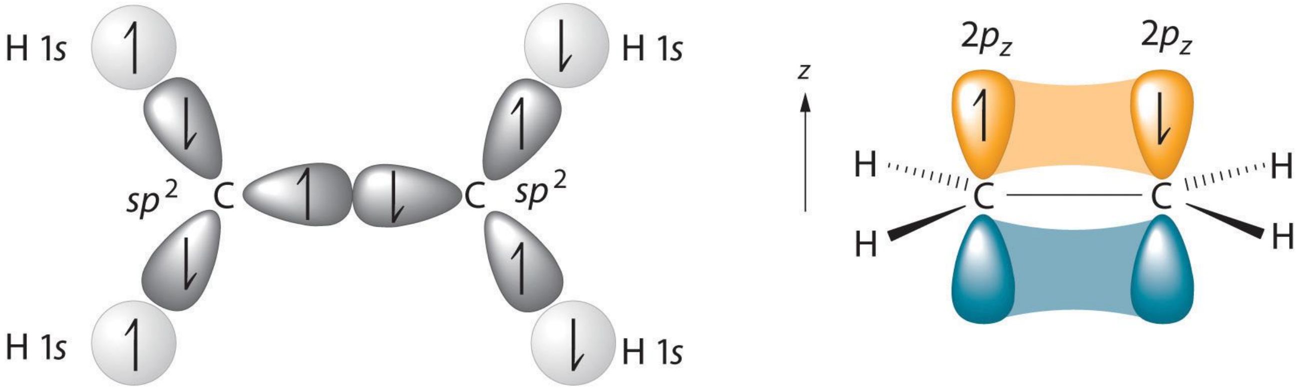
A vinyl group

An allyl group

Structure and Bonding in Ethene

Molecular structure of ethene

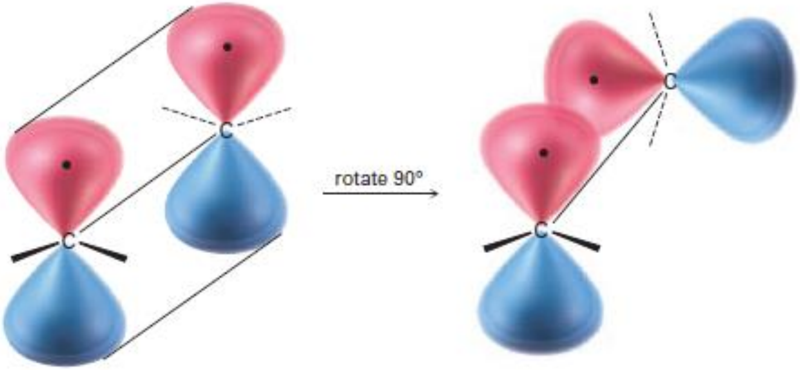




(a) C_2H_4 σ-bonded framework

(b) C_2H_4 π bonding

Cis-Trans Isomerism in Alkenes

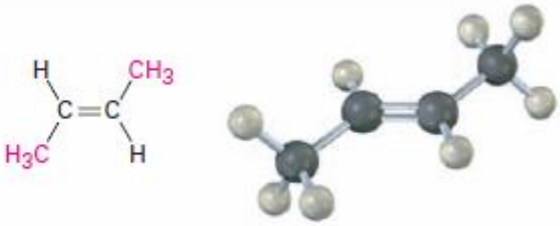


π bond
(*p* orbitals are parallel)

Broken π bond after rotation
(*p* orbitals are perpendicular)

The π bond must break for rotation to take place around a carbon–carbon double bond.

cis-2-Butene

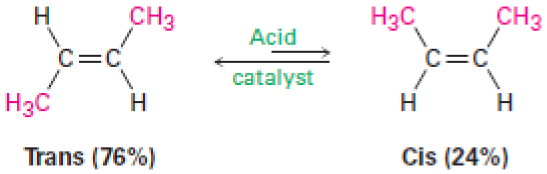


trans-2-Butene

*Substituents on the same side of the double bond is called **cis-2-butene***

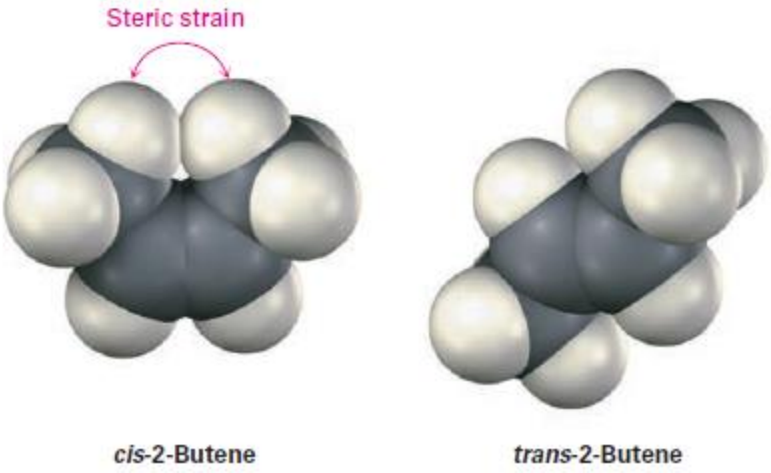
*Substituents on opposite sides is **trans-2- butene***

Stability of Alkenes



Trans (76%) Cis (24%)

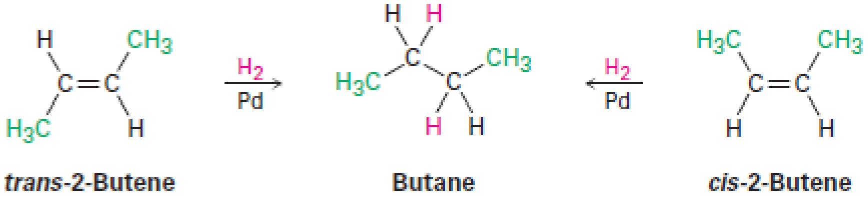
*The **trans isomer** is more stable than the cis isomer by 2.8 kJ/mol (0.66 kcal/mol) at room temperature, corresponding to a 76:24 ratio.*

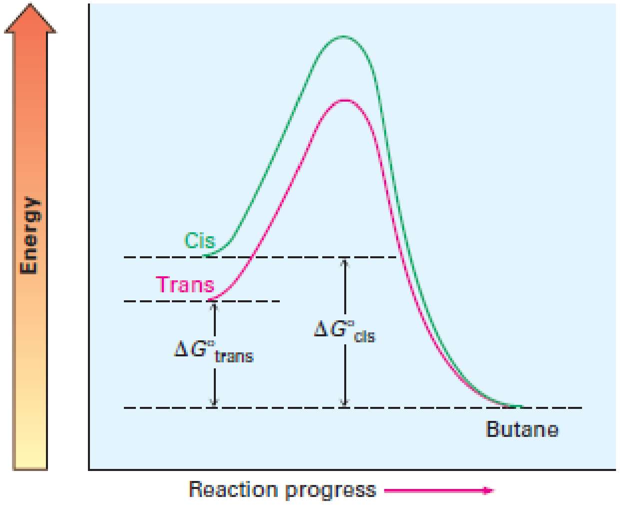


cis-2-Butene *trans*-2-Butene

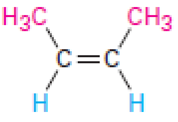
***Cis alkenes** are less stable than their trans isomers because of steric strain between the two larger substituents on the same side of the double bond*

Stability of Alkenes: Hydrogenation

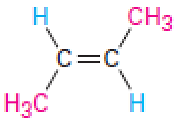




Energy diagrams *for hydrogenation of cis- and trans-2-butene. The cis isomer is higher in energy than the trans isomer by about 2.8 kJ/mol and therefore releases more energy in the reaction.*



Cis isomer
$\Delta H^\circ_{hydrog} = -120$ kJ/mol



Trans isomer
$\Delta H^\circ_{hydrog} = -116$ kJ/mol

Physical Properties of Alkenes

Comparison of Melting Points of Alkenes and Alkanes

Compound	**Melting point (ºC)**
Butane	-138
trans-2-Butene	-106
cis-2-Butene	-139
Pentane	-130
trans-2-Pentene	-135
cis-2-Pentene	-180
Hexane	-95
trans-2-Hexene	-133
cis-2-Hexene	-141
trans-3-Hexene	-115
cis-3-Hexene	-138

*The double bond in **cis-disubstituted alkenes** imposes a U-shaped bend in the molecule that disrupts packing and reduces the melting point.*

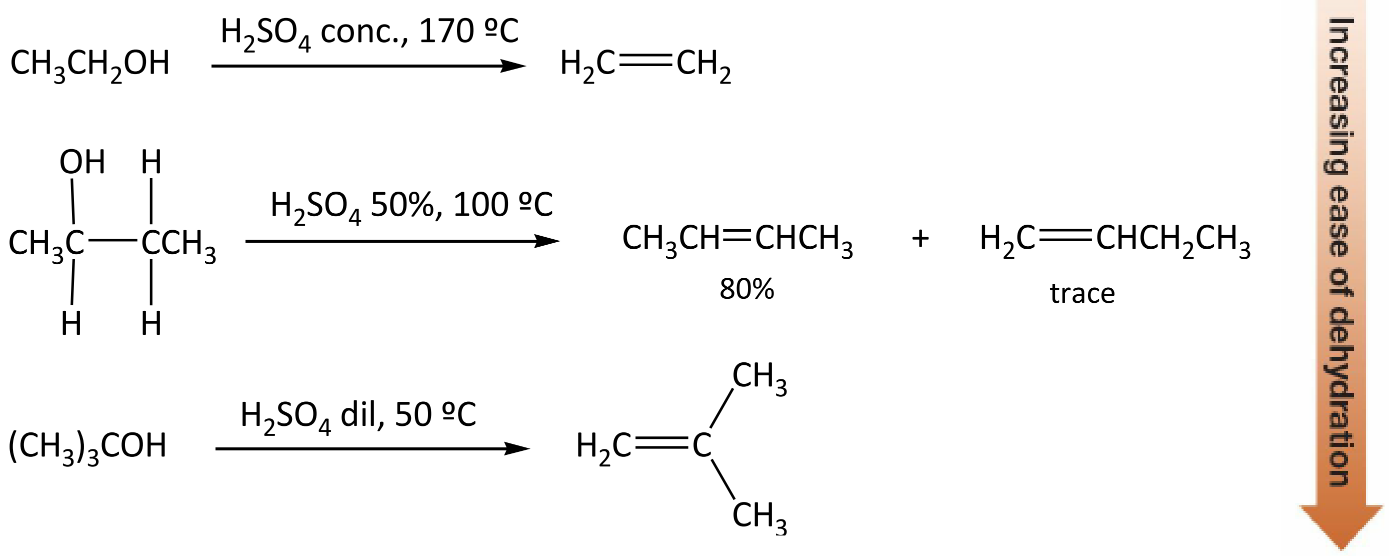
Synthesis of Alkenes

Elimination Reactions

Relative Reactivity of Alcohols in Dehydration Reactions

R = primary < secondary < tertiary

Increasing ease of dehydration



Primary alcohol $CH_3CH_2OH \xrightarrow{H_2SO_4\ \text{conc., } 170\ ºC} H_2C{=}CH_2$

Secondary alcohol $CH_3\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}CH_3 \xrightarrow{H_2SO_4\ 50\%,\ 100\ ºC} \underset{80\%}{CH_3CH{=}CHCH_3} + \underset{\text{trace}}{H_2C{=}CHCH_2CH_3}$

Tertiary alcohol $(CH_3)_3COH \xrightarrow{H_2SO_4\ \text{dil, } 50\ ºC} H_2C{=}C(CH_3)_2$

Reactivity of Alkenes

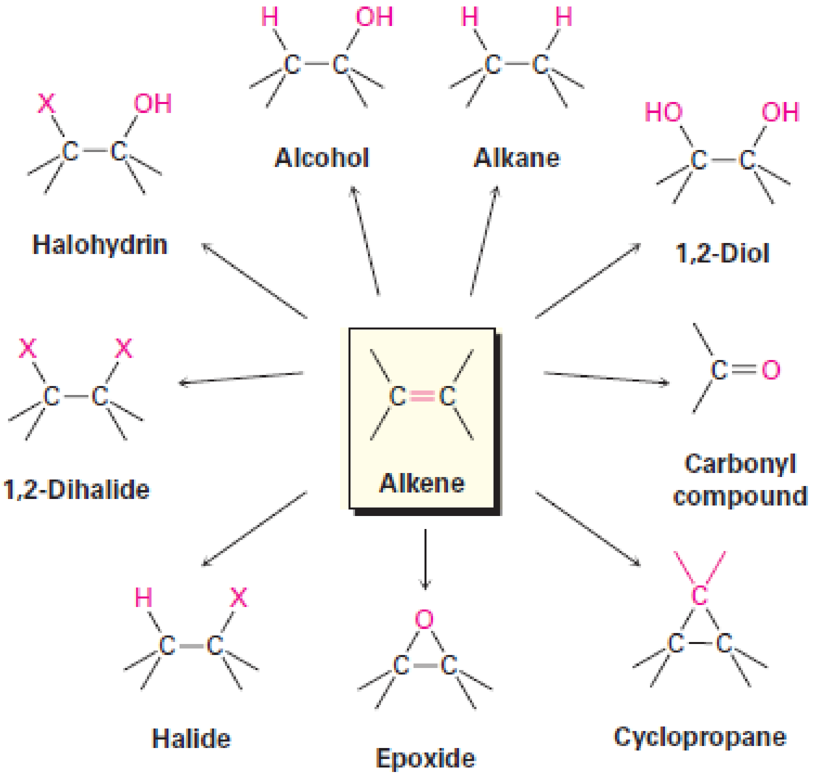
Hydration

Reduction: Hydrogenation

Addition of HOX

Halogenation of alkenes

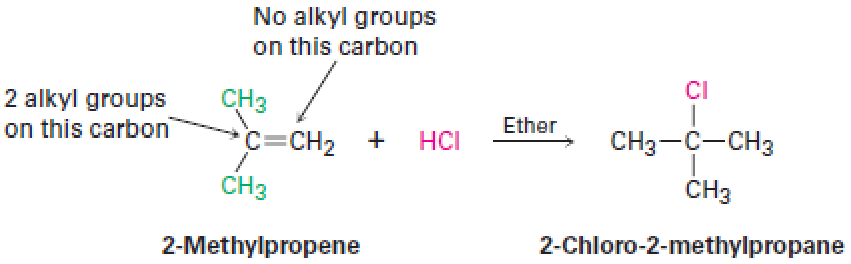
Oxidation: Carbonyl Compounds



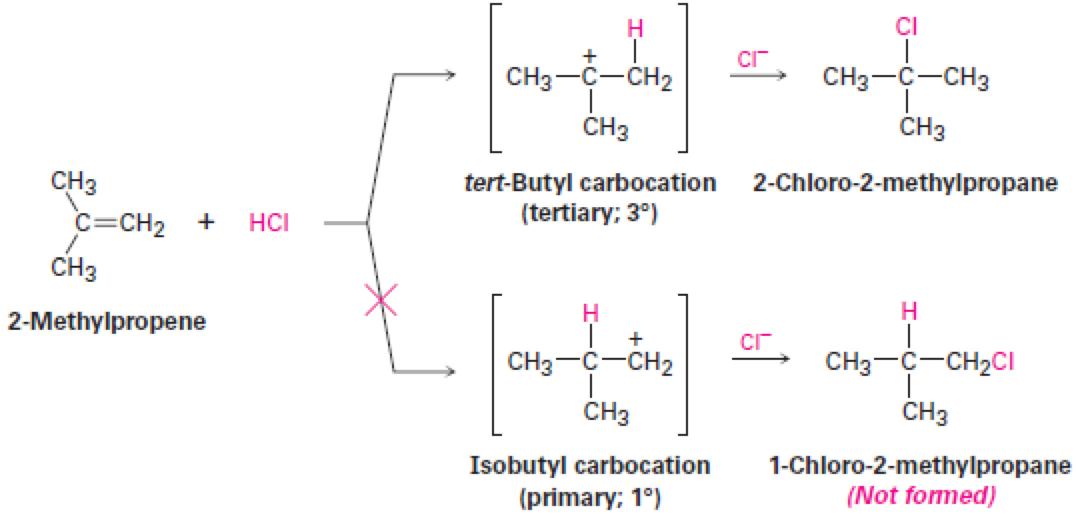
Oxidation: Epoxidation

Orientation of Electrophilic Additions: Markovnikov’s Rule

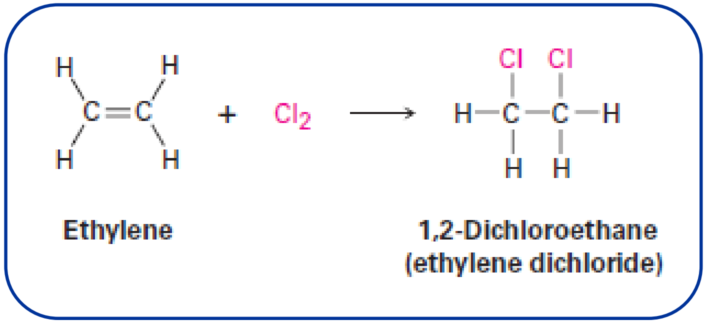
Markovnikov’s Rule*: In the addition of HX to an alkene, the H attaches to the carbon with fewer alkyl substituents and the X attaches to the carbon with more alkyl substituents*

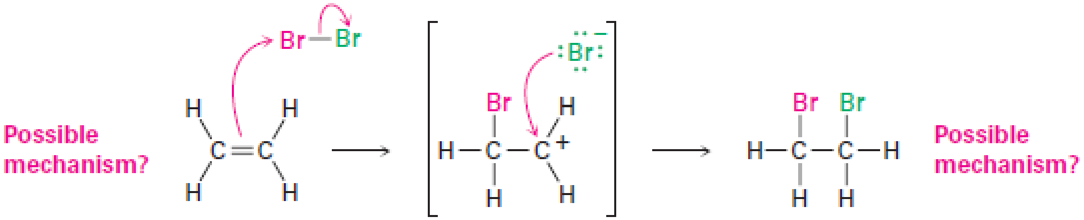


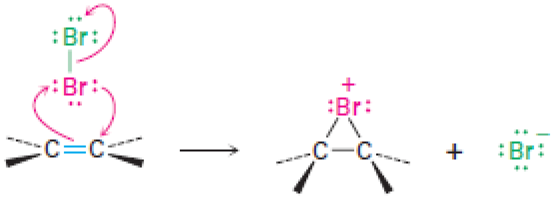
In the addition of HX to an alkene, the more highly substituted ***carbocation*** *is formed as the intermediate rather than the less highly substituted one.*



Halogenation of Alkenes: Addition of X_2

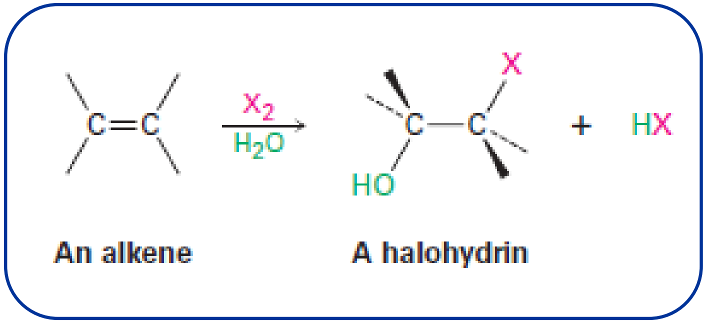




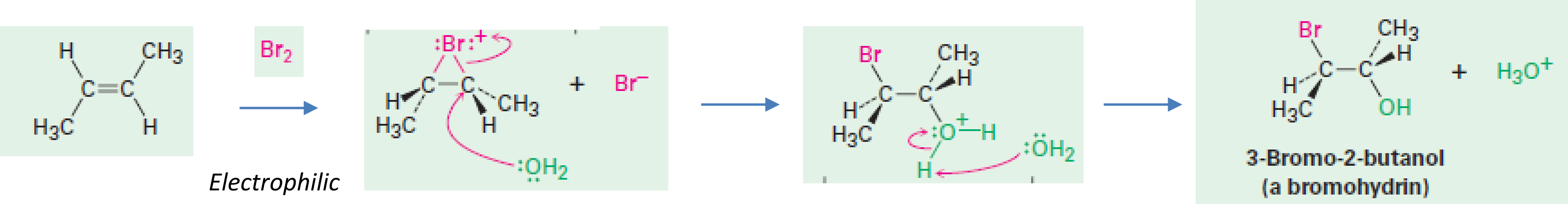


***Mechanism**: The reaction intermediate is not a carbocation but is instead a bromonium ion*

Halohydrins from Alkenes: Addition of XOH



Mechanism:



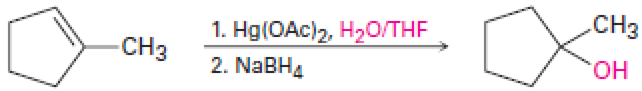
Water acts as a nucleophile

Electrophilic addition

Bromonium ion intermediate

Loss of a proton

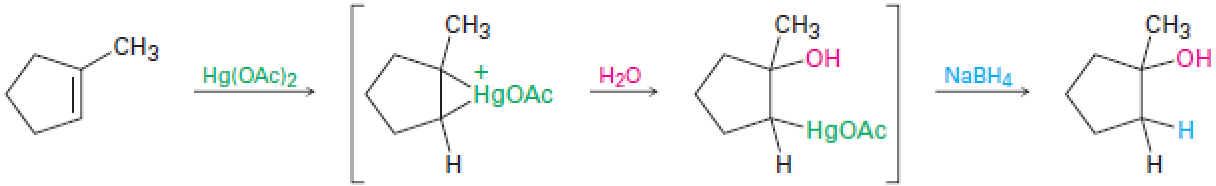
Hydration of Alkenes: Addition of H_2O by Oxymercuration



1-Methylcyclopentene

1-Methylcyclopentanol (92%)

Mechanism:



1-Methyl-cyclopentene

Mercurinium ion

Organomercury compound

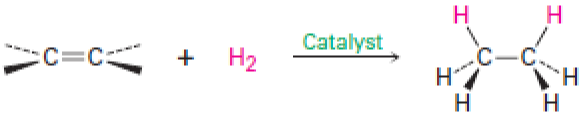
1-Methyl-cyclopentanol (92% yield)

Electrophilic addition of Hg

Nucleophilic addition of water

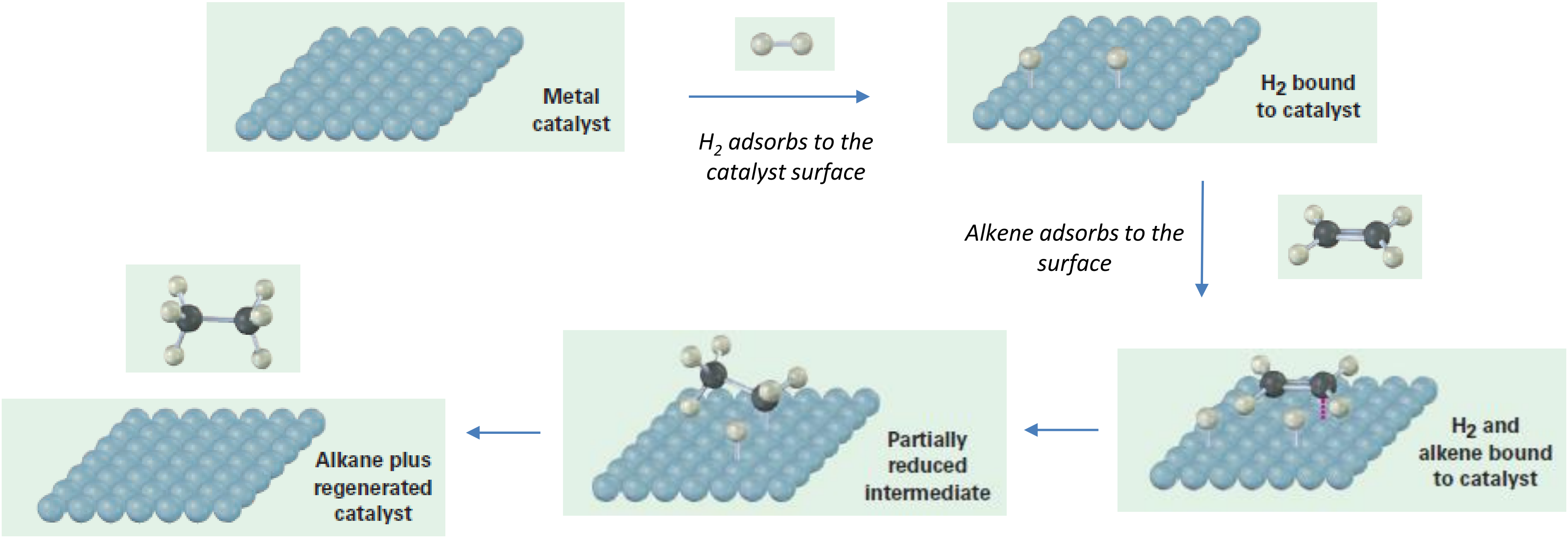
Demercuration with $NaBH_4$

Reduction of Alkenes: Hydrogenation



An alkene **An alkane**

Mechanism:



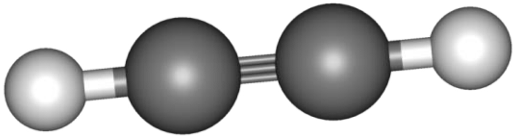
H_2 adsorbs to the catalyst surface

Alkene adsorbs to the surface

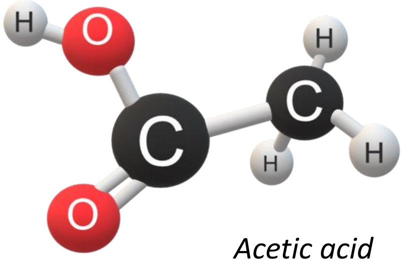
Transference of a hydrogen atom

Introduction

***Alkyne**: hydrocarbon that contains a carbon-carbon triple bond.*

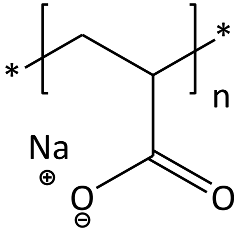


Acetylene



Acetic acid

Oxy-Acetylene Gas Welding



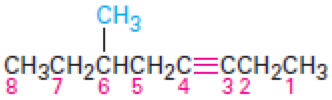
Acrylic polymers

Naming Alkynes

<u>Step 1</u>. Name the parent hydrocarbon. Find the longest carbon chain containing the triple bond, and name the compound accordingly, using the suffix -yne:

<u>Step 2</u>. Number the carbon atoms in the chain. Begin at the end nearer the triple bond. This rule ensures that the triple bond carbons receive the lowest possible numbers

<u>Step 3</u>. Write the full name. If more than one triple bond is present, indicate the position of each and use one of the suffixes -diyne, -triyne, and so on.



$$\underset{8}{CH_3}\underset{7}{CH_2}\underset{6}{\overset{\overset{CH_3}{|}}{C}H}\underset{5}{CH_2}\underset{4}{C}{\equiv}\underset{3}{C}\underset{2}{CH_2}\underset{1}{CH_3}$$

Begin numbering at the end nearer the triple bond.

6-Methyl-3-octyne

(New: 6-Methyloct-3-yne)

***Substituents**: As with alkyl and alkenyl substituents derived from alkanes and alkenes, respectively, alkynyl groups are also possible.*

Butyl
(an alkyl group)

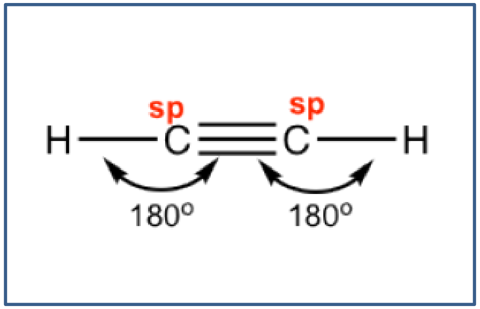
1-Butenyl
(a vinylic group)

(New: But-1-enyl)

1-Butynyl
(an alkynyl group)

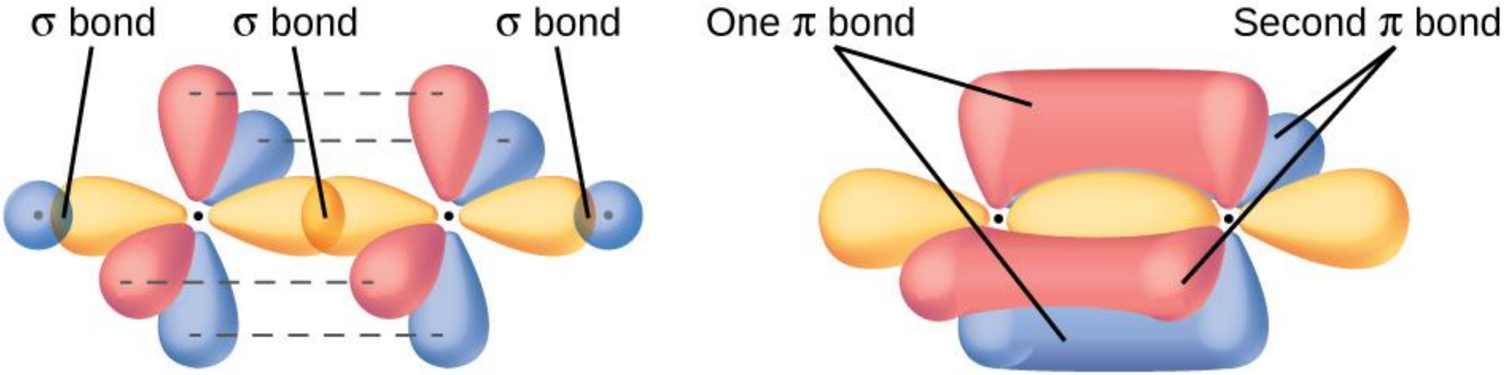
(New: But-1-ynyl)

Structure and Bonding in Ethyne



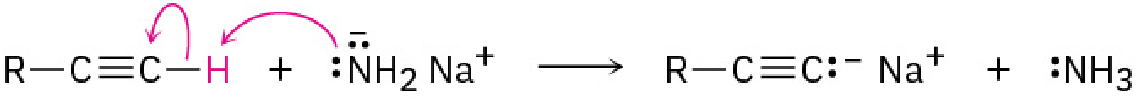
Molecular structure of ethyne

sp hybridization



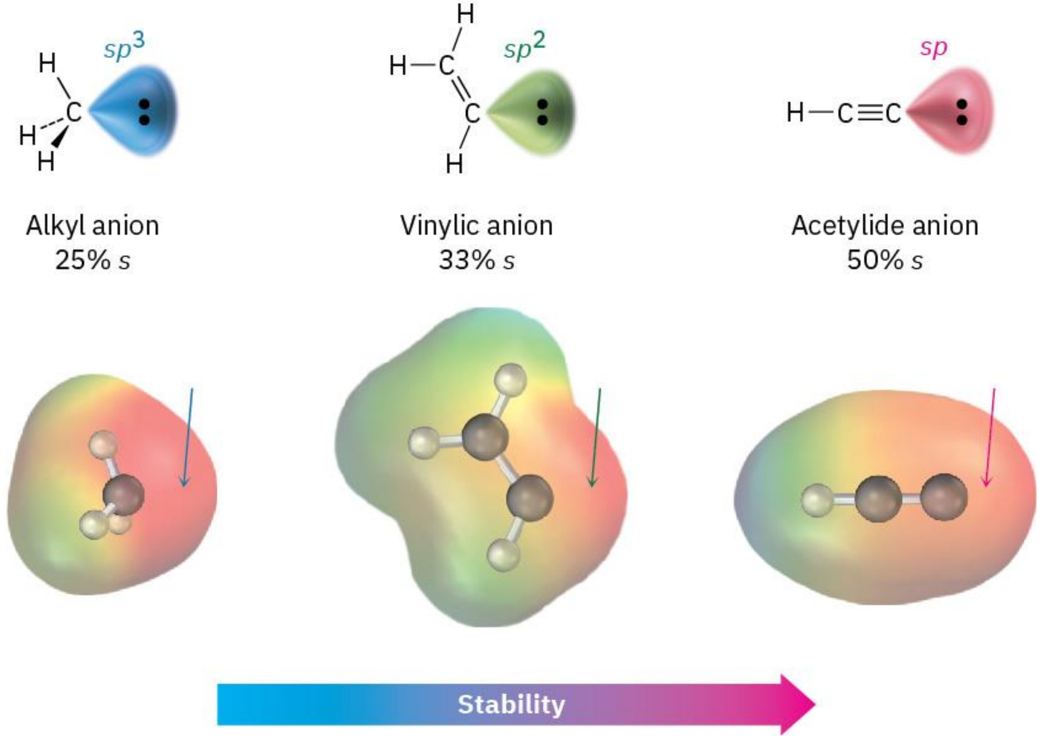
Physical Properties of Alkynes

Acidity of Alkynes



$$R-C\equiv C-H + :\ddot{N}H_2\ Na^+ \longrightarrow R-C\equiv C:^-\ Na^+ + :NH_3$$

Acetylide anion



Alkyl anion
25% *s*

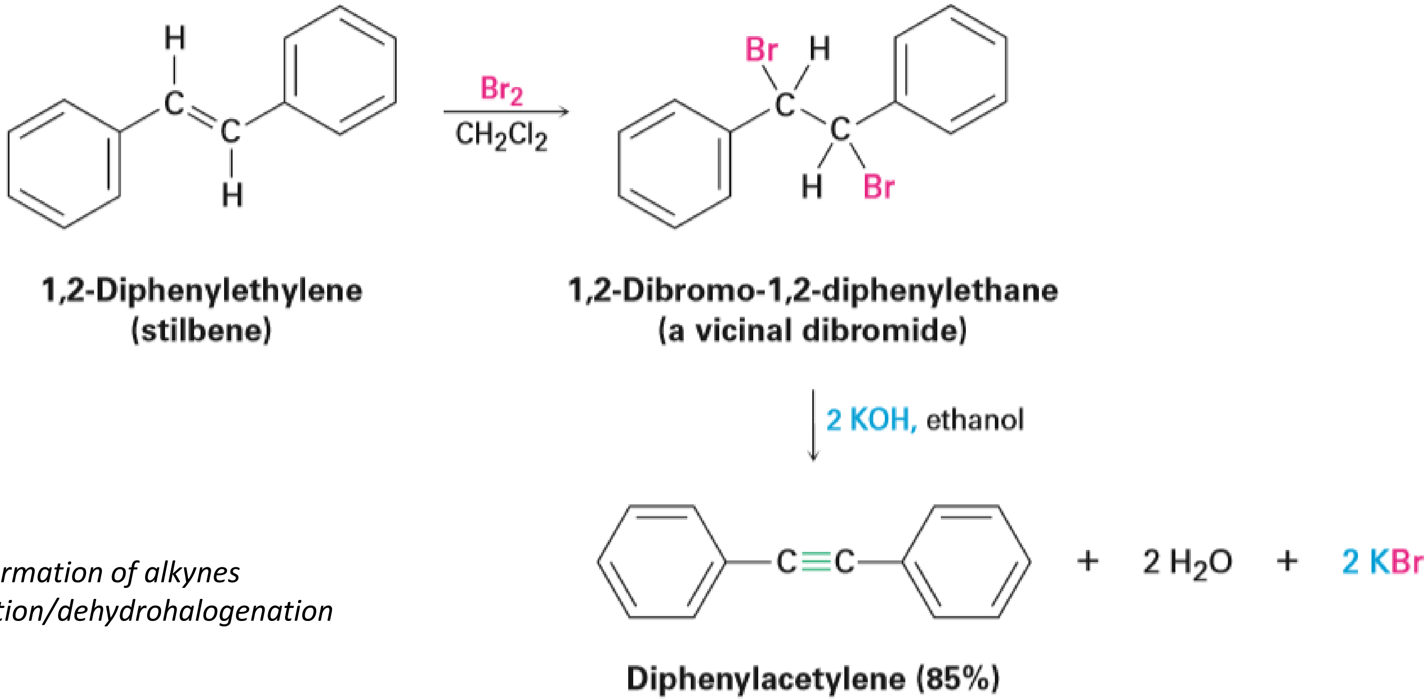
Vinylic anion
33% *s*

Acetylide anion
50% *s*

Acidity of Simple Hydrocarbons

Family	Example	K_a	pK_a	
Alkyne	$HC\equiv CH$	10^{-25}	25	**Stronger acid**
Alkene	$H_2C=CH_2$	10^{-44}	44	↑
Alkane	CH_4	10^{-60}	60	**Weaker acid**

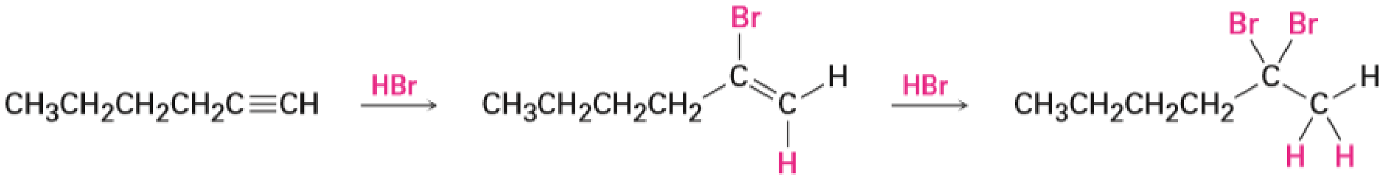
Synthesis of Alkynes



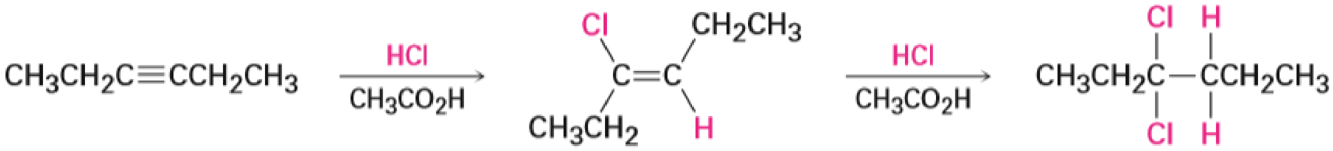
Formation of alkynes
Halogenation/dehydrohalogenation

Reactivity of Alkynes

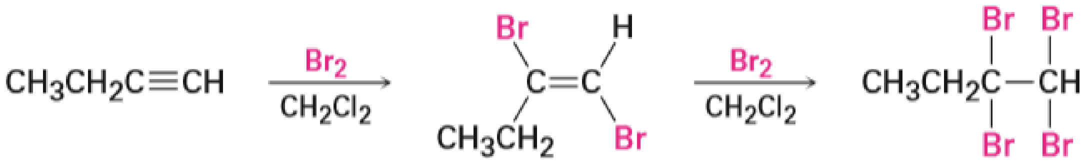
Addition of HX and X_2



1-Hexyne 2-Bromo-1-hexene 2,2-Dibromohexane

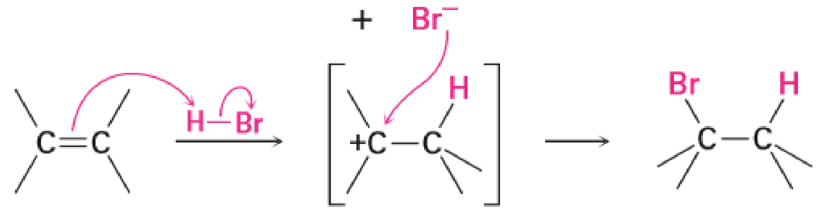


3-Hexyne (*Z*)-3-Chloro-3-hexene 3,3-Dichlorohexane



1-Butyne (*E*)-1,2-Dibromo-1-butene 1,1,2,2-Tetrabromobutane

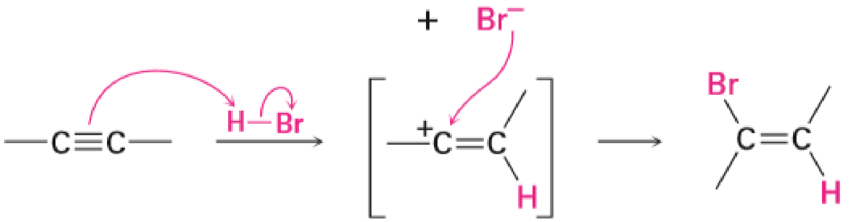
Mechanism:



An alkene

An alkyl carbocation

An alkyl bromide

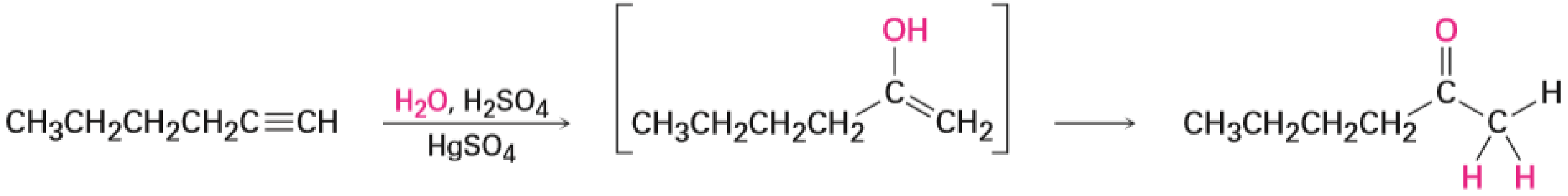


An alkyne

A vinylic carbocation

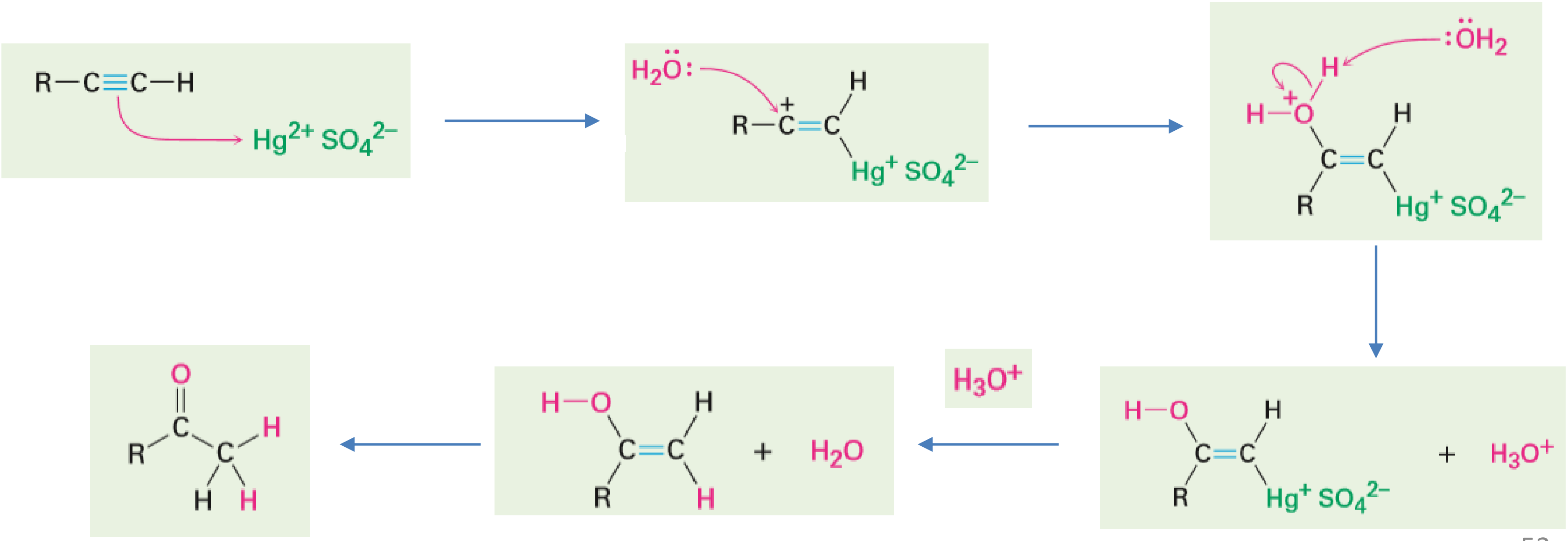
A vinylic bromide

Mercury (II)-Catalyzed Hydration of Alkynes



1-Hexyne **An enol** **2-Hexanone (78%)**

Mechanism:



Reduction of Alkynes

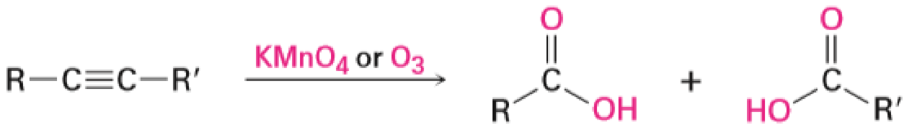
$$HC\equiv CH \xrightarrow[\text{Catalyst}]{H_2} H_2C{=}CH_2 \qquad \Delta H^\circ_{\text{hydrog}} = -176\ \text{kJ/mol}\ (-42\ \text{kcal/mol})$$

$$H_2C{=}CH_2 \xrightarrow[\text{Catalyst}]{H_2} CH_3{-}CH_3 \qquad \Delta H^\circ_{\text{hydrog}} = -137\ \text{kJ/mol}\ (-33\ \text{kcal/mol})$$

Reduction to alkenes and alkanes

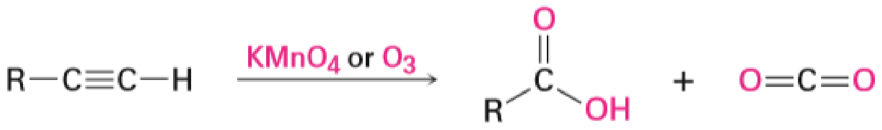
Oxidative Cleavage of Alkynes

An internal alkyne

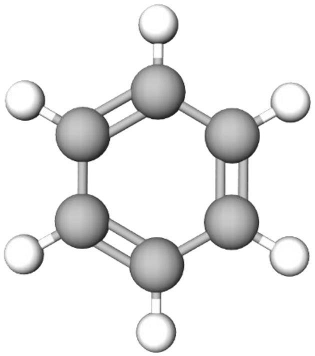


Oxidation to carboxylic acids

A terminal alkyne

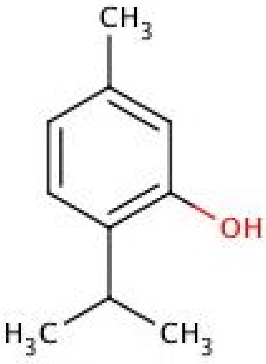


Introduction

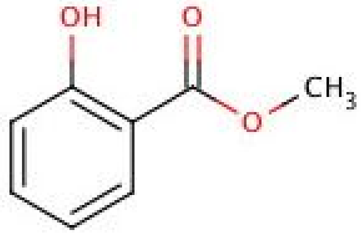


Benzene

Vanillin



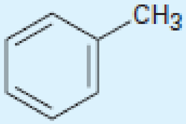
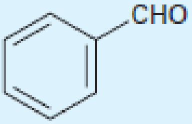
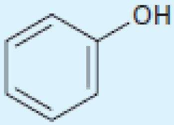
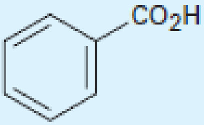
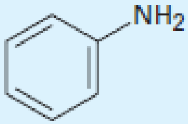
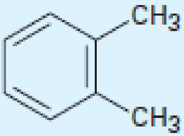
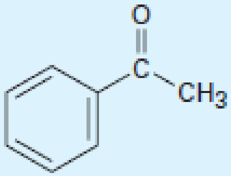
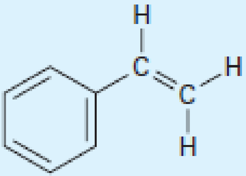
Thymol



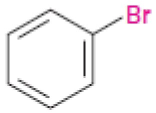
Methyl salicylate (wintergreen)

Naming Aromatic Compounds

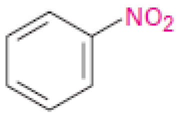
Common Names of Some Aromatic Compounds

Structure	Name	Structure	Name
	Toluene (bp 111 °C)		Benzaldehyde (bp 178 °C)
	Phenol (mp 43 °C)		Benzoic acid (mp 122 °C)
	Aniline (bp 184 °C)		ortho-Xylene (bp 144 °C)
	Acetophenone (mp 21 °C)		Styrene (bp 145 °C)

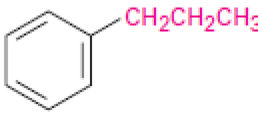
*1. **Monosubstituted benzenes** are named systematically in the same manner as other hydrocarbons, with -benzene as the parent name.*



Bromobenzene

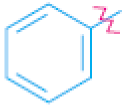


Nitrobenzene

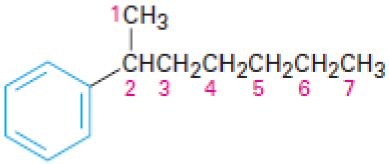


Propylbenzene

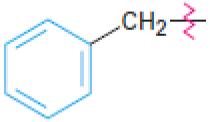
*2. **Alkyl-substituted** benzenes are sometimes referred to as arenes and are named in different ways depending on the size of the alkyl group. The name phenyl, sometimes abbreviated as Ph or F (Greek phi), is used for the -C_6H_5 unit when the benzene ring is considered as a substituent.*



A phenyl group

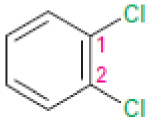


2-Phenylheptane

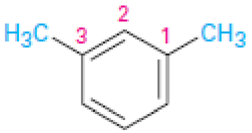


A benzyl group

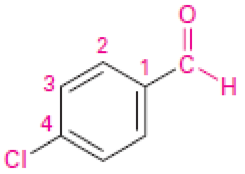
*3. **Disubstituted** benzenes are named using one of the prefixes ortho (o), meta (m), or para (p).*



ortho-Dichlorobenzene
1,2 disubstituted

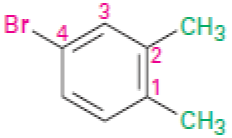


meta-Dimethylbenzene
(*meta*-xylene)
1,3 disubstituted

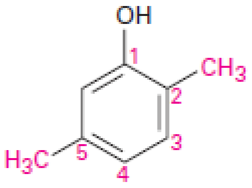


para-Chlorobenzaldehyde
1,4 disubstituted

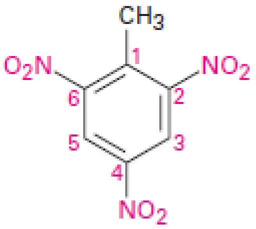
*4. Benzenes with **more than two substituents** are named by choosing a <u>point of attachment as carbon 1</u> and numbering the substituents on the ring so that the second substituent has as low a number as possible.*



4-Bromo-1,2-dimethylbenzene

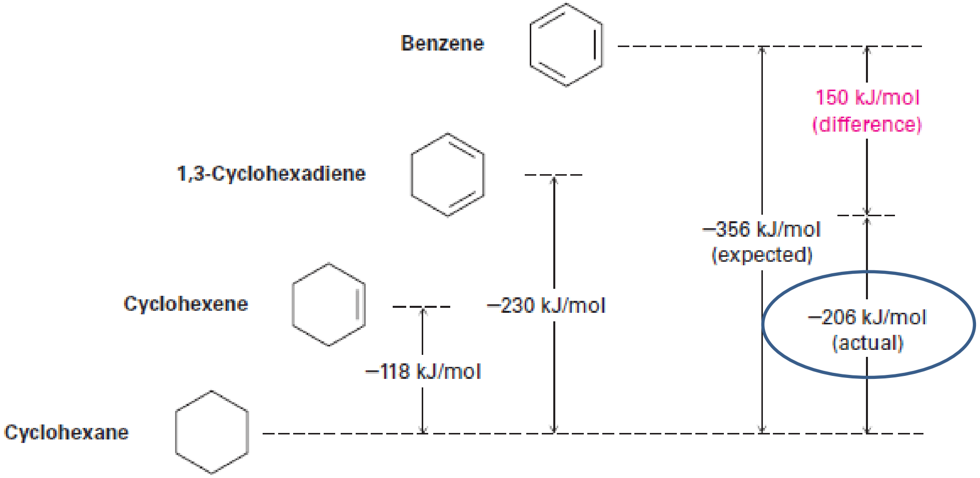


2,5-Dimethylphenol



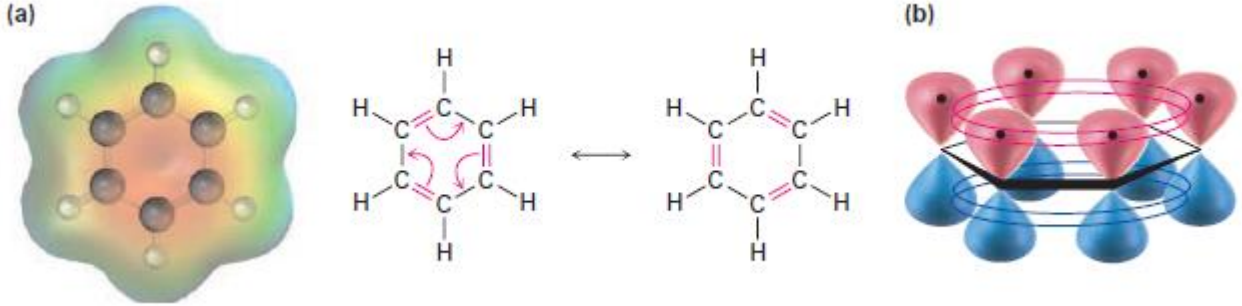
2,4,6-Trinitrotoluene (TNT)

Stability of benzene



Heats of hydrogenation

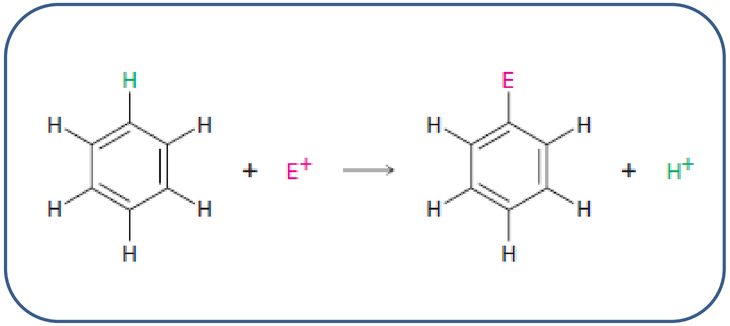
Benzene is more stable than expected by 150 kJ/mol.



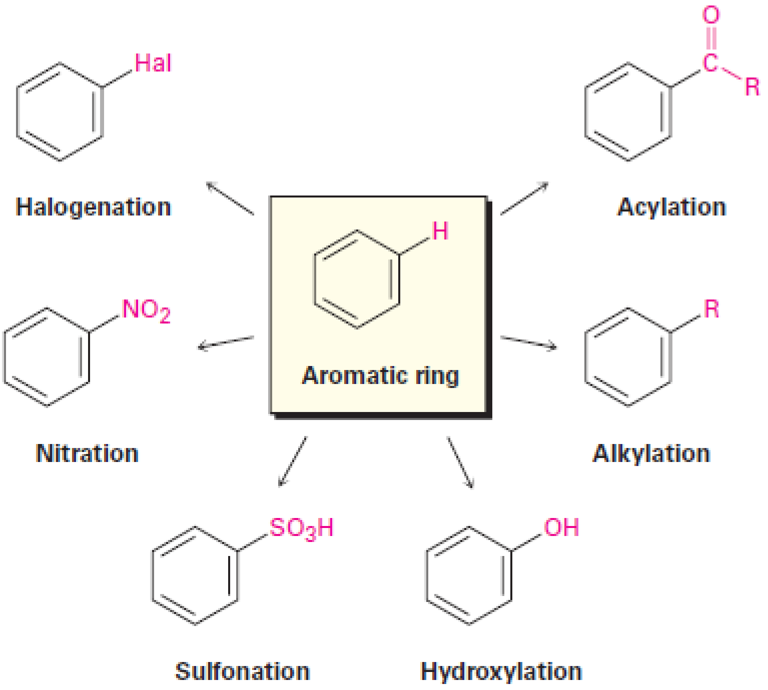
a) An electrostatic potential map of benzene and b) an orbital picture.

Reactivity

Electrophilic Aromatic Substitution

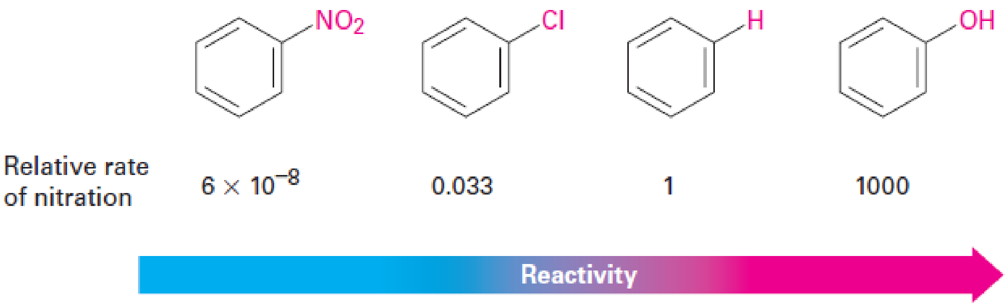


An electrophile (E) reacts with an aromatic ring and substitutes for one of the hydrogens



Substituent Effects in Electrophilic Substitutions

Substituents affect the
reactivity of the aromatic ring

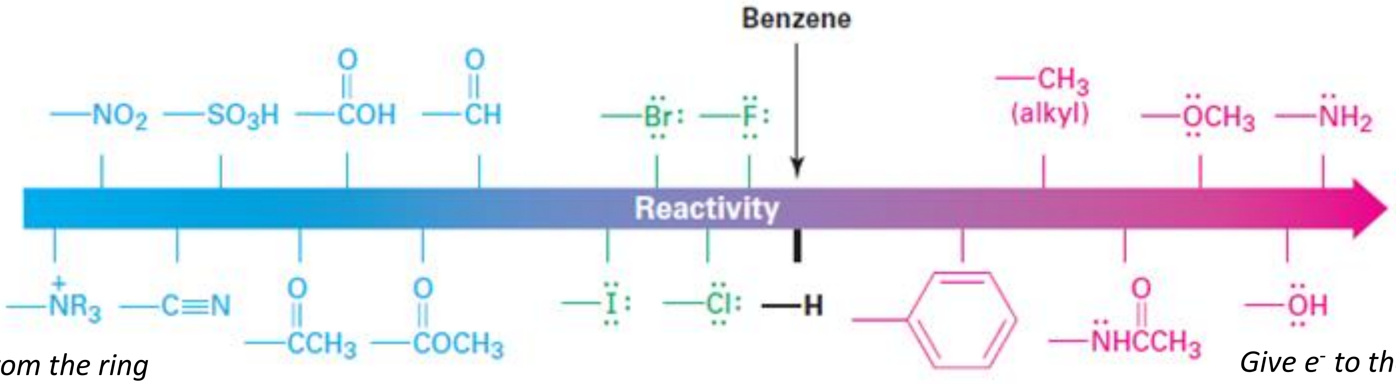


Substituents affect the
orientation *of the reaction*

-meta

-ortho and -para

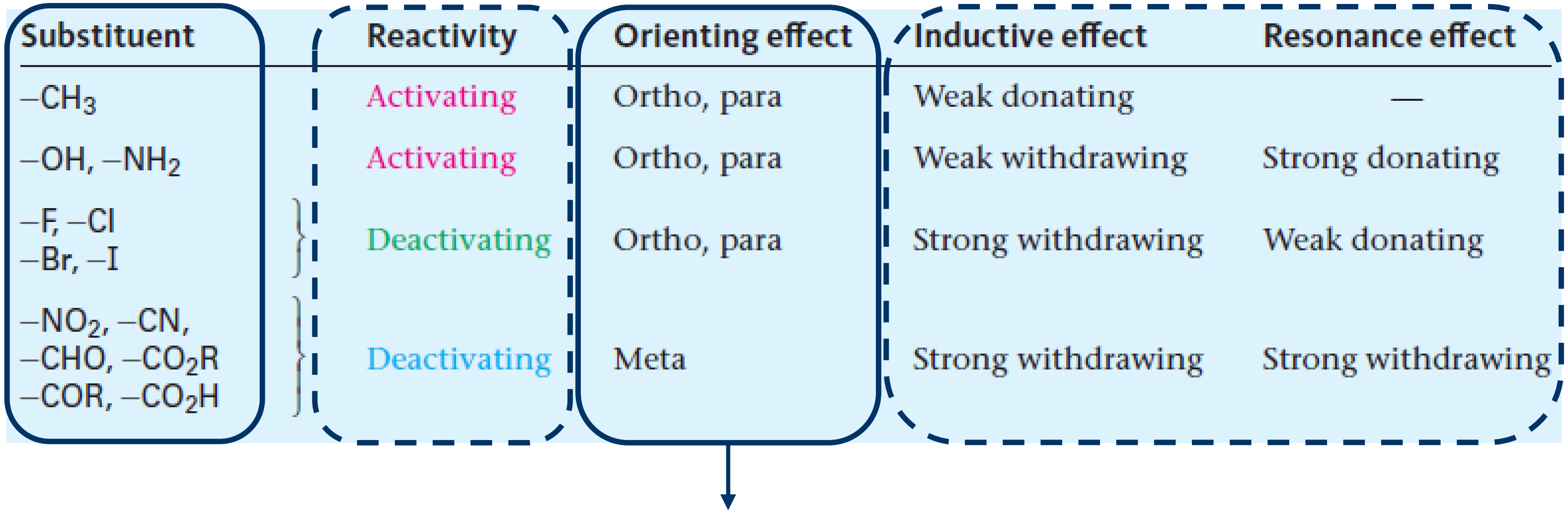
-ordo and -para



Accept e- from the ring
Deactivating groups

Give e- to the ring
Activating groups

A Summary of Substituent Effects in Aromatic Substitution



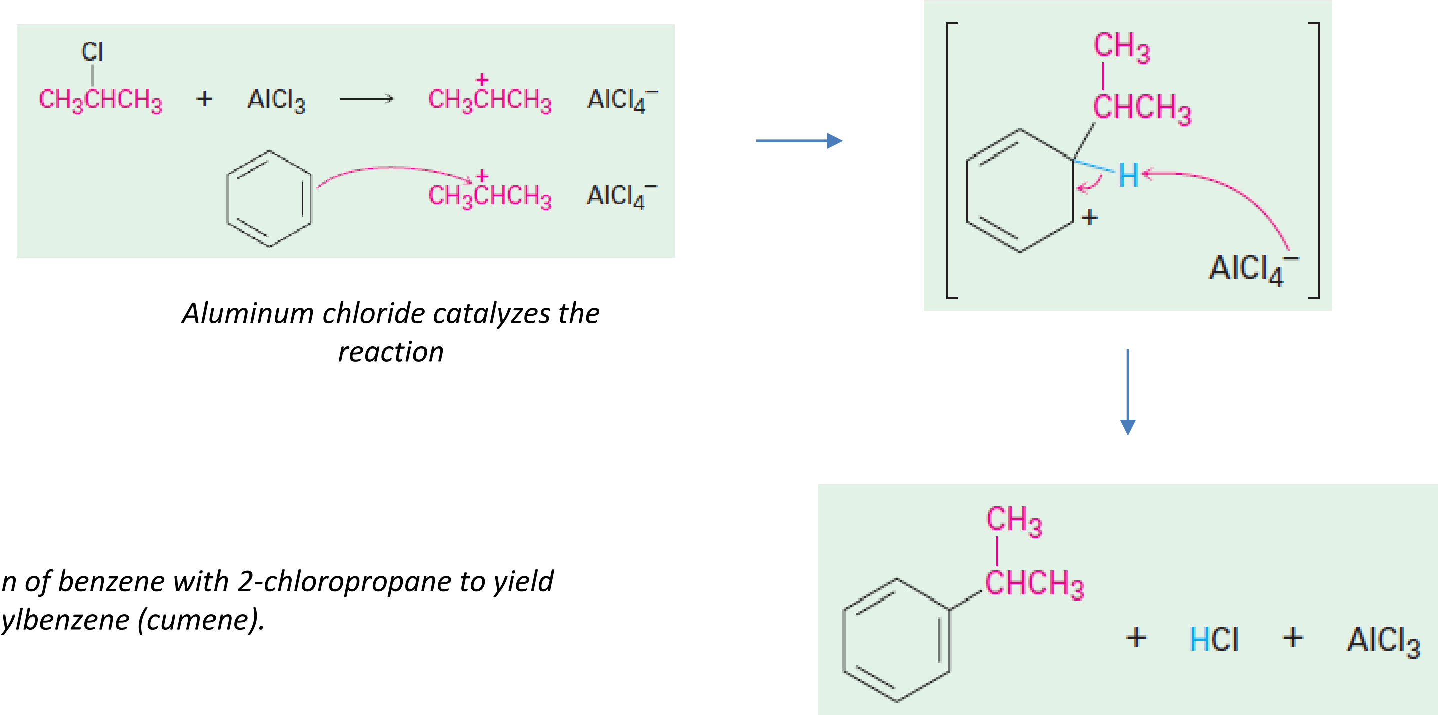
Substituent	Reactivity	Orienting effect	Inductive effect	Resonance effect
$-CH_3$	Activating	Ortho, para	Weak donating	—
$-OH$, $-NH_2$	Activating	Ortho, para	Weak withdrawing	Strong donating
$-F$, $-Cl$ $-Br$, $-I$	Deactivating	Ortho, para	Strong withdrawing	Weak donating
$-NO_2$, $-CN$, $-CHO$, $-CO_2R$ $-COR$, $-CO_2H$	Deactivating	Meta	Strong withdrawing	Strong withdrawing

Reactivity
Position of the substituent in the ring

Alkylation and Acylation of Aromatic Rings: The Friedel-Crafts Reaction

***Alkylation** of Aromatic Rings: the introduction of an alkyl group (-**R**) onto the benzene ring*

Mechanism

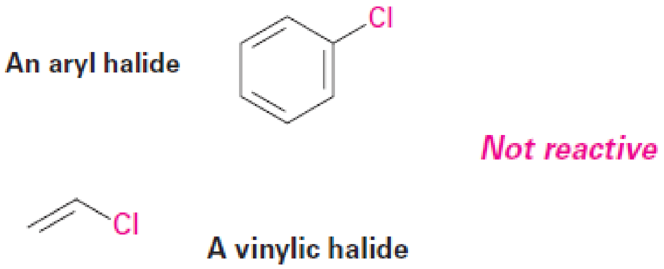


Aluminum chloride catalyzes the reaction

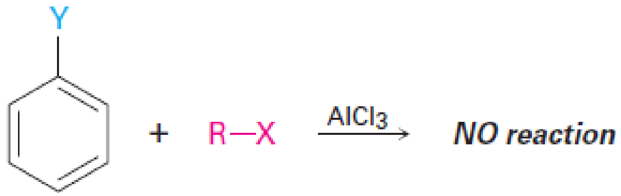
Reaction of benzene with 2-chloropropane to yield isopropylbenzene (cumene).

Limitations:

*1. Only **alkyl halides** can be used. Aromatic (aryl) halides and vinylic halides don't react because aryl and vinylic carbocations are too high in energy to form under Friedel–Crafts conditions.*

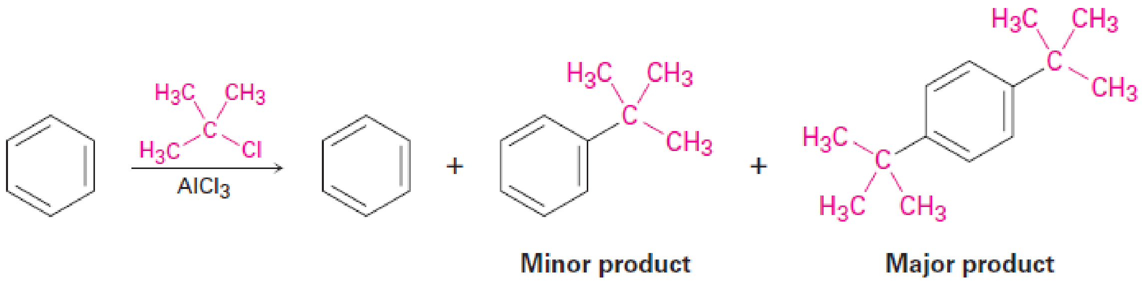


*2. Friedel–Crafts reactions don't succeed on aromatic rings that are substituted either by a **strongly electron-withdrawing group**.*

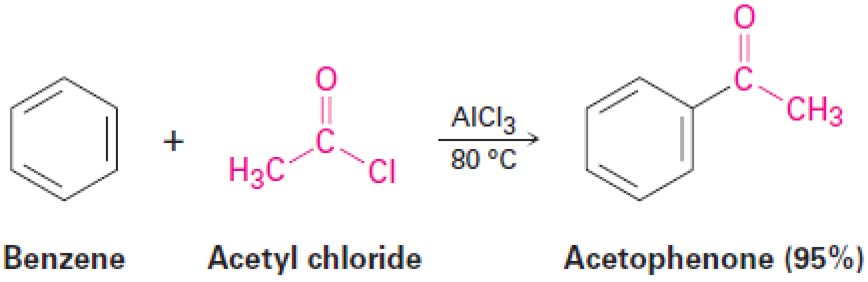


where Y = $-\overset{+}{N}R_3$, $-NO_2$, $-CN$, $-SO_3H$, $-CHO$, $-COCH_3$, $-CO_2H$, $-CO_2CH_3$ ($-NH_2$, $-NHR$, $-NR_2$)

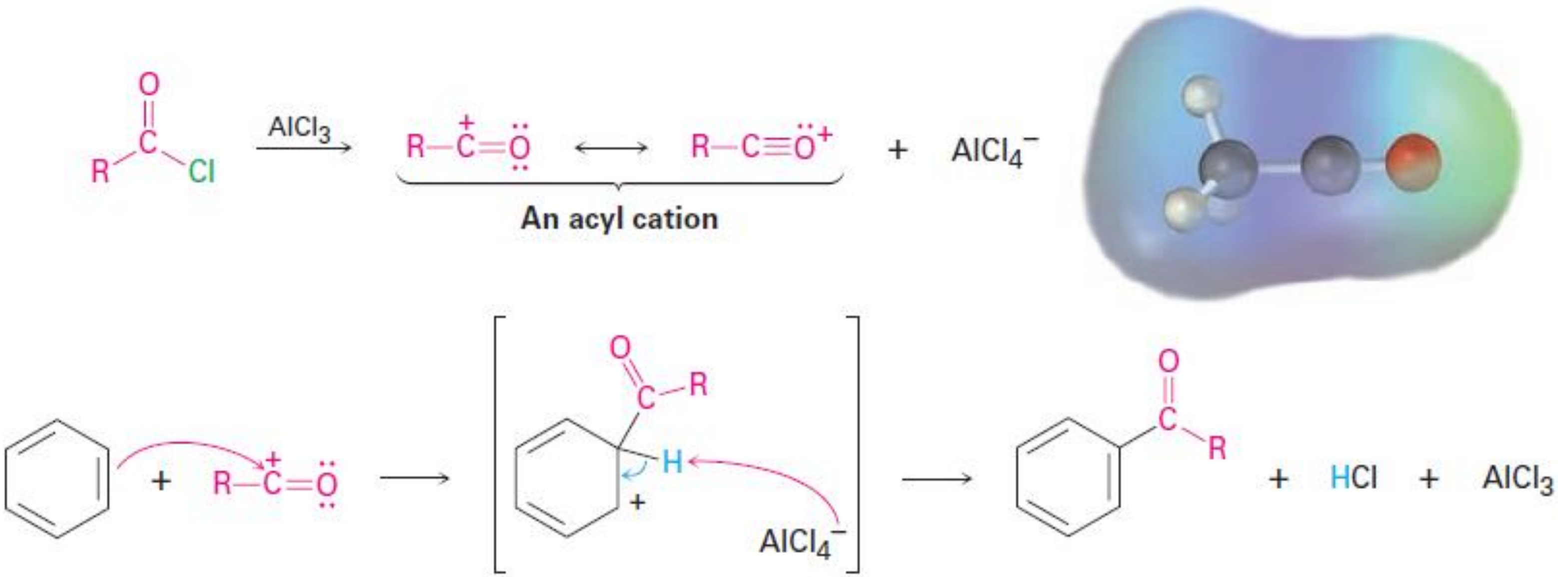
*3. Once the first alkyl group is on the ring, a **second substitution** reaction is facilitated.*



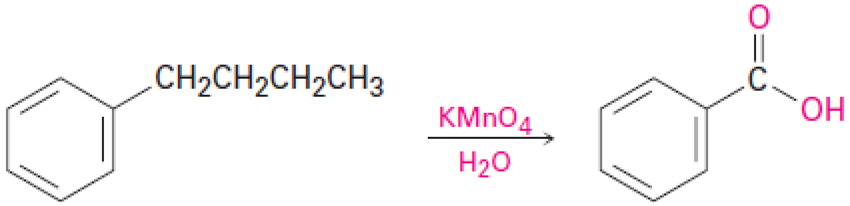
***Acylation** of Aromatic Rings: the introduction of an acyl group (-**COR**) onto the benzene ring*



Mechanism



Oxidation



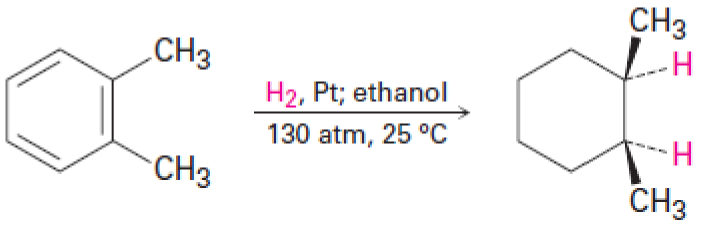
Butylbenzene

Benzoic acid (85%)

*The net effect is conversion of an alkylbenzene (**Ar-R**) into a benzoic acid (**Ar-CO_2H**)*

Oxidizing: MnO_4

Reduction



***o*-Xylene**

***cis*-1,2-Dimethyl-cyclohexane**

***Platinum catalyst** with hydrogen gas at several hundred atmospheres pressure*

Reducing: H_2

Image Credits

Slide 3:

- Structure of alkanes: 1840460mahesh, CC BY-SA 4.0, https://commons.wikimedia.org/wiki/File:Alkane_4_structure.jpg.

Slides 3 (table), 4-9, 11, 13, 16, 17, 21-23, 25, 26-29, 32, 33, 35-37, 40-45, 47, 49-54, 56-66:

- Organic Chemistry. A tenth Edition. John McMurry, Cornell University (Emeritus), CC BY-SA 4.0, https://openstax.org/details/books/organic-chemistry.

Slides 10, 15 (graph), 24 (table), 26 (graph), 34 (σ and π bonds), 48 (sp hybridization):

- Chem 12A: Organic Chemistry Fall 2022. Andy Wells, Chabot College, Open Education Resource (OER) LibreTexts Project, https://chem.libretexts.org/Courses/Chabot_College/Chem_12A:_Organic_Chemistry_Fall_2022.

Slides 14, 15, 19 (rearrangement), 28 (example), 30, 39, 47 (acrylic polymers structure):

- Images made by the authors.

Slides 18, 19, 34 (ethene structure), 49 (ethyne structure):

- Organic Chemistry I. Xin Liu. Kwantlen Polytechnic University, Surrey BC, CC BY-SA 4.0, https://open.umn.edu/opentextbooks/textbooks/1119.

Slide 31:

- Ethylene 3D structure: Claudio Pistilli, CC0 1.0, https://eo.wikipedia.org/wiki/Dosiero:Ethylene_3D_2.png.
- Propylene 3D structure: Claudio Pistilli, CC0 1.0, https://eo.m.wikipedia.org/wiki/Dosiero:Propylene_3D_2.png.
- Oleic acid structure: 3D structure, CNX OpenStax, CC BY 4.0, https://commons.wikimedia.org/wiki/File:Figure_02_03_05.jpg; bond-line structure, Johannes Botne, CC BY-SA 3.0, https://snl.no/oljesyre.

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- Acetylene 3D structure: MarinaVladivostok, CC0 1.0, https://commons.wikimedia.org/wiki/File:Acetylene_ball-and-stick.png.
- Acetic acid 3D structure: Christinelmiller, CC BY-SA 4.0, https://commons.wikimedia.org/wiki/File:Vinegar_Acetic_Acid_CH3COOH.png.
- Oxy acetylene gas welding: Paul Anderson, CC BY 2.0, https://commons.wikimedia.org/wiki/File:Oxy-Acetylene_welding_set.jpg.
- Dyes (acrylic polymers): Chris Larson, CC BY-SA 4.0, https://www.musson.com/supersat-sample-kit.html.

Slide 55:

- Benzene 3D structure: Herman Bergwerf, CC0 1.0, https://ndla.no/subject:1:f18b0daa-6507-4025-8998-b8a11c8ccc70/topic:5:f604b380-5cdb-4227-885e-bc9b57cb3237/topic:98043c9d-c278-4bf2-bf0f-abff61c3d155/resource:be046bcc-74e1-4ef1-8450-370c6752882d.
- Vanillin, thymol, and methyl salicylate chemical structure: C5perez, CC0 1.0, https://commons.wikimedia.org/wiki/File:Tast1.jpg.
- Vanillin flower: pantherkatz, CC BY-ND 2.0, https://www.flickr.com/photos/17405338@N00/2201862437.
- Thymol leaves: US Department of Agriculture, CC BY 2.0, https://www.flickr.com/photos/usdagov/8411805215.
- Wintergreen: pl@ntnet, CC BY-SA 4.0, https://identify.plantnet.org/k-world-flora/species/Gaultheria%20procumbens%20L./data.