Organic I

Lecture 4

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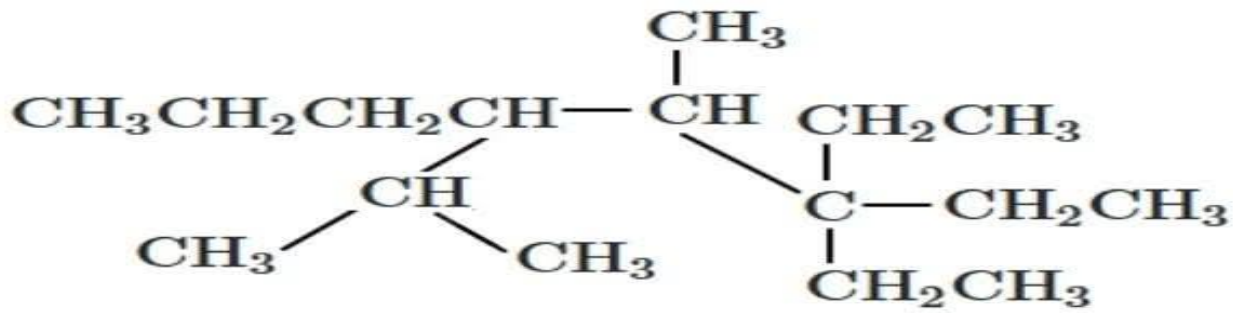
Q3: The IUPAC name of the compound



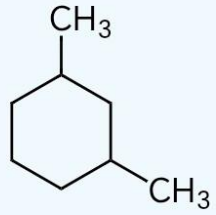
1. 3,3-diethyl-4-methyl-5 (methylethyl)octane

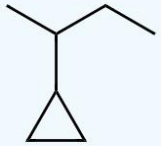
2. 3,3-diethyl-5-isopropyl-4-methyloctane

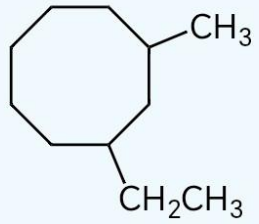
3. 4-isopropyl-5-methyl-6,6-diethyloctane

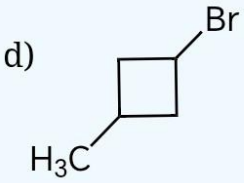
4. 6,6-diethyl-4-isopropyl-5-methyloctane

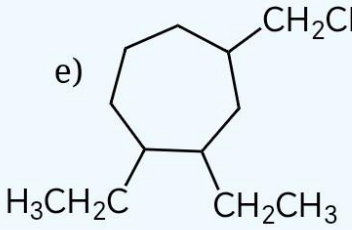
Give the IUPAC names for the following cycloalkane structures.

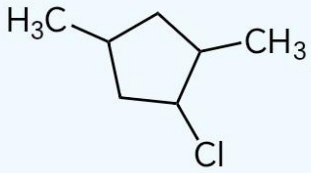
a) 

b) 

c) 

d) 

e) 

f) 

a) 1,3-Dimethylcyclohexane

b) 2-Cyclopropylbutane

c) 1-Ethyl-3-methyl-cyclooctane

d) 1-Bromo-3-methylcyclobutane

e) 1,2,4-Triethylcycloheptane

f) 1-Chloro-2,4-dimethylcyclopentane

Preparation of alkanes

1) From Alkenes (Catalytic Hydrogenation):

e.g.:

$$H_3CHC{=}CH_2 \xrightarrow{H_2 / Ni} CH_3CH_2CH_3$$



2) From Alkyl Halides:

A) By Reduction:

e.g.

$$CH_3\text{-}\underset{\displaystyle Br}{\underset{|}{CH}}\text{-}CH_2\text{-}CH_3 \xrightarrow{Zn / CH_3COOH} CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

B) Via Grignard Reagent:

e.g.:

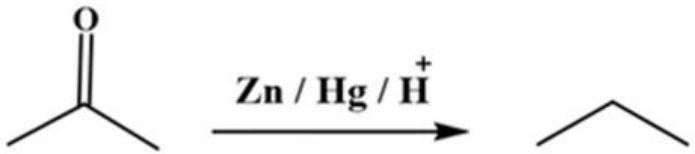
$$CH_3Br \xrightarrow[ether]{Mg} \overset{\ominus}{CH_3}\overset{\oplus}{MgBr} \begin{cases} \xrightarrow{H_2O} CH_4 + Mg(OH)Br \\ \xrightarrow{CH_3CH_2Br} CH_3CH_2CH_3 + MgBr_2 \end{cases}$$

N.B:

- C- (N, O, Halogen) ⟶ +ve charge
- C- (Li, Mg) ⟶ -ve charge

3) From Carbonyl compounds (Clemmensen Reduction):

e.g.



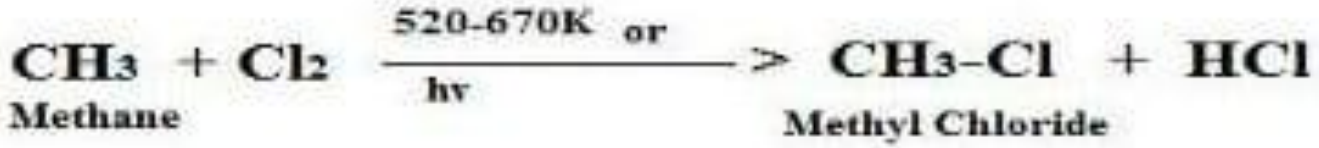
Physical properties of Alkanes:

1) The first four members of alkanes are gases at R.T., while from C5 to C17 are liquids and those which above C17 are solids.

2) Branched alkanes have *lower boiling points* than unbranched alkanes.

3) Alkanes are nonpolar compounds, so they don't dissolve in water (polar solvent) but soluble in benzene (nonpolar solvent).

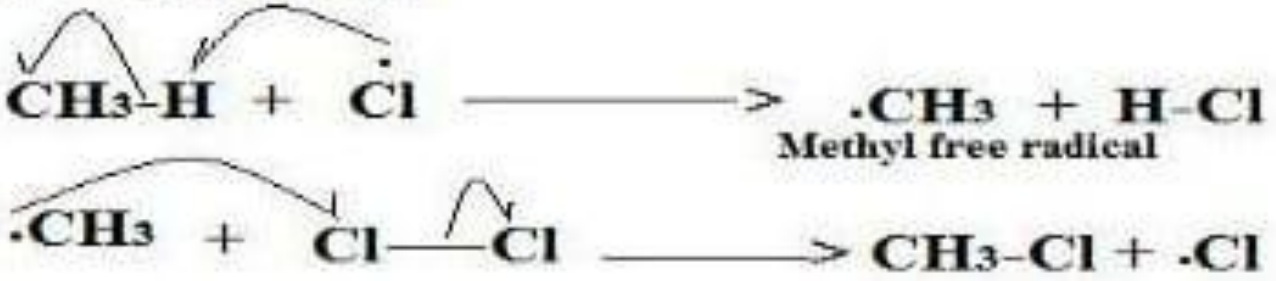
1- Halogenation (free radical substitution reaction)



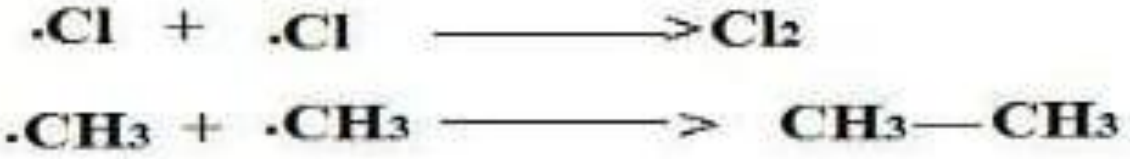
Step 1: Initiation



Step 2: Propagation

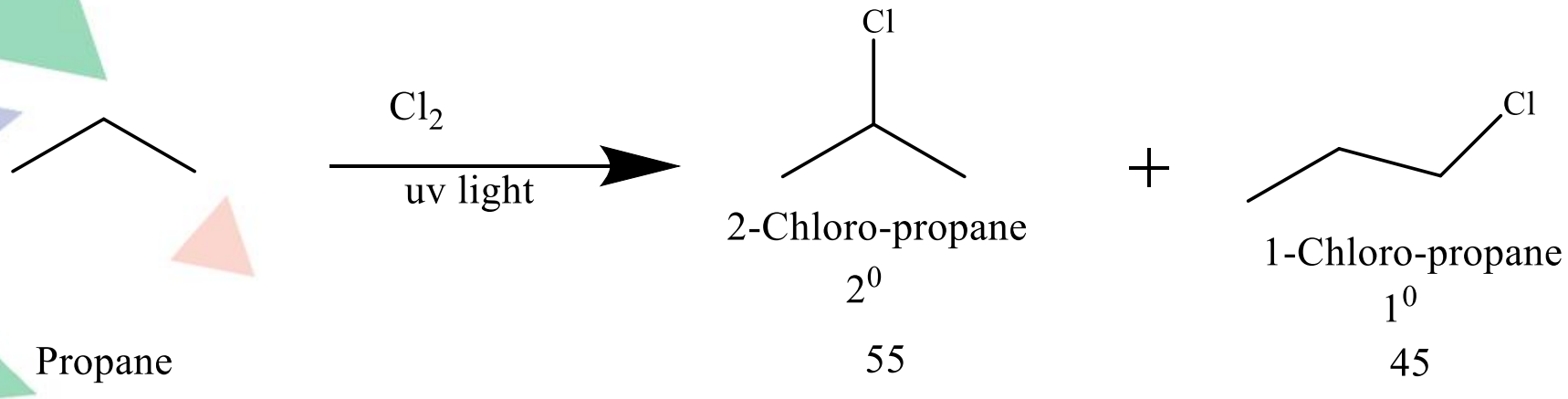


Step 3: Termination

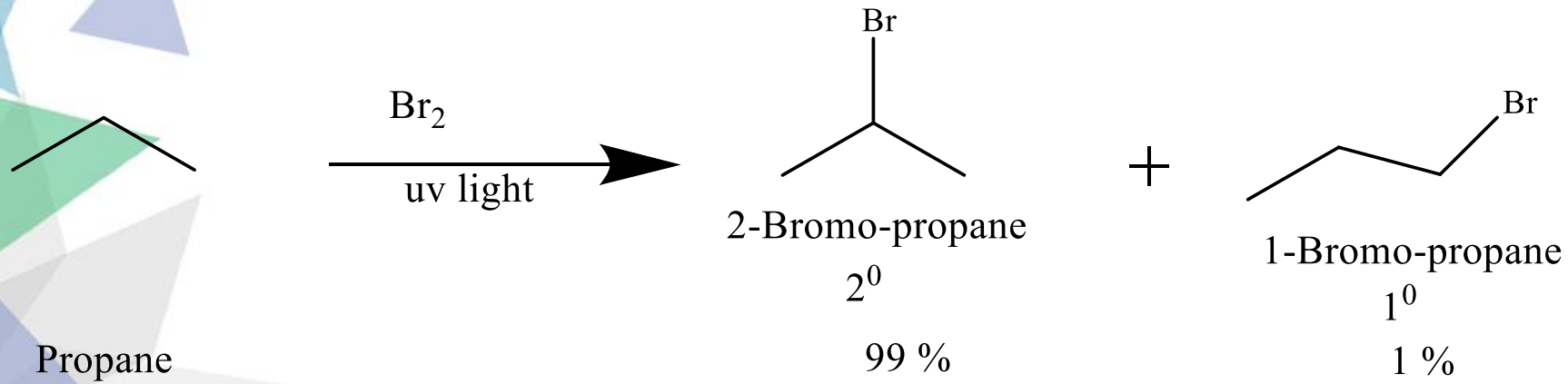


F> Cl >Br >I

Chlorine is more reactive than bromine and less selective



Bromine is less reactive and more selective



From previous examples we should know:

a) When there is **one type** of Hs, as in CH_4, there will be **One product** only of alkyl halides as there is one type of alkyl free radical only ($CH_3\cdot$).

b) When there are **two types** of Hs, as in $CH_3CH_2CH_3$ or $CH_3CH(CH_3)CH_3$, there will be **Two products (Major and Minor)** of alkyl halides as there are *two* types of alkyl free radicals.

Stability of carboradicals and carbocations

Factors that affect stability of radical and cation

1- Hyperconjugation

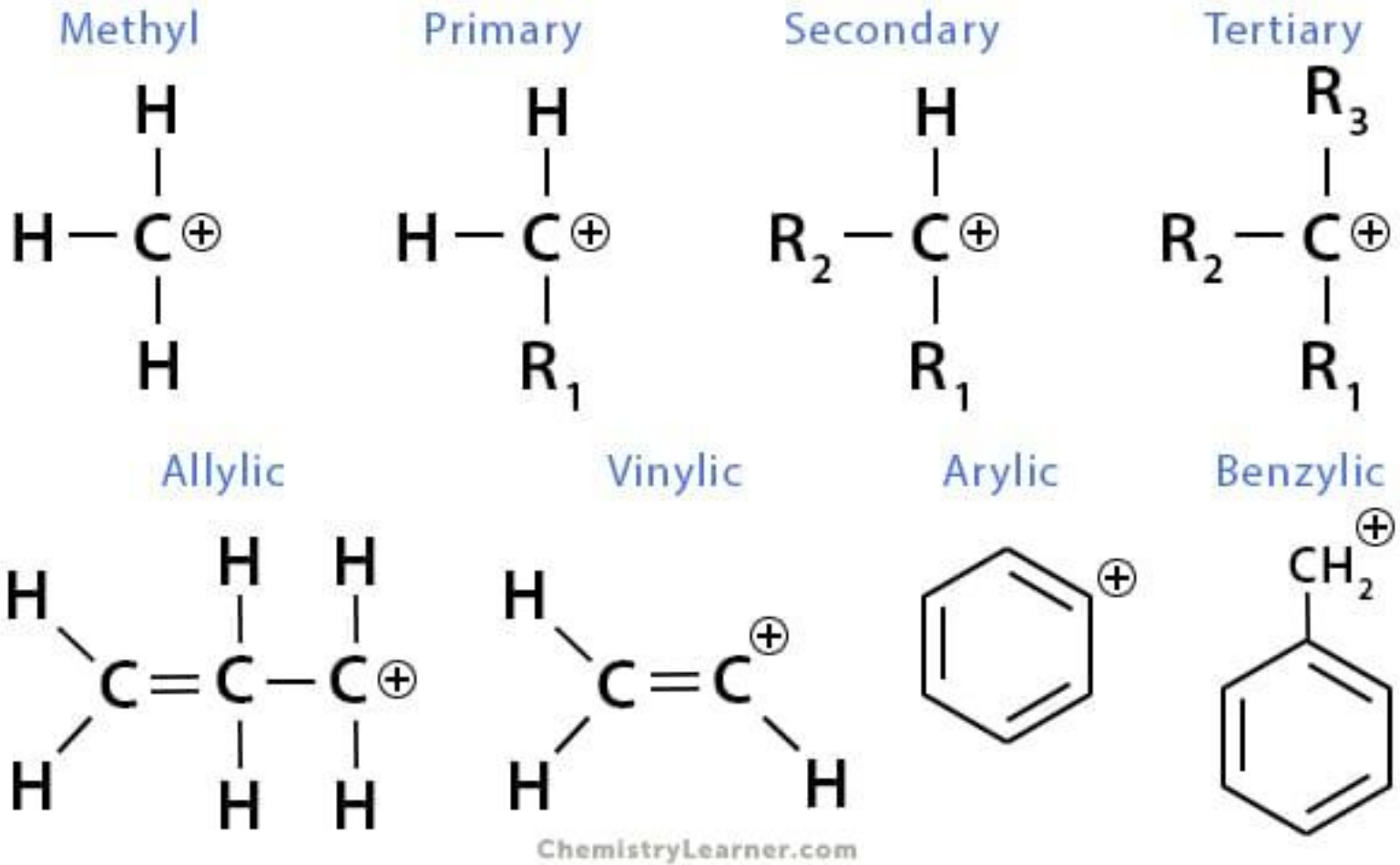
2- Inductive effect

3- Resonance

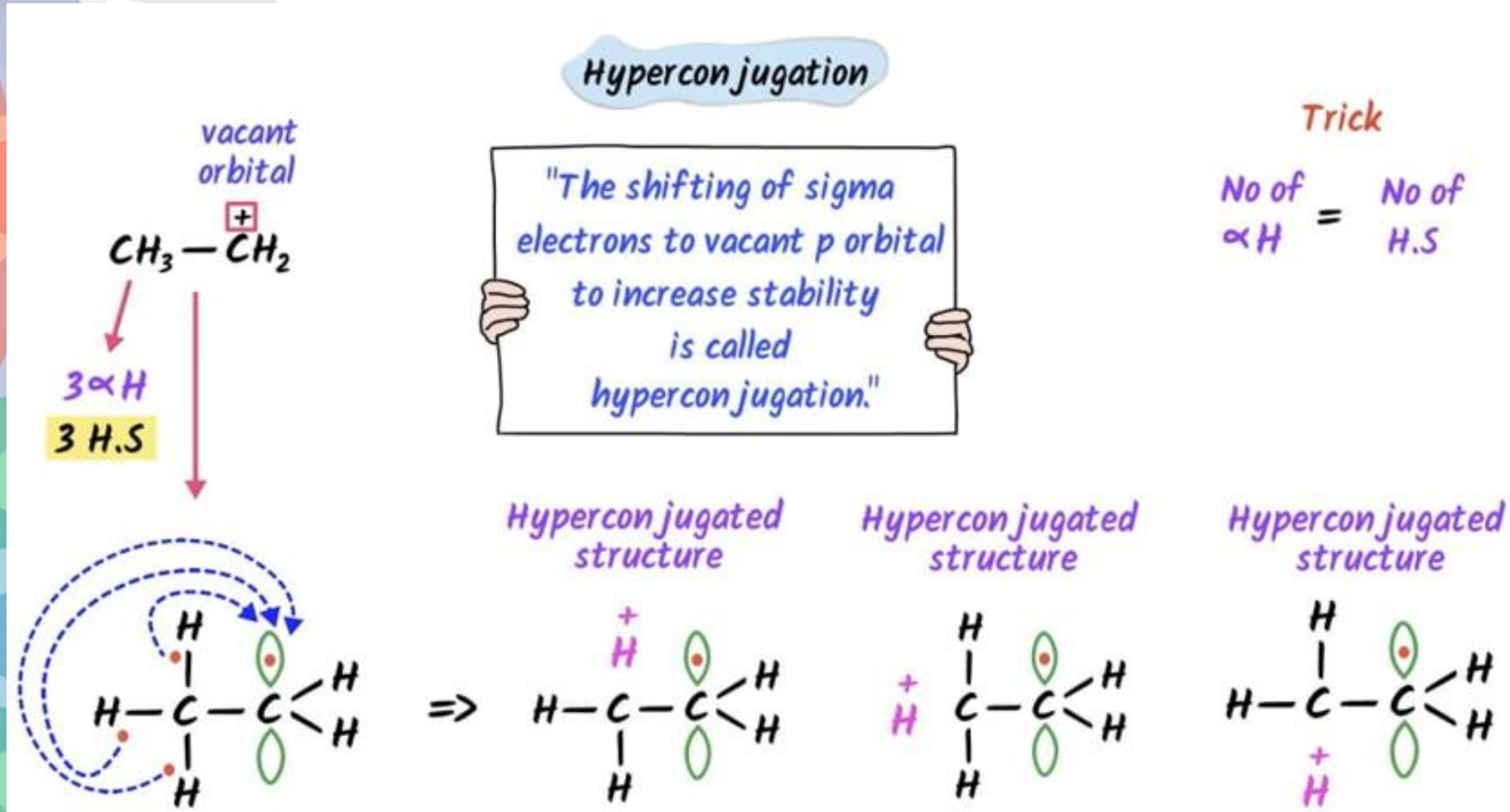
4- S-Character

5- Electronegativity

Types of Carbocation

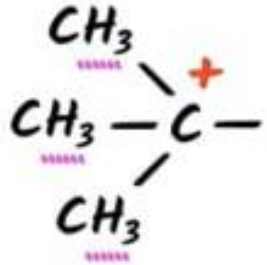
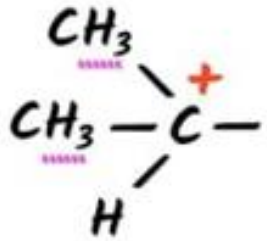
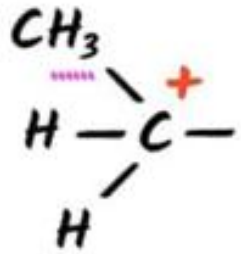


1- Hyperconjugation



Stability of Carbocations

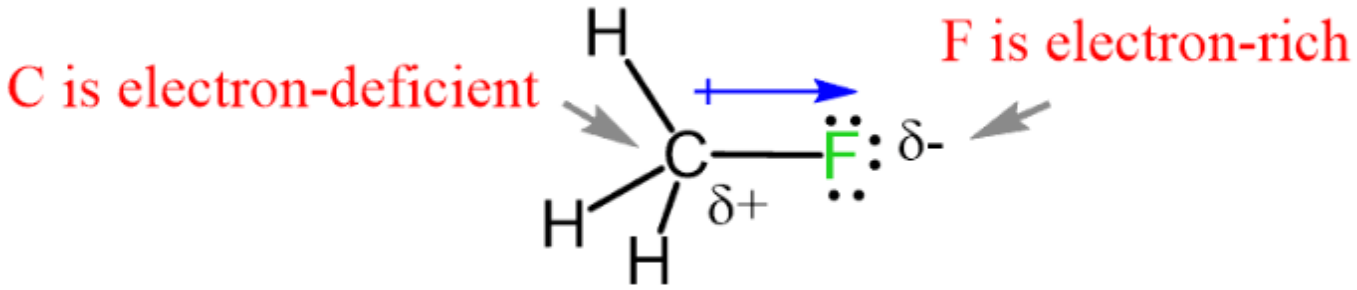
Resonance > Hyperconjugation > Inductive effect

Tertiary carbocation	Secondary carbocation	Primary carbocation	Methyl carbocation
			
9∝H	6∝H	3∝H	No alpha hydrogen
9 H.S	6 H.S	3 H.S	

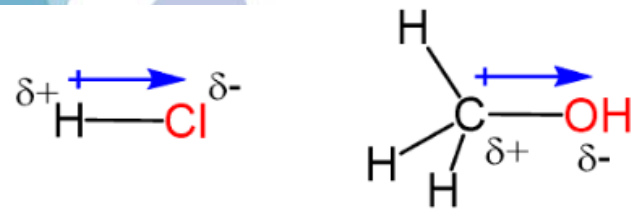
More Hyp Structures = More Stability

2- Inductive effect

Recall from pervious lecture that a **polar covalent bond** is formed when two atoms with **different electronegativities** are connected. In these bonds, the shared electron pair of the covalent bond is **not in the middle** of the two atoms. There is a higher density towards the more electronegative element, and as a result, both **elements have partial charges.** Mainly, the more electronegative atom bears a **partial negative**, and the other atom has **a partial positive charge** which are indicated by the **delta plus (δ+)** and delta minus **(δ-)** symbols:

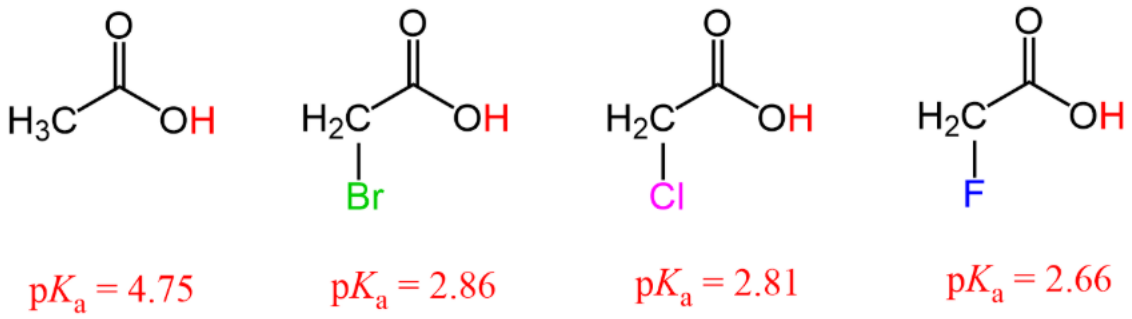


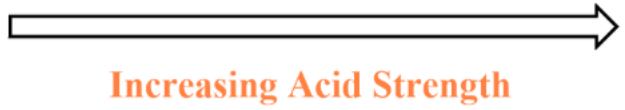
C-F is plar vovalent bond

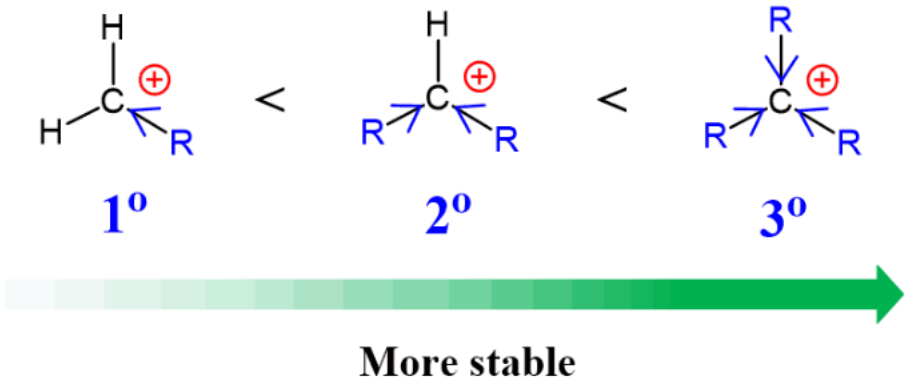


More examples of polar covalent bonds

This essentially is the **inductive effect**: it is **partial transfer of electrons through sigma (σ) bonds.** If the atom or the group **donates electron density,** it is said to have a **positive inductive effect (+*I*).** Atoms or groups that **pull electron density** from another atom or a group through sigma bond(s), are **electron-withdrawing** and denoted as **–*I* groups.**







Inductive effect

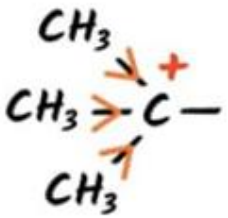
NO2
F
OH
OCH3
NH2
Cl
Br

Akyl groups

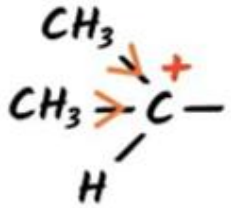
Electron withdrawing group
-I effect

Electron donating group
+I effect

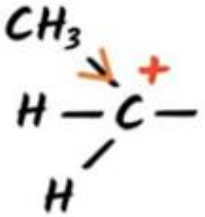
Inductive effect



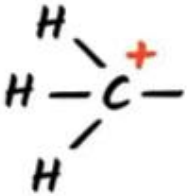
3 es donors



2 es donors



1 e donor



No es donor

Inductive effect

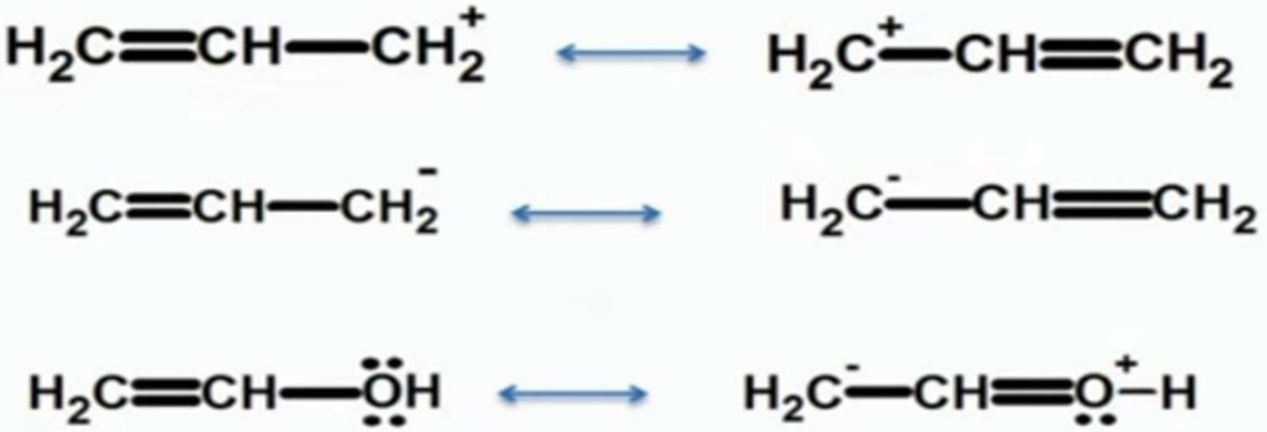
To attract or donate electron to create polarity...

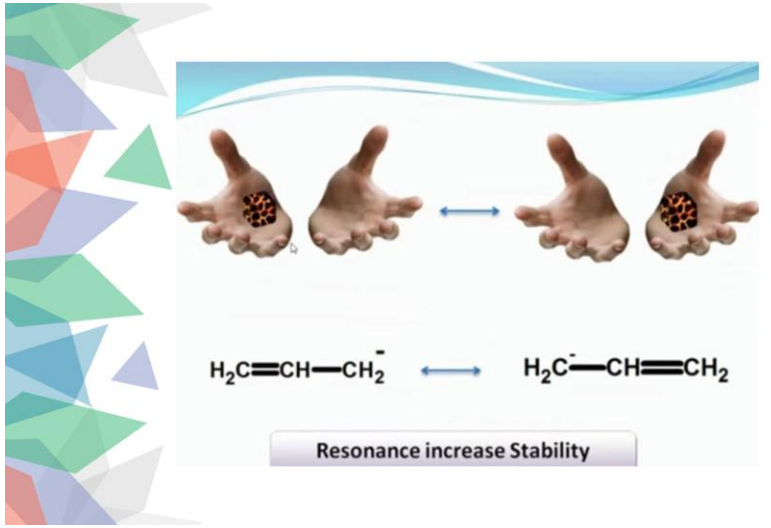
$CH_3 >$ Weak electron donor

3- Resonance

Mesomeric effect

- Complete transfer of electrons through pi bond
  "double ,triple bond"





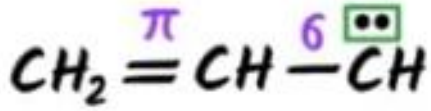
Substituent	Inductive effect	Resonance effect
$-CH_3$	Weak donating	—
$-OH, -NH_2$	Weak withdrawing	Strong donating
$-F, -Cl$ $-Br, -I$	Strong withdrawing	Weak donating
$-NO_2, -CN,$ $-CHO, -CO_2R$ $-COR, -CO_2H$	Strong withdrawing	Strong withdrawing

Stability of Carbocations

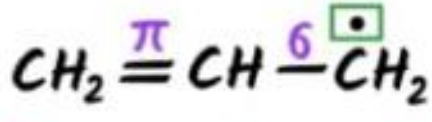
Complete concept of stability of carbocations.

Resonance

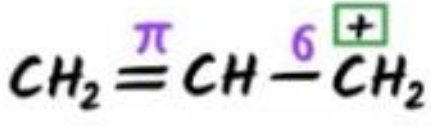
It is possible in 4 types of compounds.



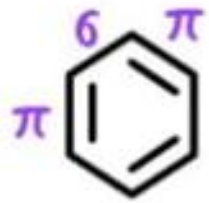
Resonance is possible.



Resonance is possible.



Resonance is possible.



Resonance is possible.

Difficult Examples

Resonance > Hyperconjugation > Inductive effect

a)



b)



c)



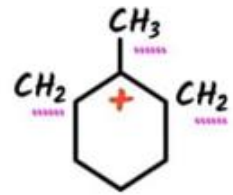
a)



3∝H

3 H.S

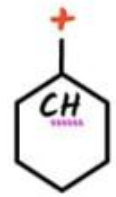
b)



7∝H

7 H.S

c)



1∝H

1 H.S

b) > a) > c)

Difficult Examples

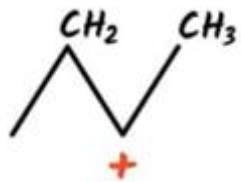
Resonance > Hyperconjugation > Inductive effect

a)



Resonance

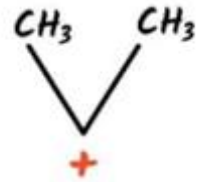
b)



5 ∝ H

5 H.S

c)



6 ∝ H

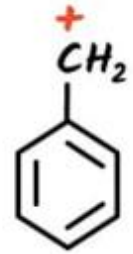
6 H.S

a) > c) > b)

Exception Case

Which is more stable .....

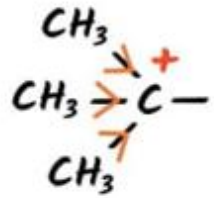
Benzylic carbocation



Resonance

<

Tertiary carbocation



9 ∝ H

9 H.S

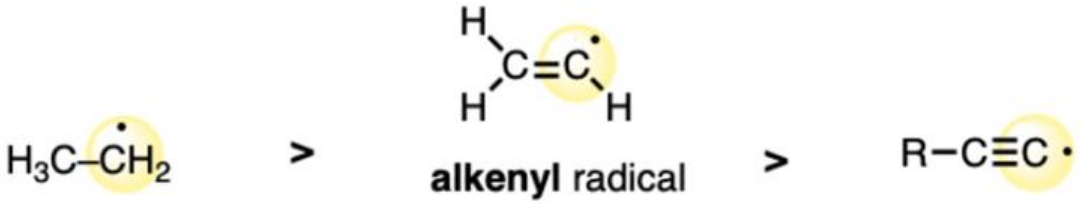
3 es donors

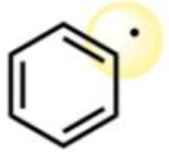
👉 Because of extensive hyperconjugation and inductive effect in it.

4- S-Character

The Role of Orbital Hybridization

- The stability of a free radical **decreases** as the orbital is held **closer** to the nucleus
- As *s*-character of the orbital increases, the stability of the radical decreases.





alkyl radical

most stable

aryl radical

alkynyl radical

least stable

- **less *s*-character of orbital**
- held further away from nucleus
- lower electron affinity of half-filled orbital = greater stability

- **more *s*-character of orbital**
- orbital **closer** to nucleus
- higher electron affinity of half-filled orbital = lesser stability

5- Electronegativity of carbocations

The Role of Electronegativity

- Across the periodic table, radical stability **decreases** in stability going from left to right *(i.e. with increasing electronegativity)*
- Why? A partially filled orbital becomes increasingly unstable the more tightly it is held to the nucleus



most stable

- **least** electronegative atom (C)

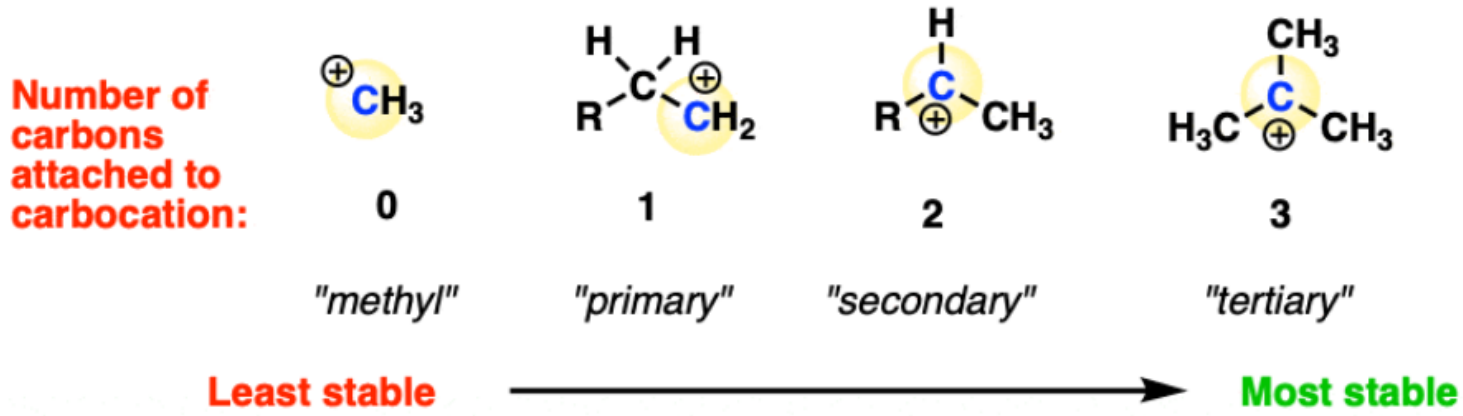
least stable

- most electronegative atom (F)

- Similar to the relationship between the amount of *s*-character; you can think of increasing *s*-character as being effectively the same as having greater electronegativity

*Higher electronegativity = greater electron affinity of the half-filled orbital, meaning it will be more **unstable***

Carbocation **stability increases** as the number of adjacent alkyl groups is **increased**



In other words, carbocation stability increases as C-H bonds are replaced with C-C bonds.

Why?

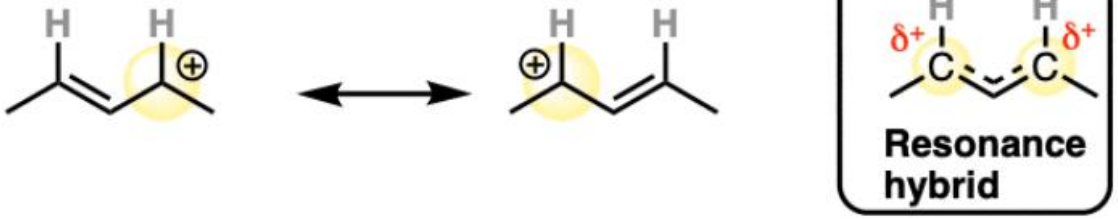
Being electron-poor, carbocations are **stabilized** through donation of electron density from neighboring **electron-rich** atoms.

As I've often told my students, "*when you're poor, it helps to have rich neighbors*".

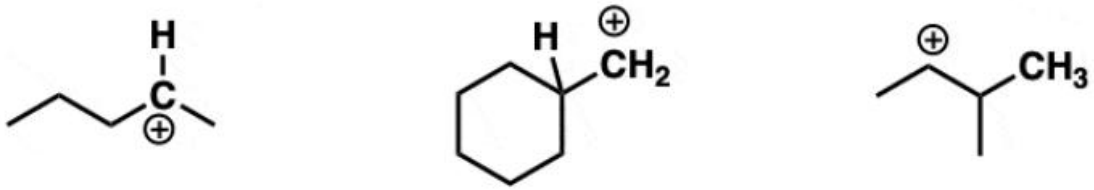
One way to rationalize this trend is through applying **inductive effects.**

• This **reduces** the overall charge density of the carbocation, making it more **stable**.

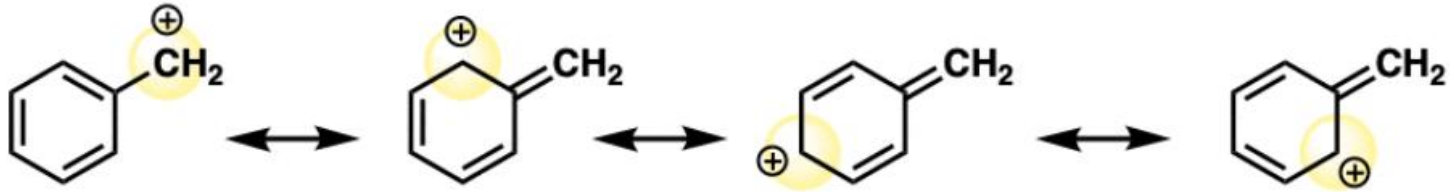
In the case below, each carbon bears a positive charge of +0.5 in the resonance hybrid



Contrast that to the carbocations below, where the positive charge **cannot** be delocalized through resonance due to the absence of neighboring p-orbitals



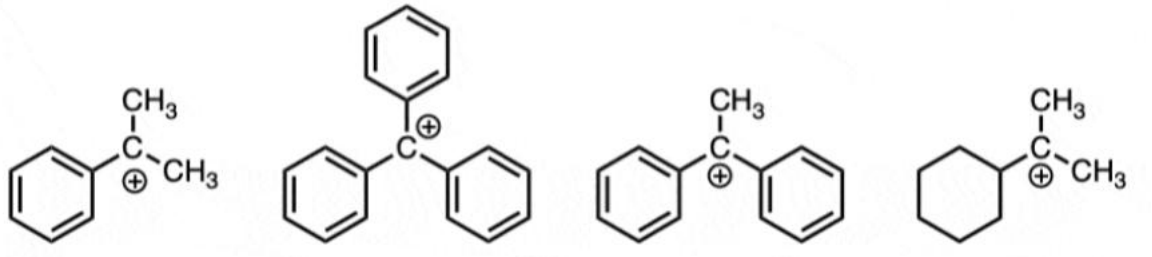
Aromatic rings (e.g. benzene) also stabilize positive charge through **resonance**



In order for resonance stabilization to occur, the empty p-orbital of the carbocation must be capable of overlap with the adjacent pi-bond

Practice problem

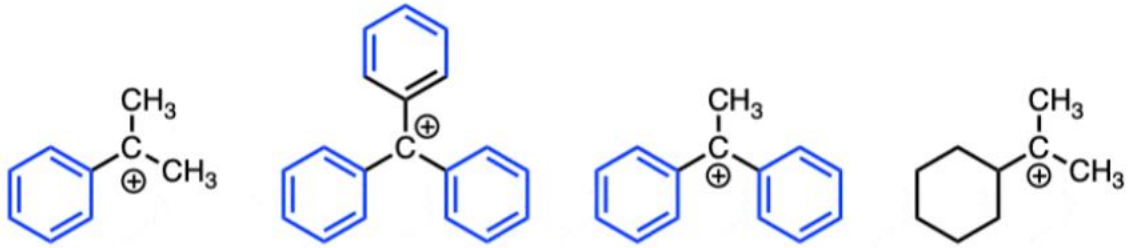
Rank the following carbocations in order of stability (1 = most stable, 4 = least stable)



A B C D

All of these carbocations are **tertiary** (attached to 3 carbons)
They differ in the number of adjacent aromatic rings (capable of stabilizing the carbocation through resonance)

The more aromatic rings the carbocation is attached to, the more stable it is.



A

3

B

1 (most stable)

Attached to 3 aromatic rings

C

2

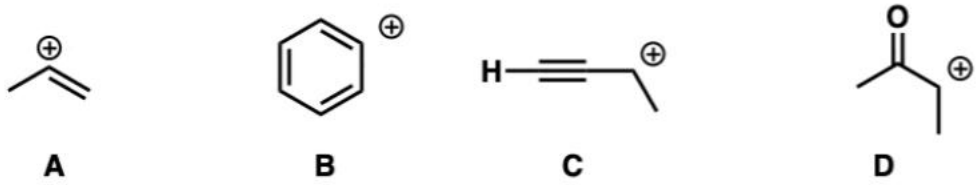
D

4 (least stable)

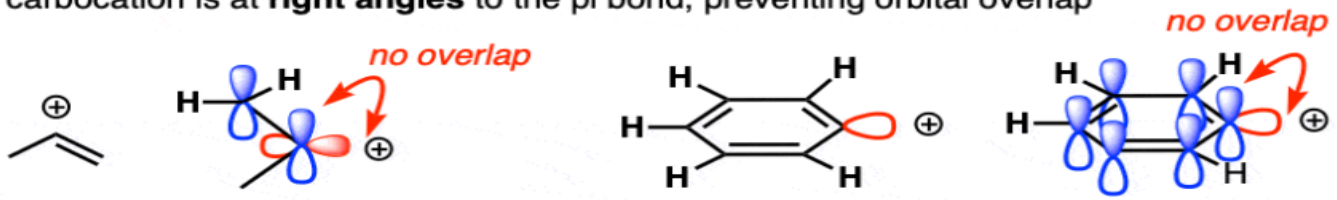
No resonance stabilization possible

Practice problem:

Are these carbocations **resonance-stabilized**? Why or why not?

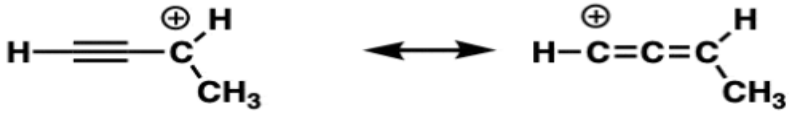


A and **B** are **not** stabilized by resonance. The empty p-orbital of the carbocation is at **right angles** to the pi bond, preventing orbital overlap



the empty p-orbital cannot overlap with pi-bond - it is in the same plane as the C–H bonds

C is stabilized by resonance since overlap **is** possible



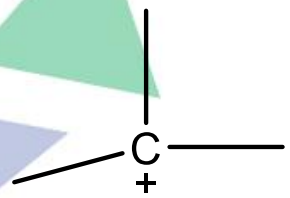
D is **not** stabilized by resonance. Although the empty p-orbital **is** capable of overlap with the pi-bond, the resonance form with a positive charge on oxygen has **less than a full octet on the very electronegative oxygen atom**, which makes it an **insignificant** resonance form.

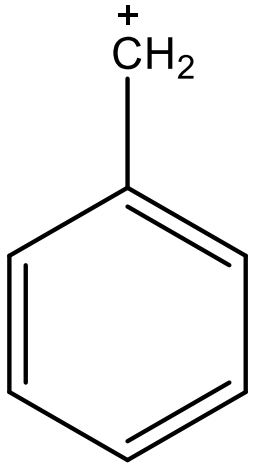


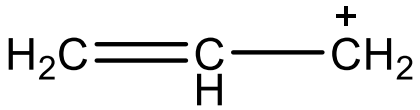
only six valence electrons
empty p-orbital on oxygen

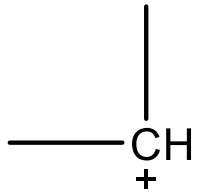
not a significant resonance form

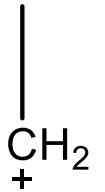
Order of carbocation stability



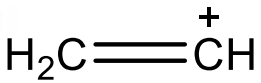


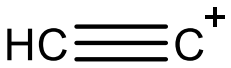




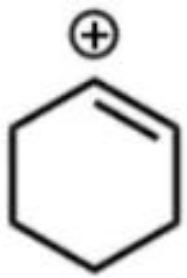


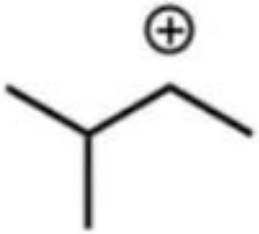






Which **carbocation** is the **most stable**?

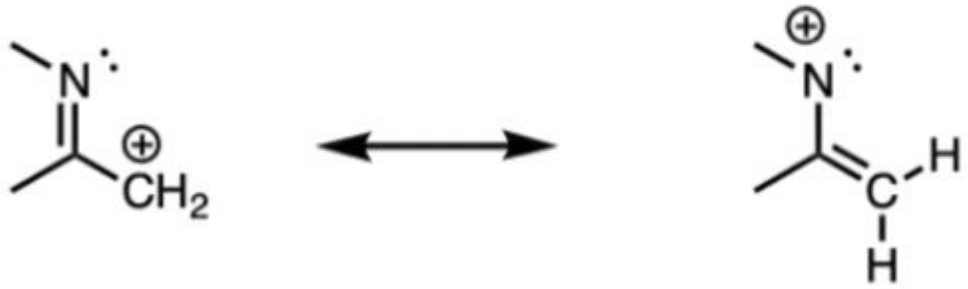
A) 

B) 

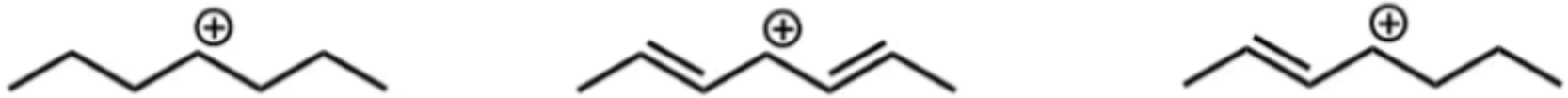
C) 

D) 

Is this carbocation **resonance-stabilized**? Why or why not?

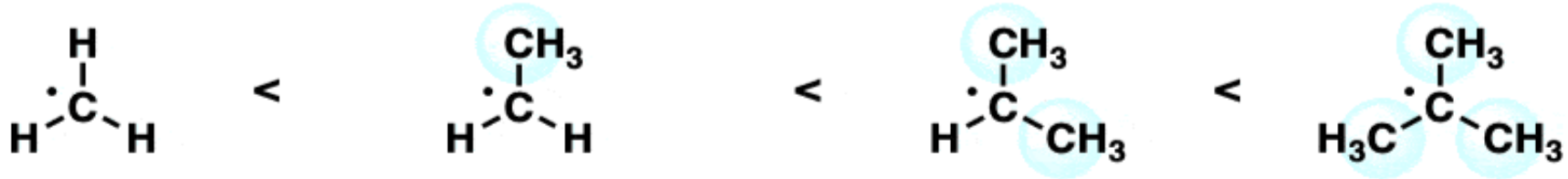


Rank the following carbocations in order of their **stability**



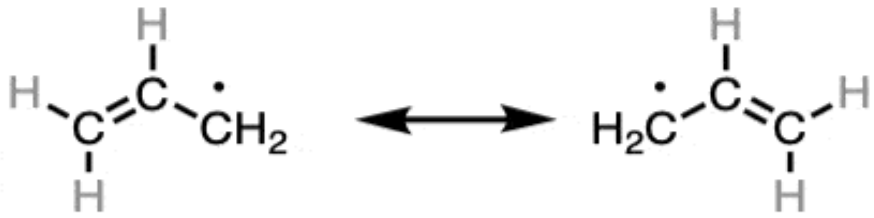
Summary: Factors Influencing Free-Radical Stability

- Free radicals are electron-deficient (have less than a full octet of electrons) and are therefore stabilized by neighboring electron donating groups such as **alkyl** groups

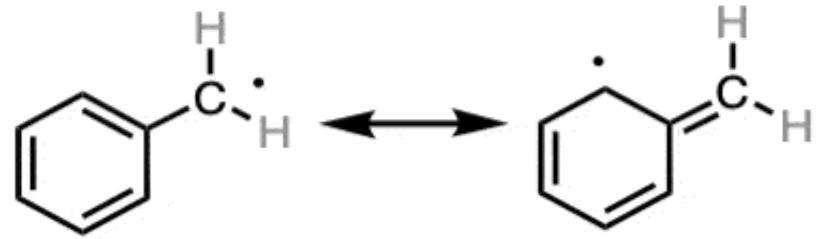


Methyl radical (Least stable) < Primary radical < Secondary radical < Tertiary radical (Most stable)

- Free radicals are also stabilized when they can be **delocalized** through resonance with an adjacent pi-bond



Allyl radical



Benzyl radical

- Bond dissociation energies (BDE's) are generally a good guide to free-radical stability. The lower the BDE, the more stable the resulting radical

Summary - Factors Affecting Carbocation Stability

Alkyl substitution

- The stability of carbocations **increases** as the number of adjacent alkyl groups **increases**

Number of carbons attached to carbocation:



0 1 2 3

"methyl" *"primary"* *"secondary"* *"tertiary"*

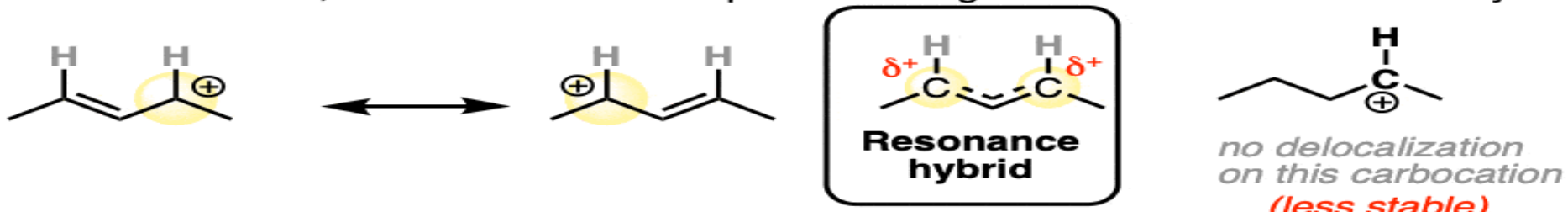
Least stable → **Most stable**

- This can be rationalized by **inductive effects** *(or alternatively through hyperconjugation)*

Resonance

- When a pi bond is adjacent to the carbocation, then the positive charge can be **spread out** over multiple carbons through **resonance**
- This **reduces** the overall charge density of the carbocation, making it more **stable**.

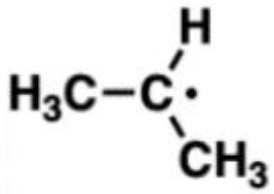
In the case below, each carbon bears a positive charge of +0.5 in the resonance hybrid

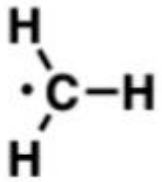


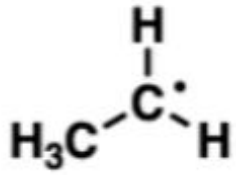
Other factors

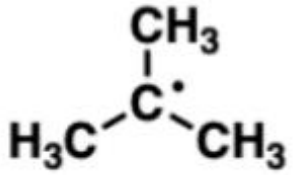
- Adjacent atoms with **lone pairs** greatly **stabilize** carbocations since the carbon can achieve a full octet of valence electrons
- Carbocation stability is decreased by adjacent **electron-withdrawing groups** that are unable to donate a lone pair of electrons (e.g. CF_3, NO_2)
- Carbocation stability **decreases** with increasing s-character (alkyl carbocations are more stable than alkenyl carbocations which are more stable than alkynyl carbocations)
- **Aromatic** carbocations are particularly **stable** and **anti-aromatic** carbocations are particularly **unstable**

Rank the following radicals from **most stable** to **least stable**.
(1 = most, 4 = least)



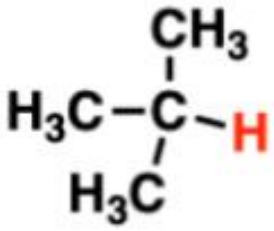




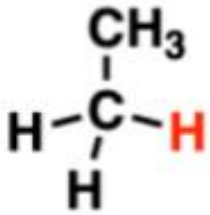


_____ _____ _____ _____

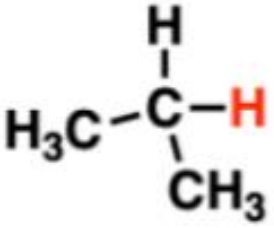
Which of the following C–H bonds requires the **most** amount of energy to break?



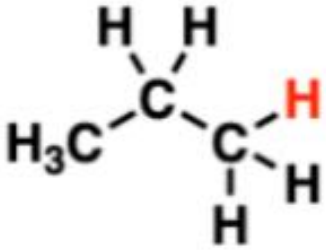
A)



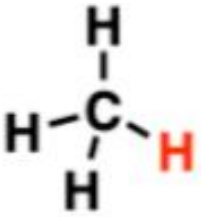
B)



C)

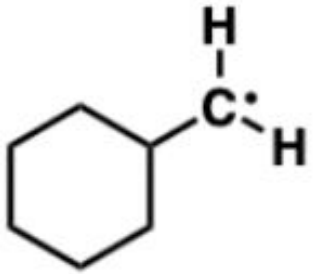


D)

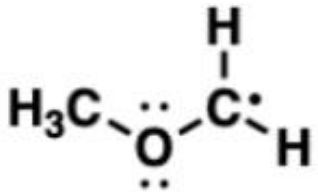


E)

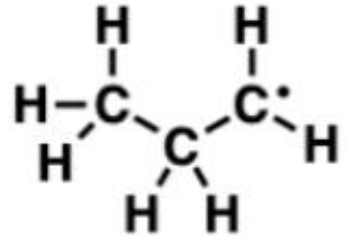
Of the following radicals, which is the **most stable**?



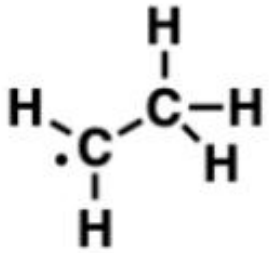
A)



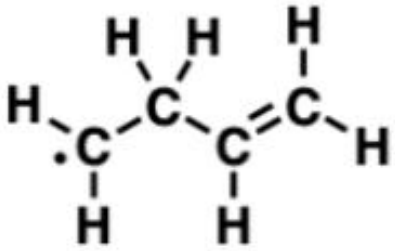
B)



C)

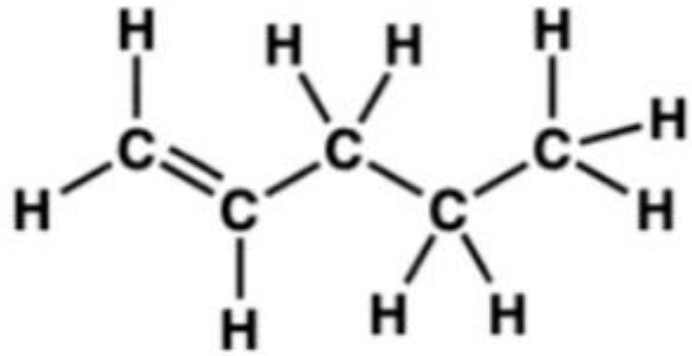


D)

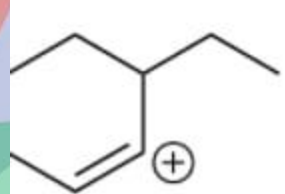


E)

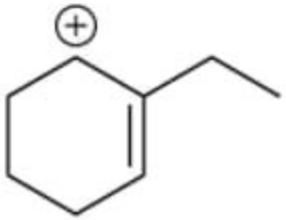
Circle the hydrogen(s) that will most likely be abstracted by a bromine radical.



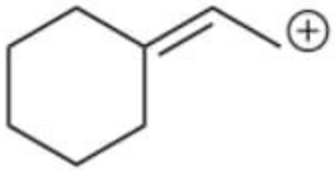
Which of the following is the most stable carbocation?



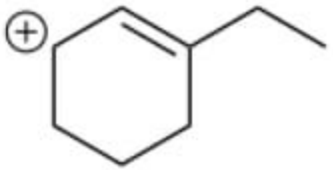
A



B



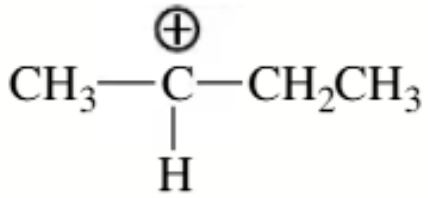
C

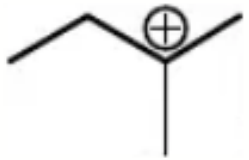


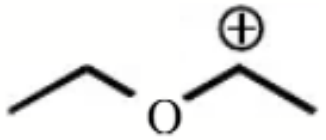
D

Practice problem

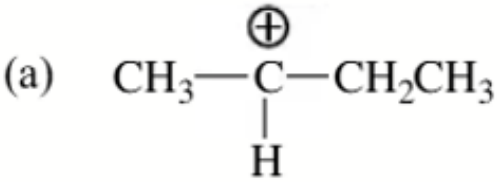
Which of the following carbocation is the most stable:

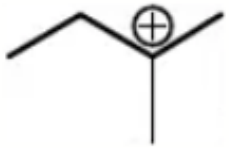
(a) 

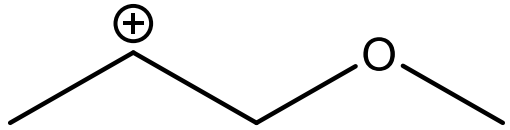
(b) 

(c) 

C is the most stable

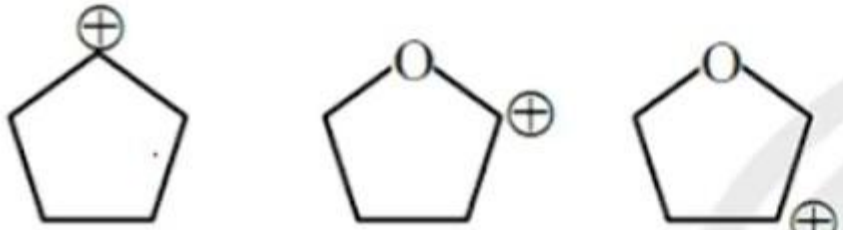
(a) 

(b) 

c- 

B is the most stable

Arrange the following carbocations in decreasing order of stability.



A B C

(A) A > C > B

(B) B > A > C

(C) C > B > A

(D) C > A > B