Disciplina: QFL0341

Estrutura e Propriedades de Compostos Orgânicos

17/setembro/2019

Ligações deslocalizadas em compostos orgânicos

Literatura

Bruice (4a ed, 2006)
p. 260: deslocalização eletrônica e ressonância – teoria do OM; reações de dienos,
p. 298: espectroscopia na região do UV-VIS;

McMurry (5a ed, 2000)
p. 522: Conjugated dienes and UV spectroscopy;

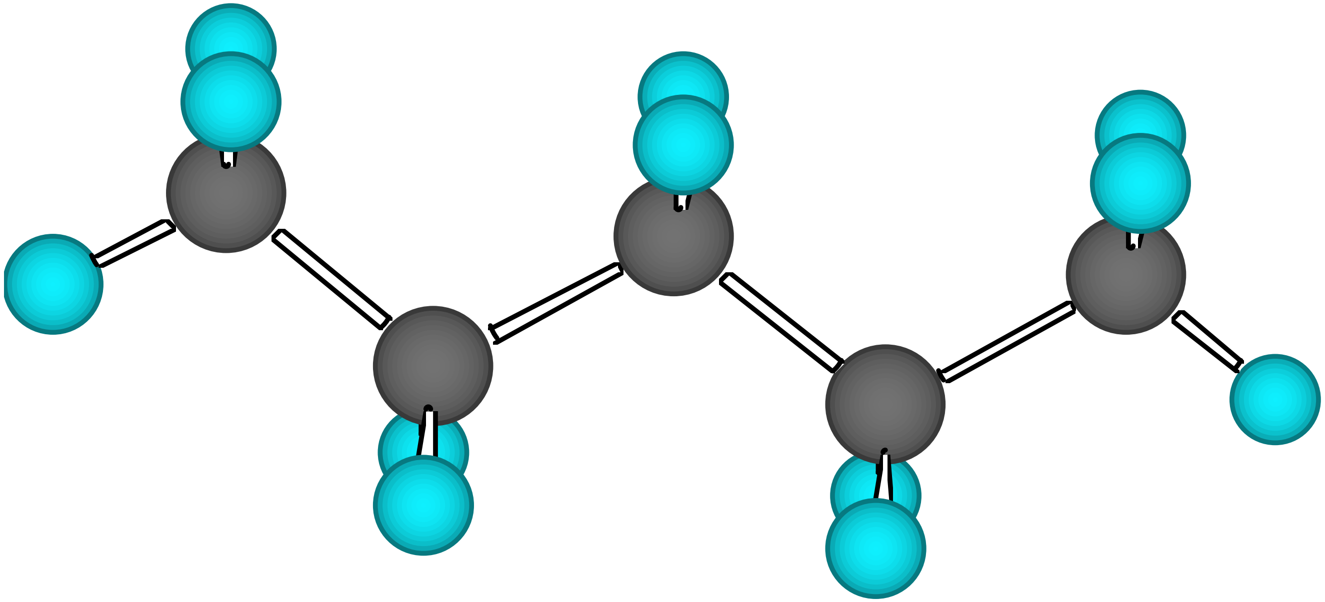
Solomons (8a ed, 2005)
p. 549: Sistemas insaturados conjugados (UV e Diels-Alder)

Vollhardt (6a ed, 2011)
p. 28: Orbitais moleculares e ligações covalentes;
p. 609: Sistemas p deslocalizados (exceto benzeno e reações eletrocíclicas);

Clayden (2001)
p. 95: Molecular orbitals;
p. 151: Delocalization and conjugation;

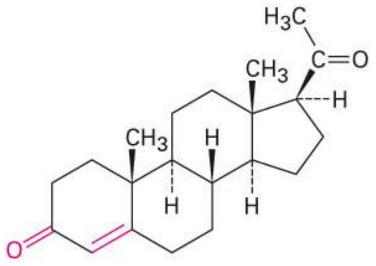
Moléculas apolares

Hidrocarbonetos (alcanos)



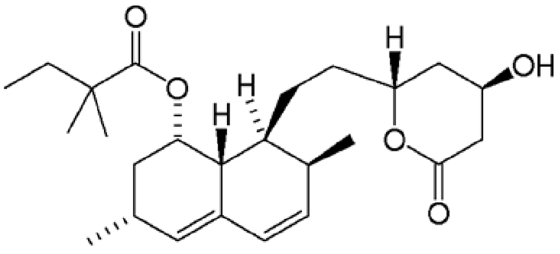
n-pentano

Conjugated compounds: common in nature

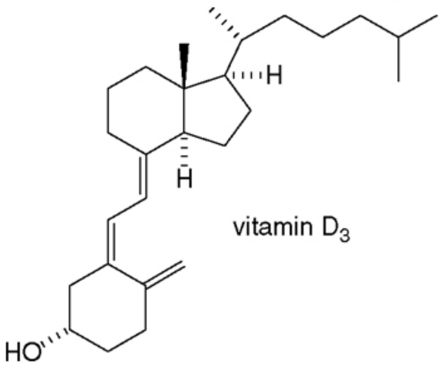


Progesterone, a conjugated enone

**Benzene,
a cyclic conjugated molecule**

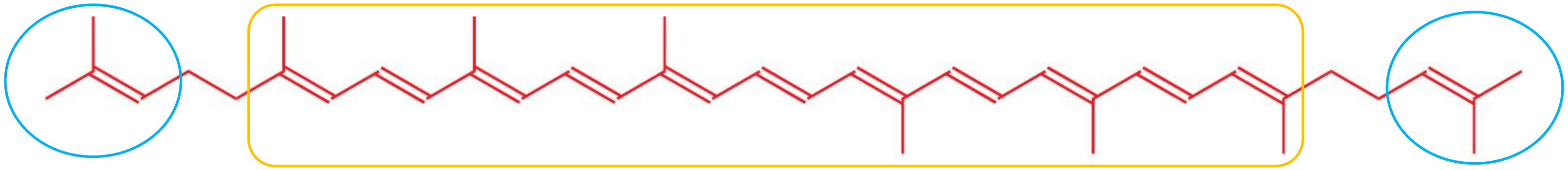


simvastatin
(Zocor)



vitamin D_3

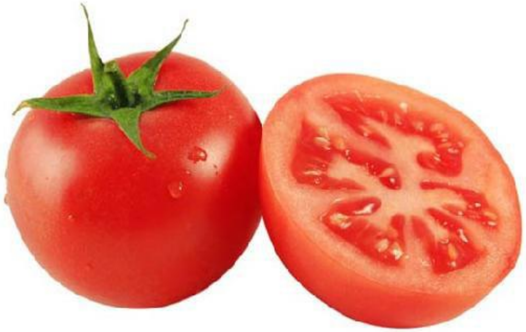
Coloured compounds are conjugated compounds



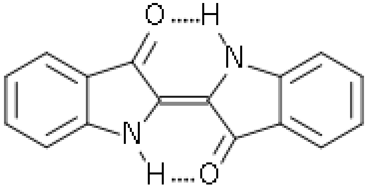
lycopene, the red pigment in tomatoes, rose hips, and other berries

Non conjugated

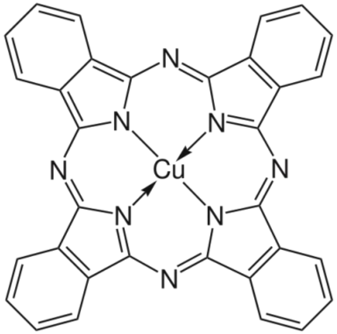
Non conjugated



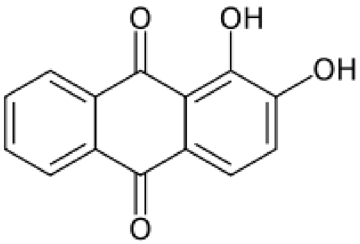
Natural and Synthetic Pigments (highly conjugated compounds)



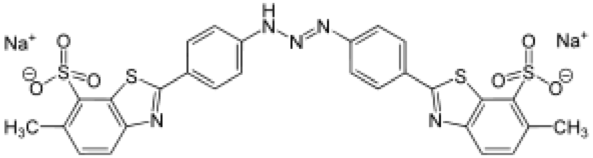
Indigofera tinctoria, (*Indigofera sumatrana*)



Phthalo Blue

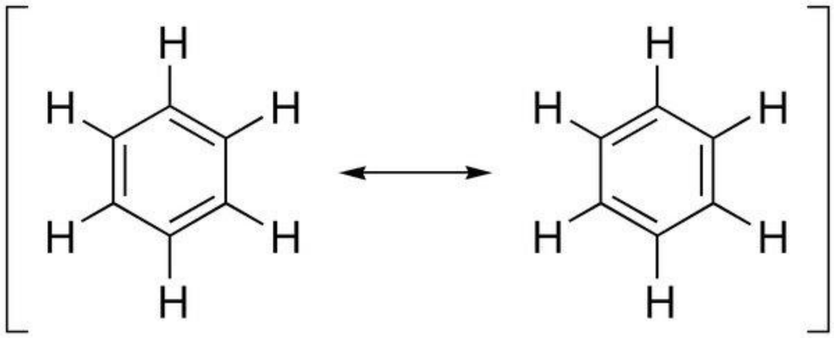


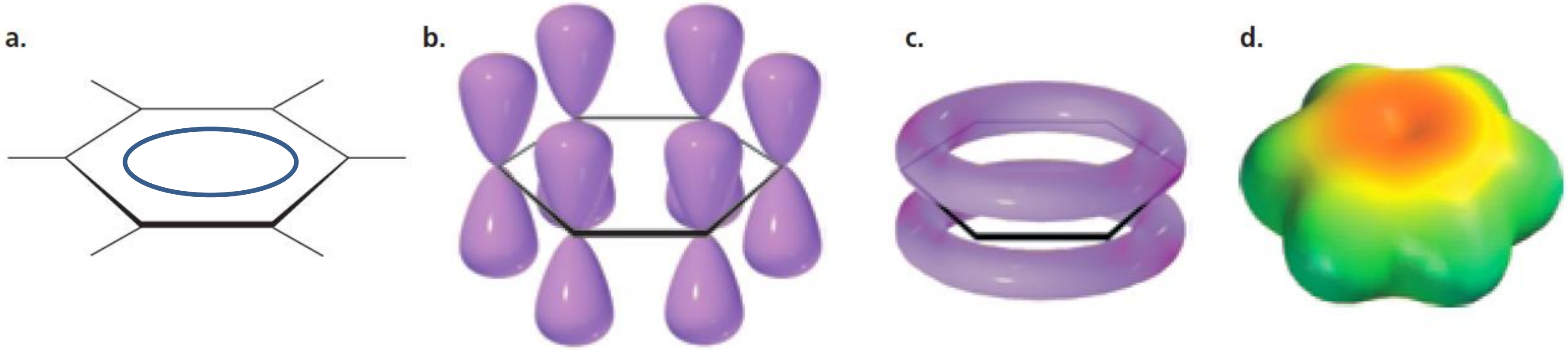
Rubia tinctorum



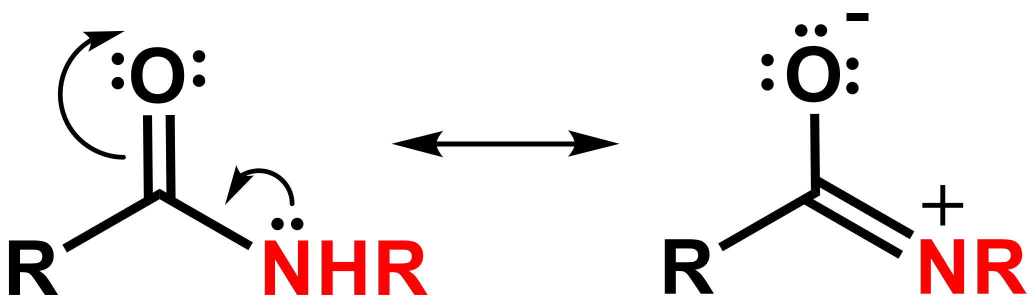
Structure of Titan yellow

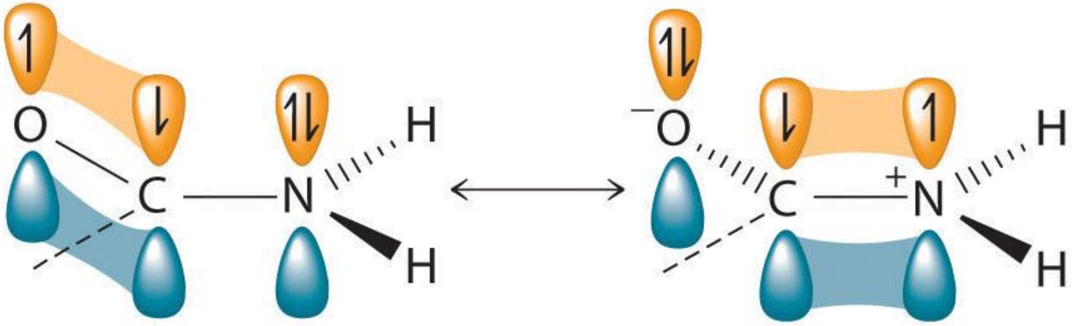
Conjugated organic compounds and delocalized bonding





Conjugation in carbonyl amides (and IR bands)





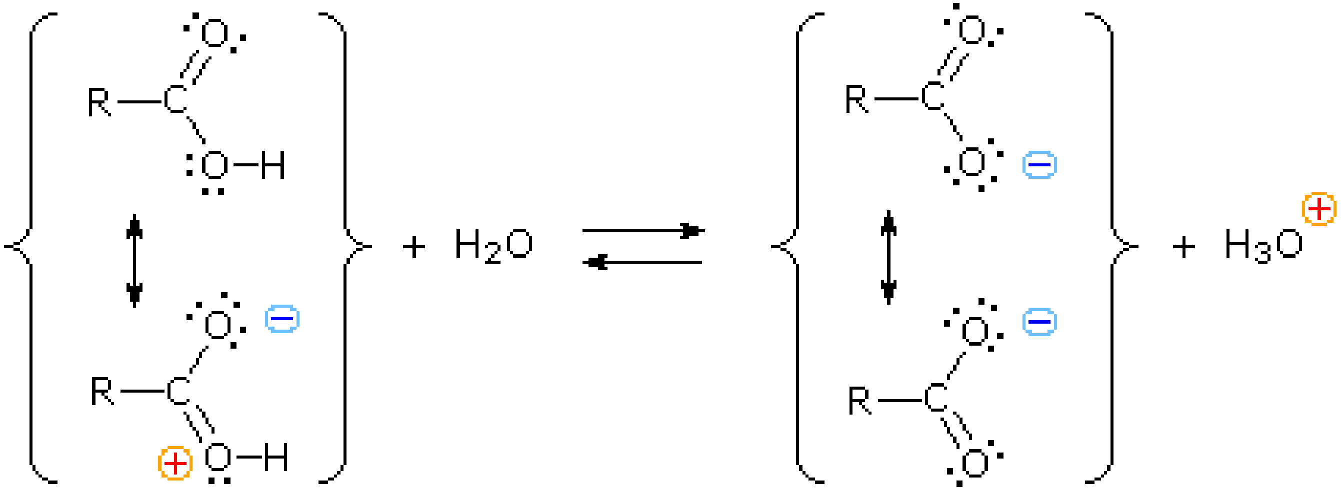
Two bands at
1660 (I)-1630(II) cm^{-1}

Amide I band:
v **C=O**
stretching,

Amide II band δ
N-H bending in
plane

The conjugation of the lone pair of electron weakens the force constant of carbonyl group!

RCO_2H versus RCO_2^-



small
resonance stabilization

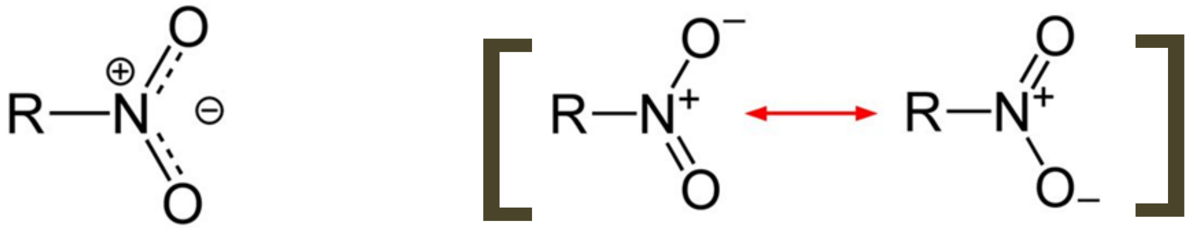
large
resonance stabilization

Charge separation

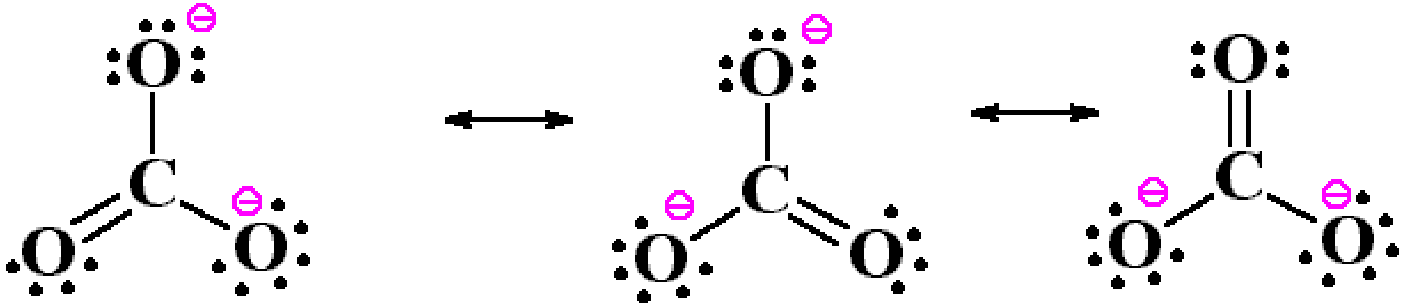
Charge delocalization

Delocalized bonding in nitrocompounds

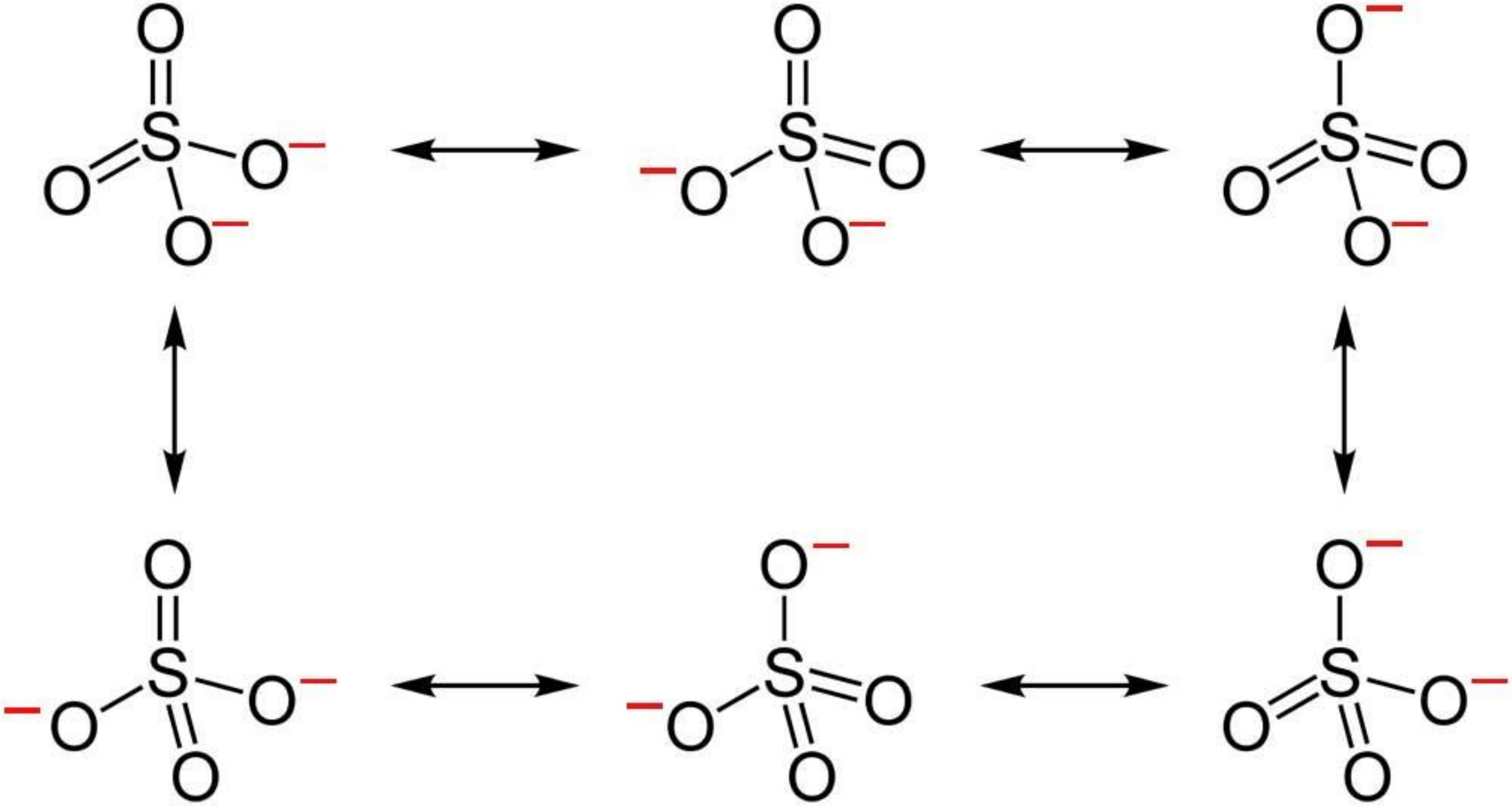
$R-NO_2$



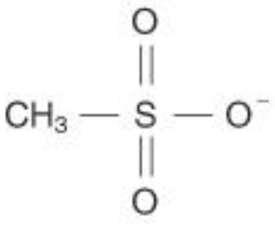
Delocalized bonding in carbonate



Delocalized bonding in sulfates



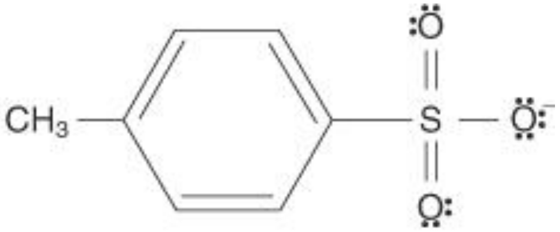
Delocalized bonding in sulfonates



methyl sulfonate

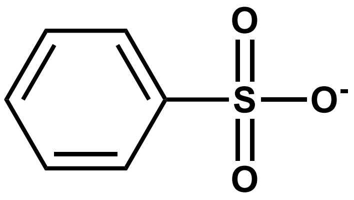
(Mesylate

Mes)



tosylate ion

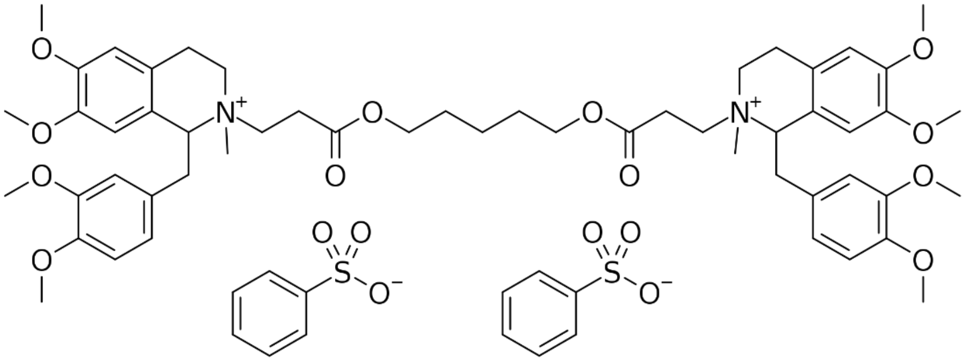
(Tos)



besylate ion

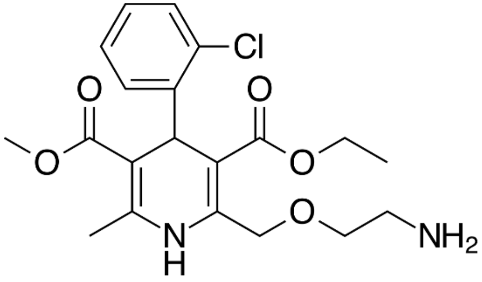
(Bz)

Íons benzenosulfonila

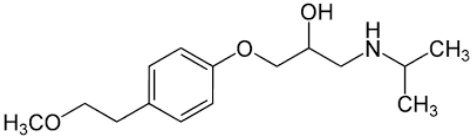


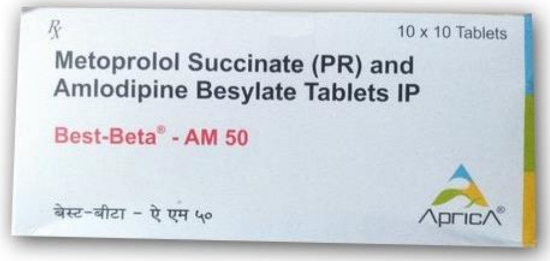
Besilato de atracúrio

É um fármaco utilizado como bloqueador neuromuscular. Em cirurgias utiliza-se como complemento de anestesia e facilitador da intubação endotraqueal, pois promove o ralaxamento muscular durante a cirurgia ou ventilação mecânica



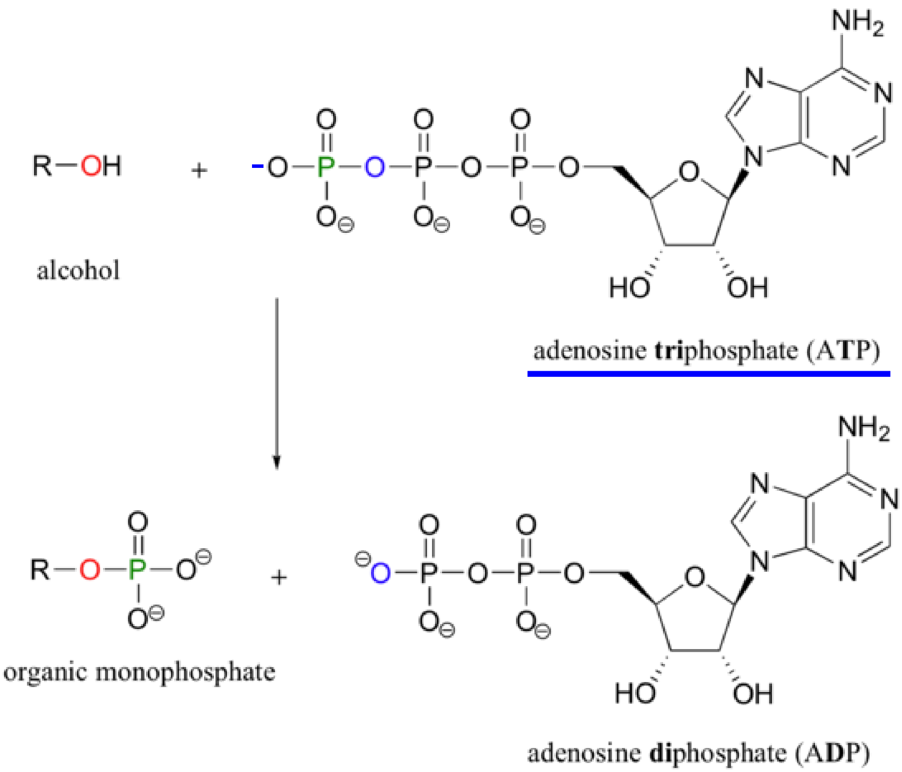
Amlodipina ou anlodipino, é uma molécula do grupo dos bloqueadores dos canais de cálcio, classe das dihidropiridinas.
É usado como vasodilatador coronário e hipotensor.

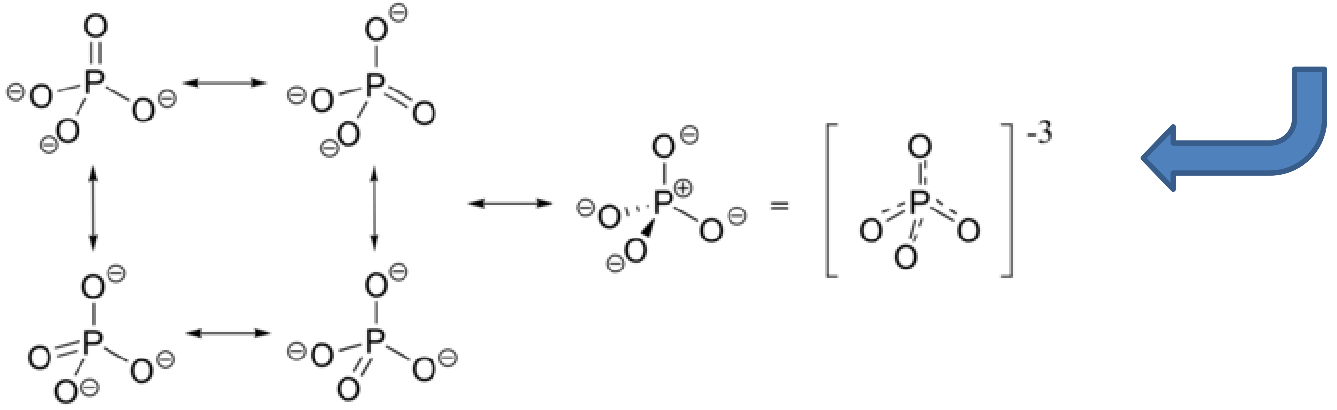


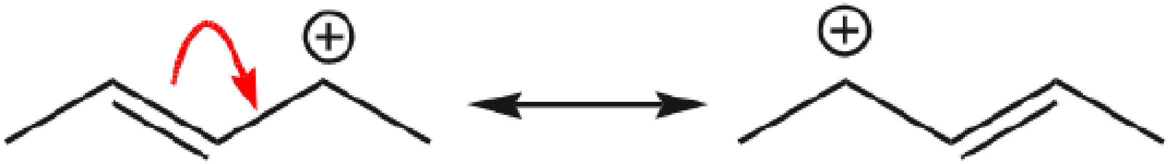


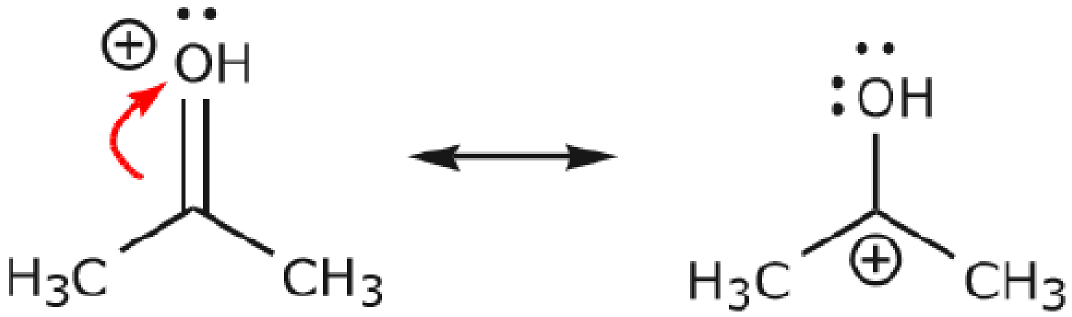
Metoprolol (um betabloqueador) é indicado para hipertensão arterial; insuficiência cardíaca; tratamento após infarto do miocárdio; angina; palpitações e profilaxia da enxaqueca.

Delocalized bonding in phosphates

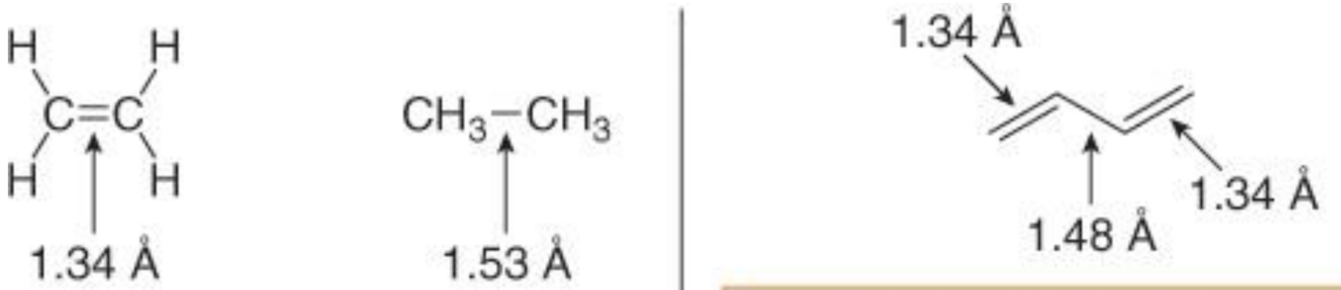




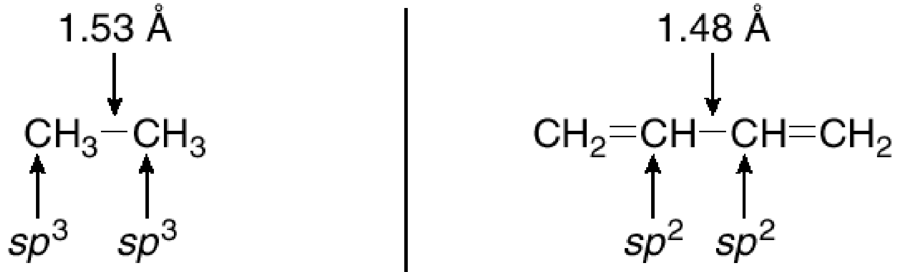



OH
H3C
CH3
OH
H3C
CH3

The carbon—carbon σ and π bond lengths in 1,3-butadiene



The C–C σ bond is **shorter** than the C–C σ bond in ethane.



25% *s*-character

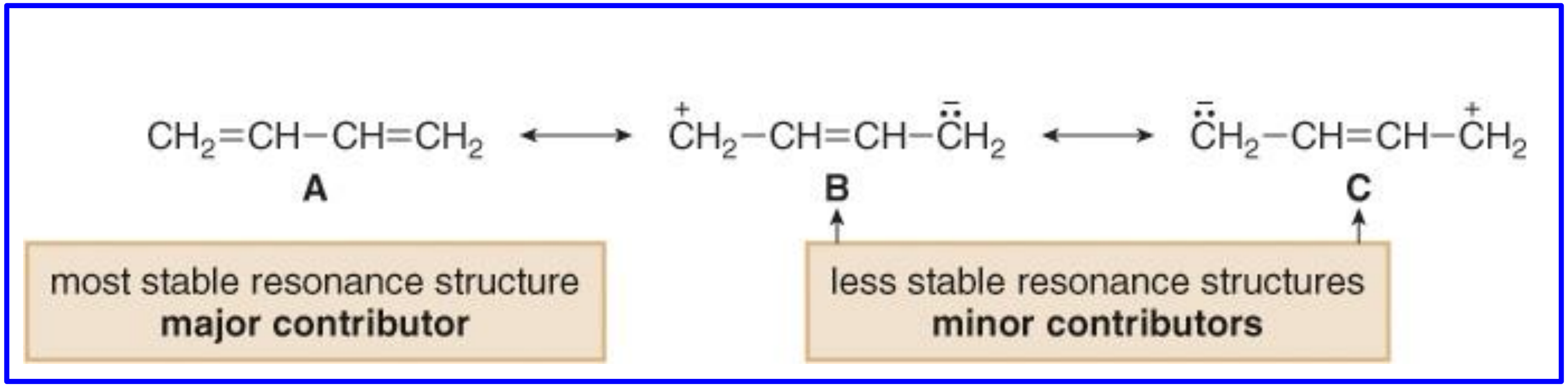
33% *s*-character

lower percent *s*-character—
longer bond

higher percent *s*-character—
shorter bond

The Carbon—Carbon σ Bond Length in 1,3-Butadiene

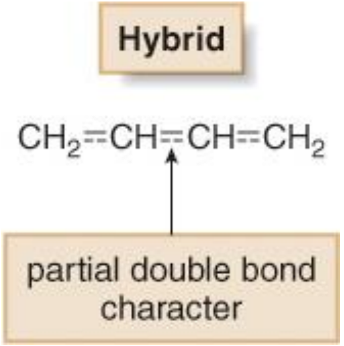
A resonance argument can also be used to explain the shorter C—C σ bond length in 1,3-butadiene.



$$\underset{\textbf{A}}{CH_2{=}CH{-}CH{=}CH_2} \longleftrightarrow \underset{\textbf{B}}{\overset{+}{C}H_2{-}CH{=}CH{-}\overset{-}{\ddot{C}}H_2} \longleftrightarrow \underset{\textbf{C}}{\overset{-}{\ddot{C}}H_2{-}CH{=}CH{-}\overset{+}{C}H_2}$$

most stable resonance structure
major contributor

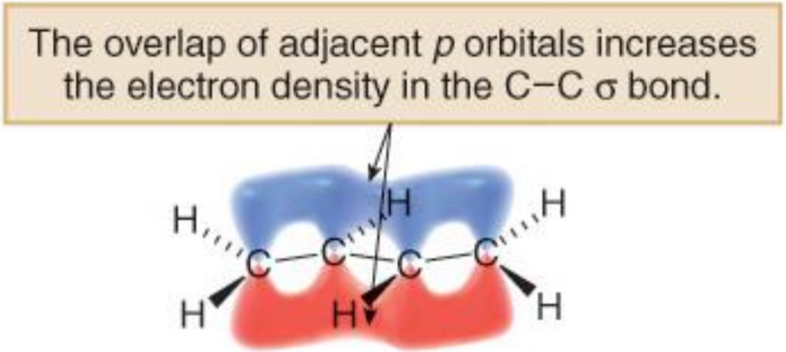
less stable resonance structures
minor contributors



Hybrid

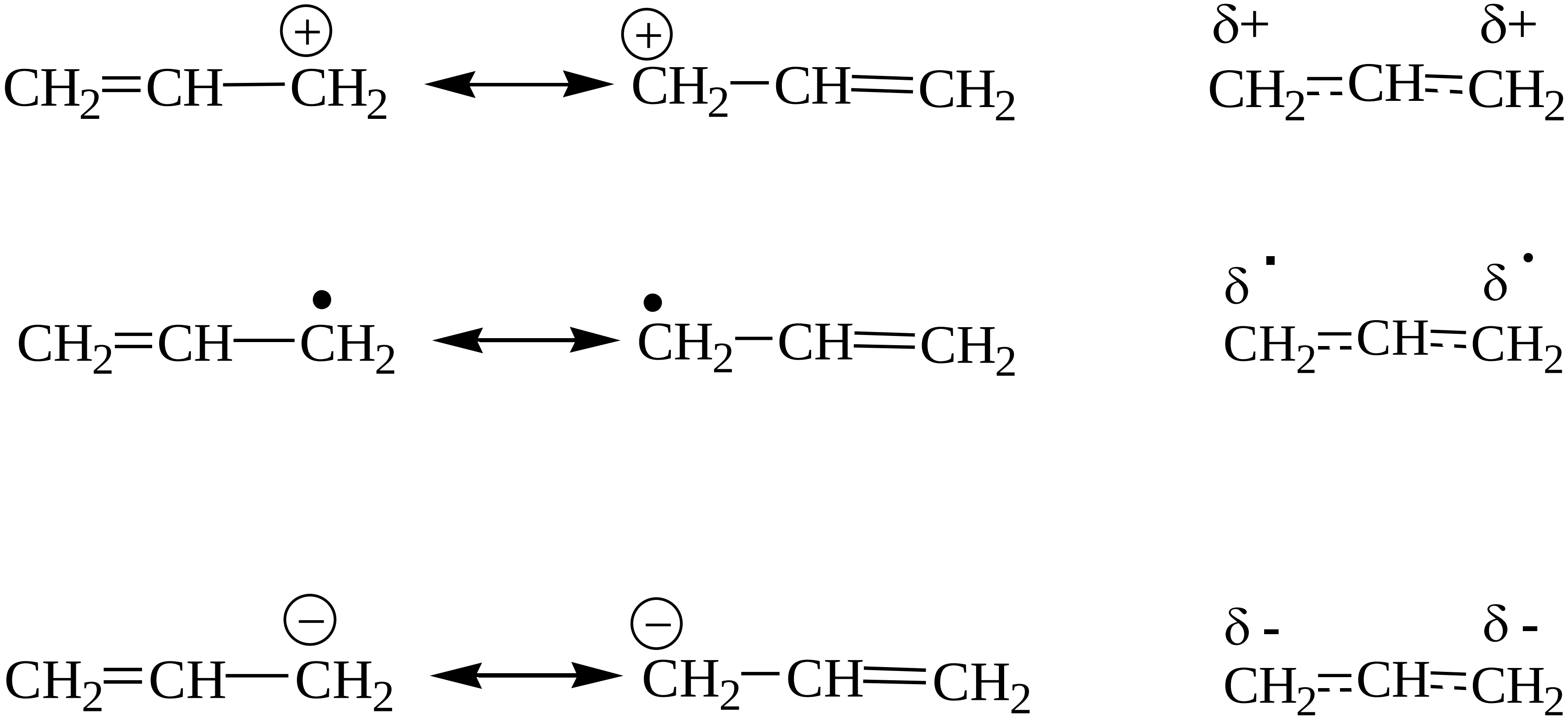
$CH_2{\overset{--}{=}}CH{\overset{--}{=}}CH{\overset{--}{=}}CH_2$

partial double bond character



The overlap of adjacent *p* orbitals increases the electron density in the C–C σ bond.

Estruturas deslocalizadas
do cátion, do radical e do ânion alílico



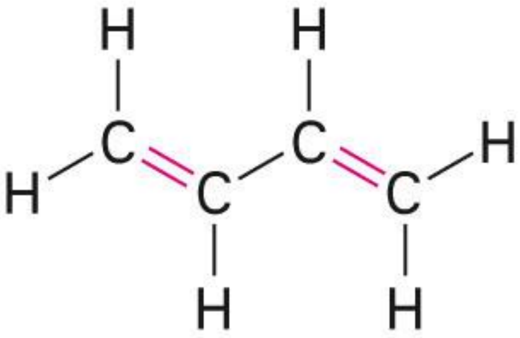
$$CH_2{=}CH{-}\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2{-}CH{=}CH_2 \qquad \overset{\delta+}{CH_2}\overset{-}{--}CH\overset{-}{--}\overset{\delta+}{CH_2}$$

$$CH_2{=}CH{-}\overset{\bullet}{C}H_2 \longleftrightarrow \overset{\bullet}{C}H_2{-}CH{=}CH_2 \qquad \overset{\delta\cdot}{CH_2}\overset{-}{--}CH\overset{-}{--}\overset{\delta\cdot}{CH_2}$$

$$CH_2{=}CH{-}\overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2{-}CH{=}CH_2 \qquad \overset{\delta-}{CH_2}\overset{-}{--}CH\overset{-}{--}\overset{\delta-}{CH_2}$$

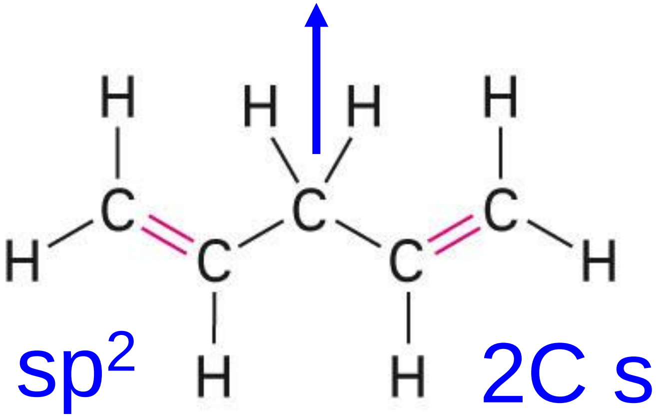
Dienos conjugados e não conjugados

4C sp^2



1,3-Butadiene
(conjugated; alternating double and single bonds)

sp^3



2C sp^2 2C sp^2

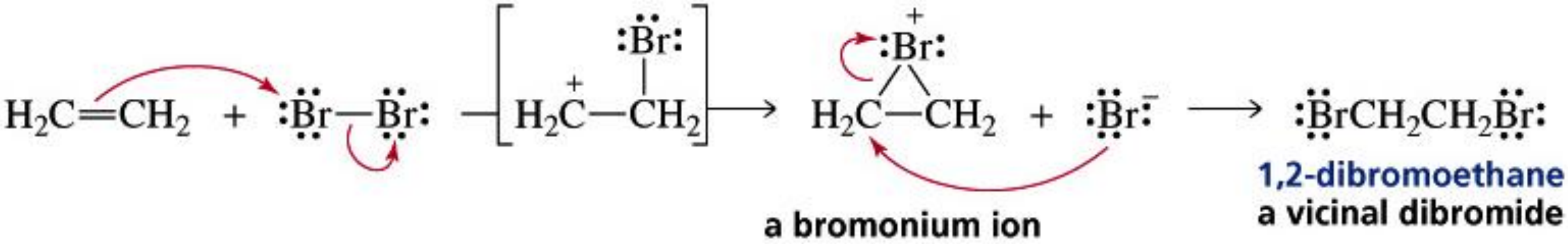
1,4-Pentadiene
(nonconjugated; nonalternating double and single bonds)

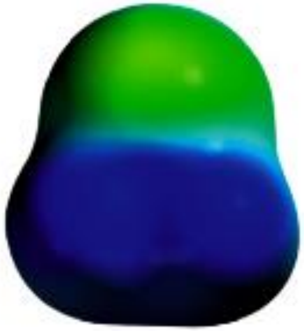
Que tipos de reações

sofrem

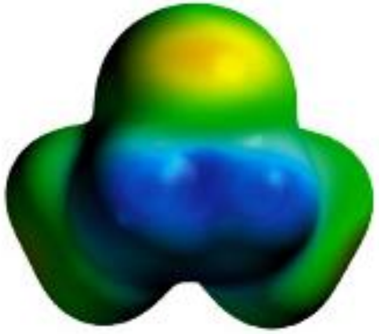
os alcenos, dienos e alcinos?

Adição de Halogênios à Alquenos



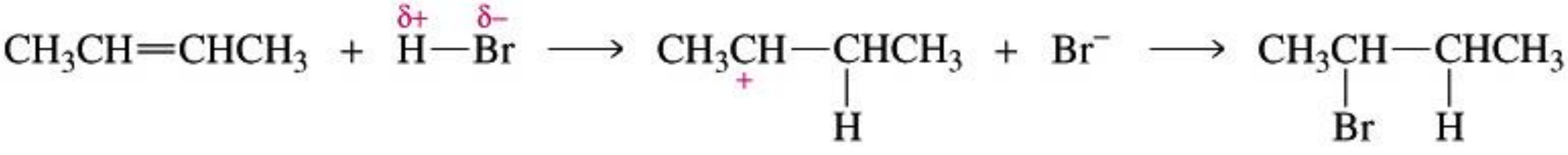


bromonium ion
of ethene



bromonium ion
of *cis*-2-butene

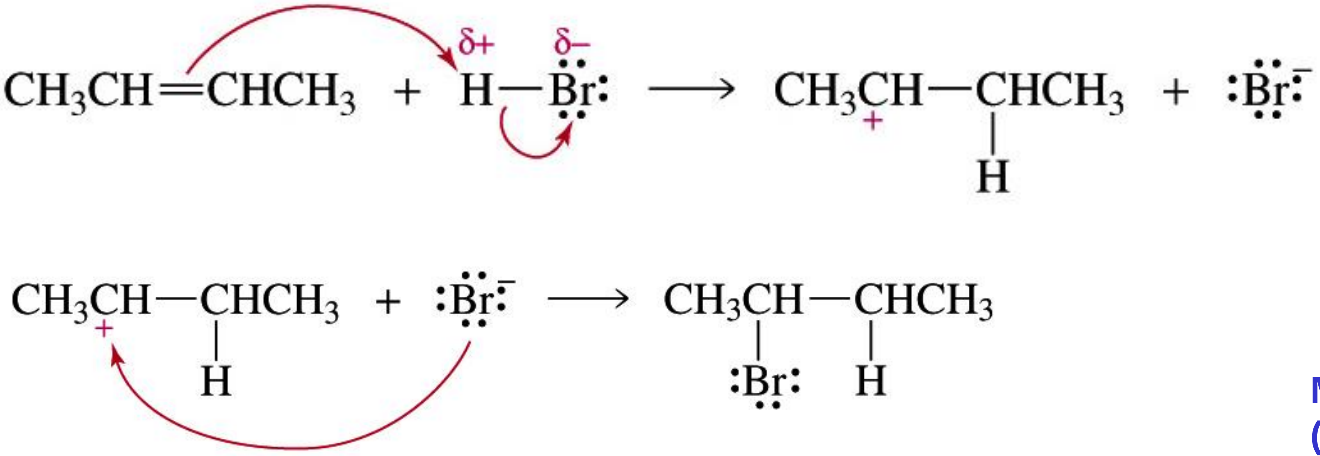
Adição Eletrofílica de HBr a Alquenos



$$CH_3CH{=}CHCH_3 + \overset{\delta+}{H}{-}\overset{\delta-}{Br} \longrightarrow CH_3\underset{+}{C}H{-}\underset{\substack{|\\ H}}{C}HCH_3 + Br^- \longrightarrow CH_3\underset{\substack{|\\ Br}}{C}H{-}\underset{\substack{|\\ H}}{C}HCH_3$$

a carbocation

2-bromobutane
an alkyl halide



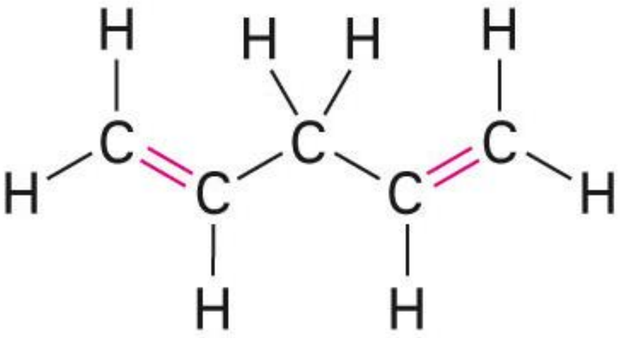
$$CH_3CH{=}CHCH_3 + \overset{\delta+}{H}{-}\overset{\delta-}{\ddot{B}r}: \longrightarrow CH_3\underset{+}{C}H{-}\underset{\substack{|\\ H}}{C}HCH_3 + :\ddot{B}r:^-$$

$$CH_3\underset{+}{C}H{-}\underset{\substack{|\\ H}}{C}HCH_3 + :\ddot{B}r:^- \longrightarrow CH_3\underset{\substack{|\\ :\ddot{B}r:}}{C}H{-}\underset{\substack{|\\ H}}{C}HCH_3$$

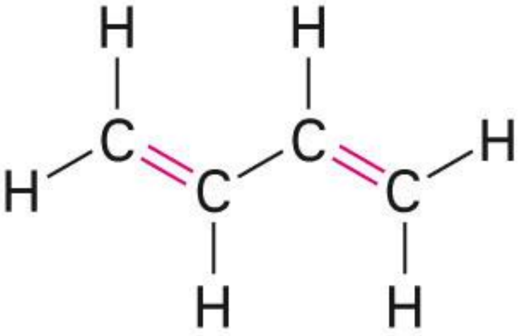
Movimento de um elétron
(para reações radicalares e em
Espectrometria de massas)

Movimento de um par de elétrons
(para reações iônicas)

Electrophilic additions to conjugated and nonconjugated and conjugated dienes



1,4-Pentadiene



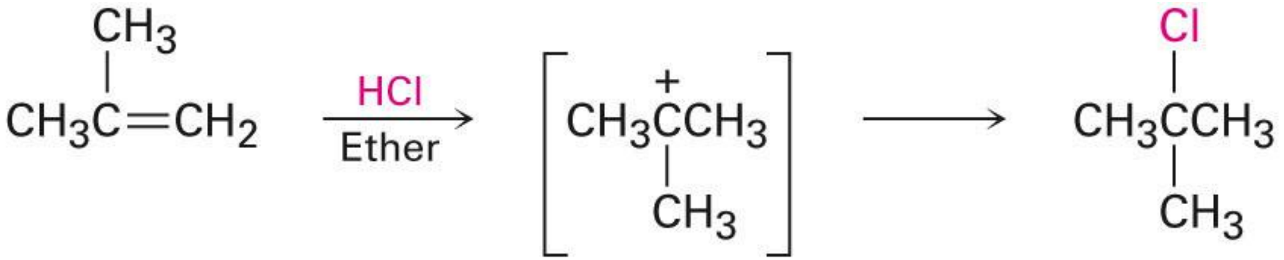
1,3-Butadiene

HCl

???

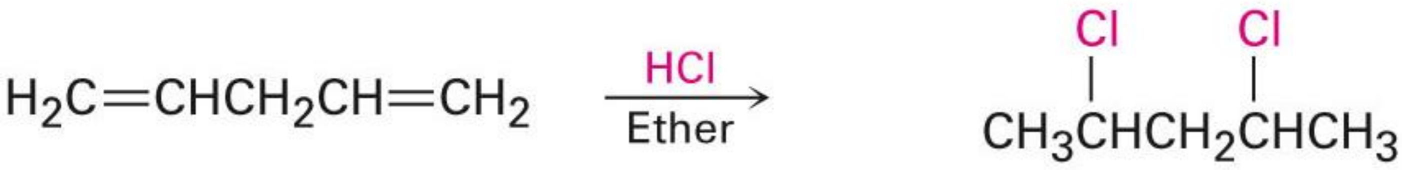
Electrophilic additions to alkenes

- Addition of electrophile to C=C (isolated double bond)
  - Markovnikov regiochemistry *via* more stable carbocation



2-Methylpropene **Tertiary carbocation** **2-Chloro-2-methylpropane**

Electrophilic additions to alkenes



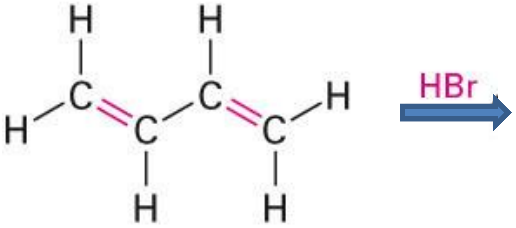
$$H_2C{=}CHCH_2CH{=}CH_2 \xrightarrow[\text{Ether}]{HCl} CH_3\overset{Cl}{\overset{|}{C}}HCH_2\overset{Cl}{\overset{|}{C}}HCH_3$$

1,4-Pentadiene (nonconjugated)

2,4-Dichloropentane

Carbocations from Conjugated Dienes

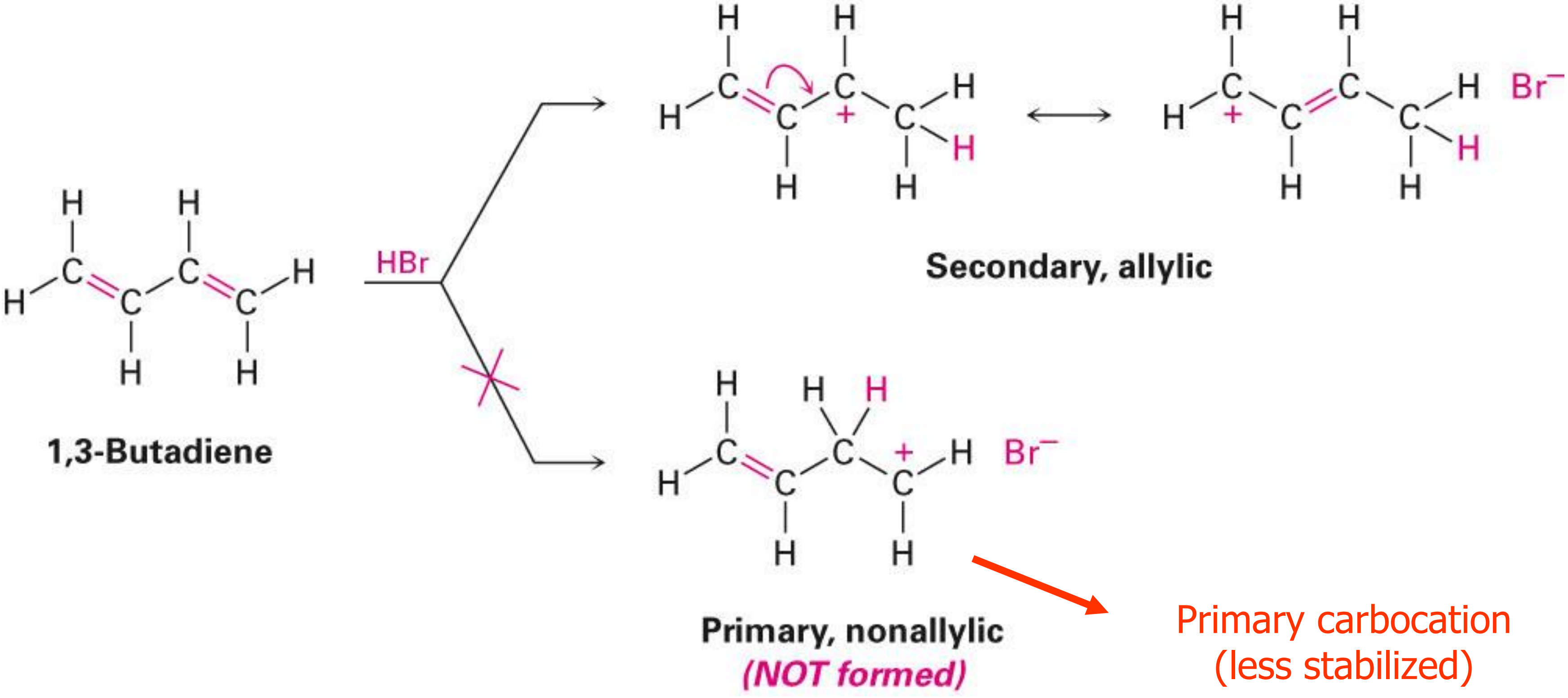
- Addition of H^+ leads to delocalized secondary allylic carbocation



1,3-Butadiene

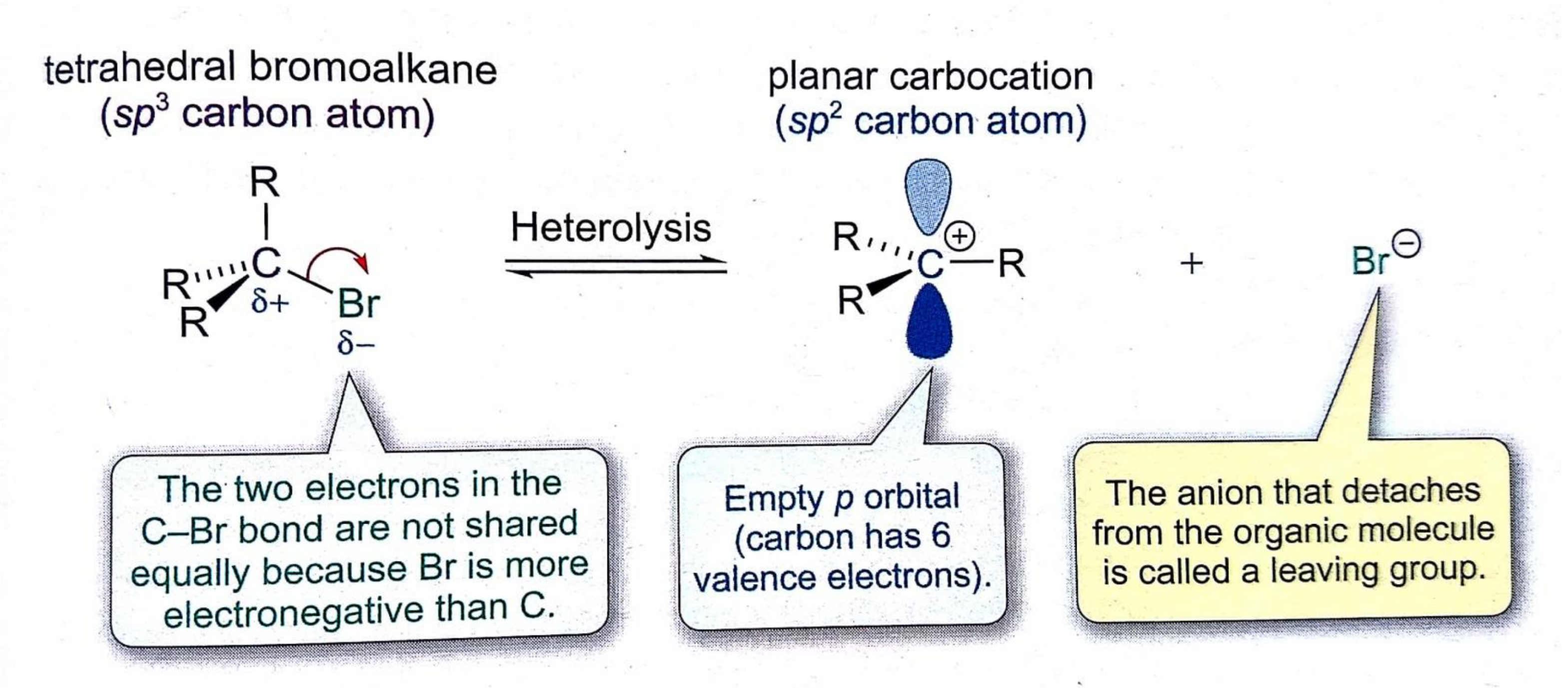
Carbocations from Conjugated Dienes

- Addition of H^+ leads to delocalized secondary allylic carbocation



Primary carbocation
(less stabilized)

Just to remember (Carbocations in saturated compounds can be produced by other ways)



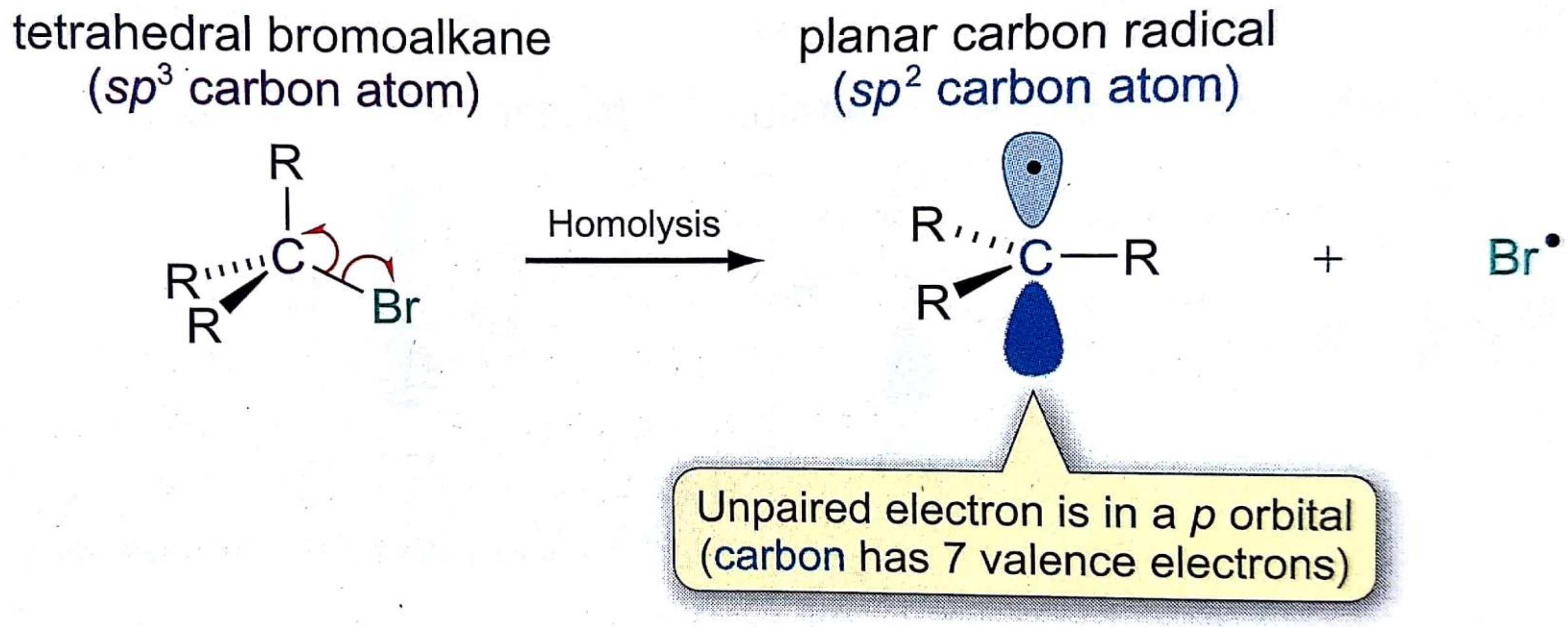
The two electrons in the C–Br bond are not shared equally because Br is more electronegative than C.

Empty *p* orbital (carbon has 6 valence electrons).

The anion that detaches from the organic molecule is called a leaving group.

Formation of other reactive species

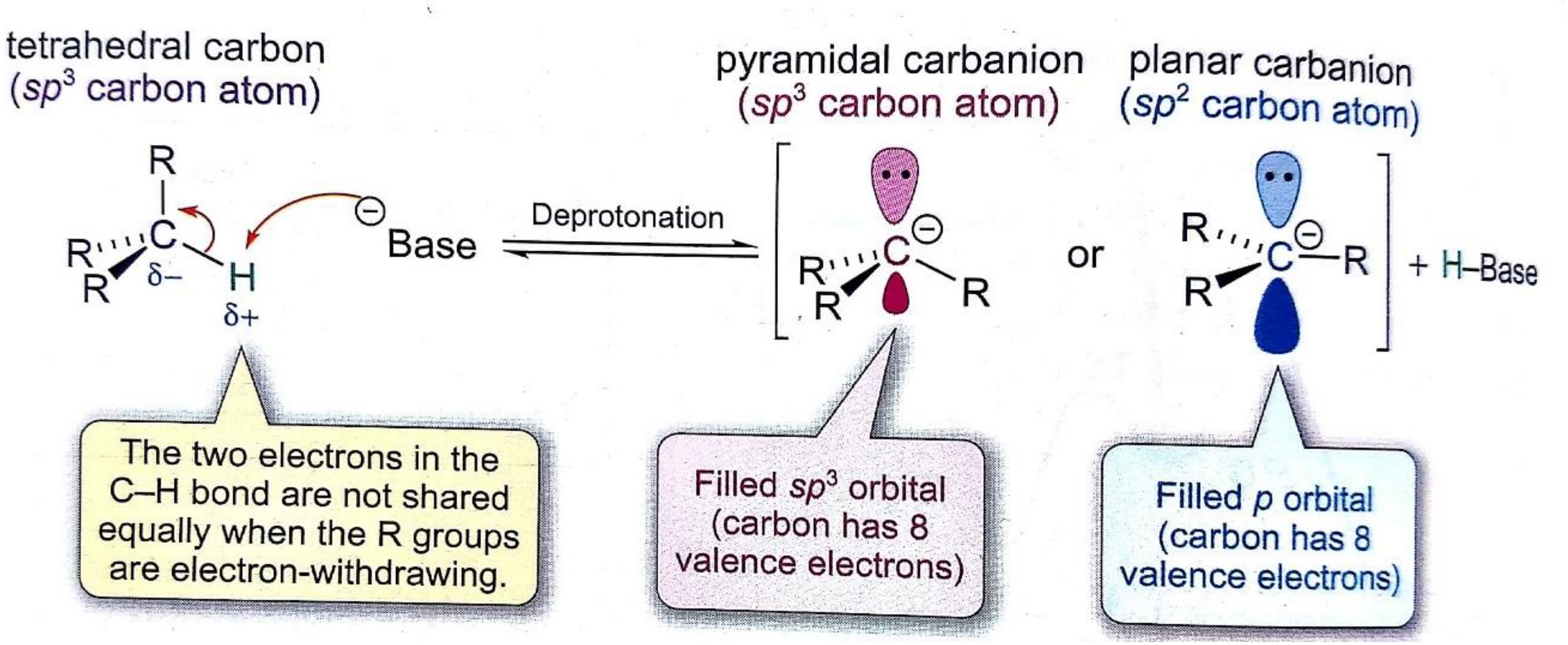
Formation of radicals by direct homolysis of C-X



Or by abstraction of radicalar hydrogen of a hydrocarbon by other radicals ($RO^{\bullet}$)

Formation of other reactive species

Formation of carbanions by deprotonation



The two electrons in the C–H bond are not shared equally when the R groups are electron-withdrawing.

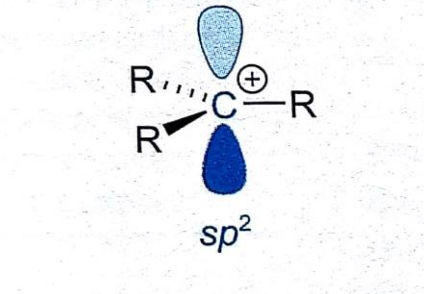
Filled sp^3 orbital (carbon has 8 valence electrons)

Filled *p* orbital (carbon has 8 valence electrons)

Geometries of reactive species

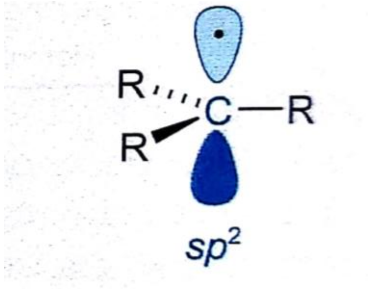
planar

Empty orbital p



carbocation

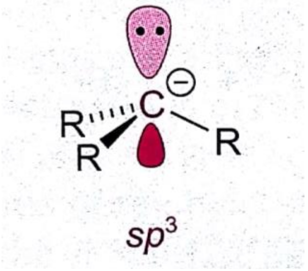
1 electron

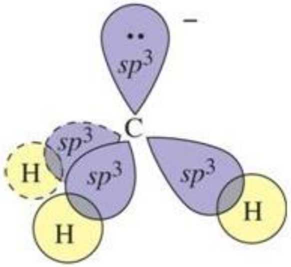


radical

pyramidal

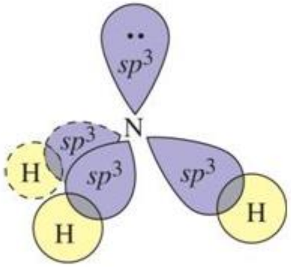
2 electrons





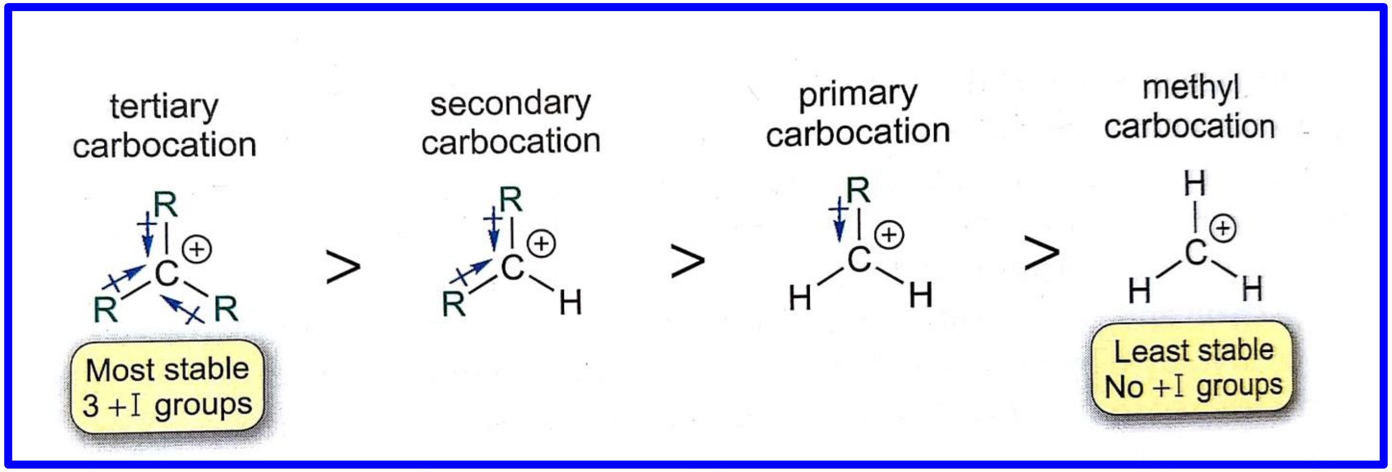
methyl anion

Similar to ammonia



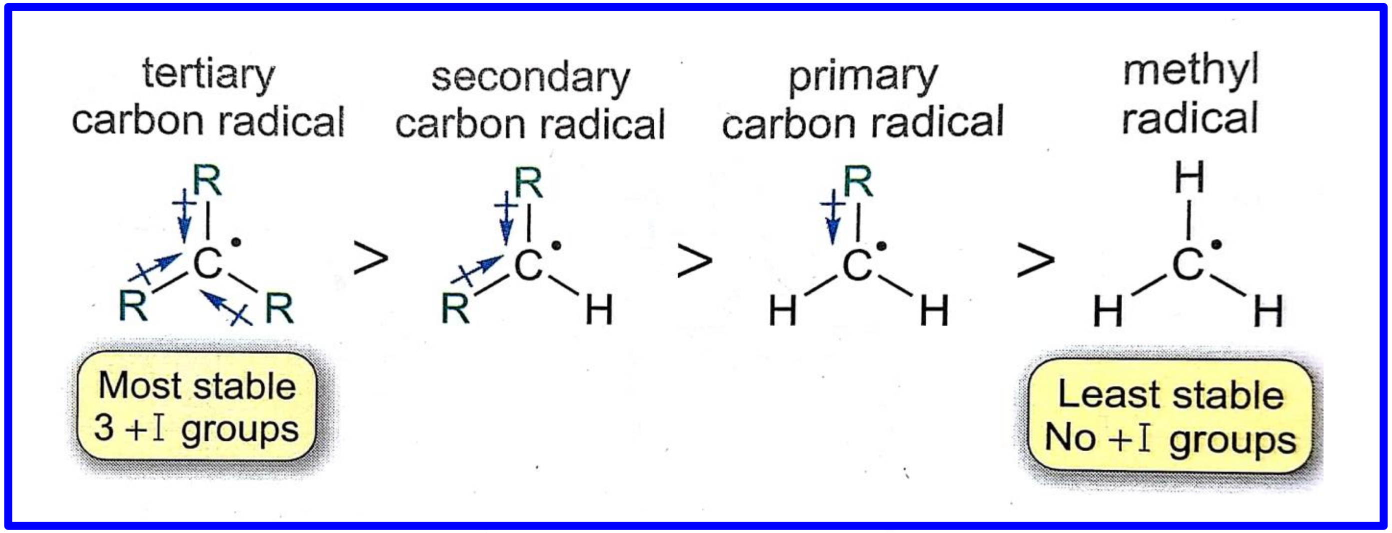
ammonia

The relative stability of carbocations and radicals are exactly the same



more stabilized

less stabilized



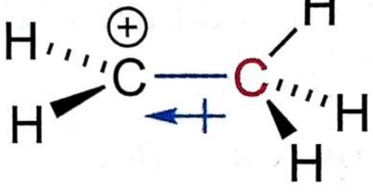
Causes for stabilization of carbocations :

1) **+ I** (inductive effects)
2) hyperconjugation

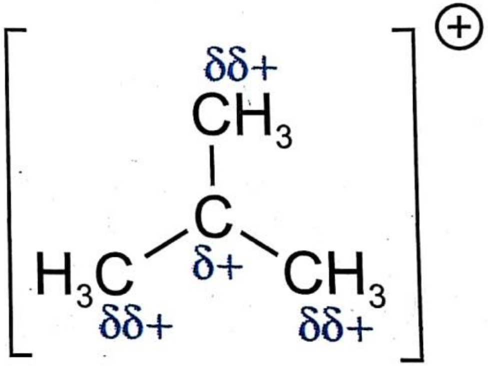
Stabilization of carbocations by **+ I** (inductive effects)

+I inductive effect

Electrons attracted from the C–C σ bond

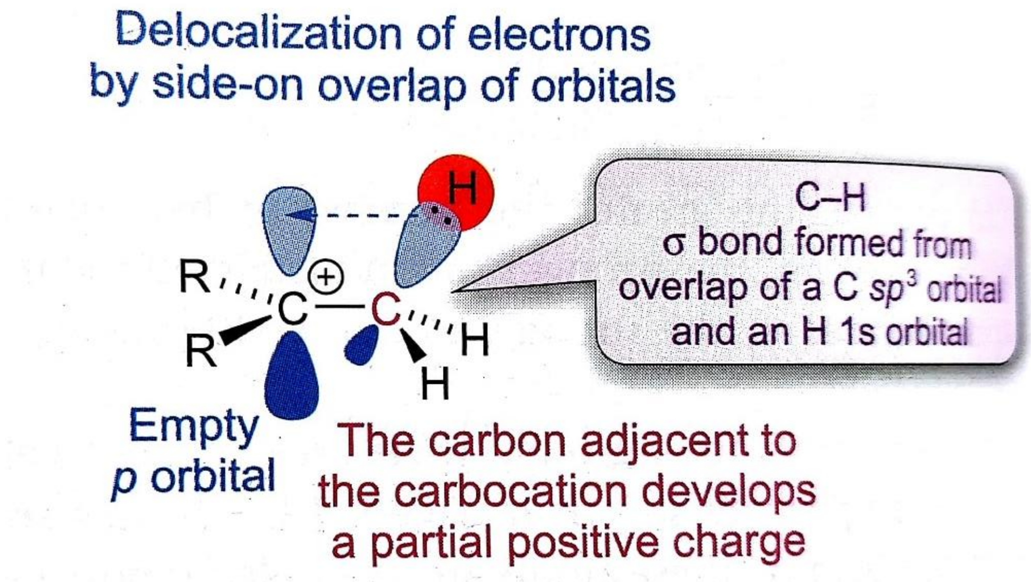


The carbon adjacent to the carbocation develops a partial positive charge

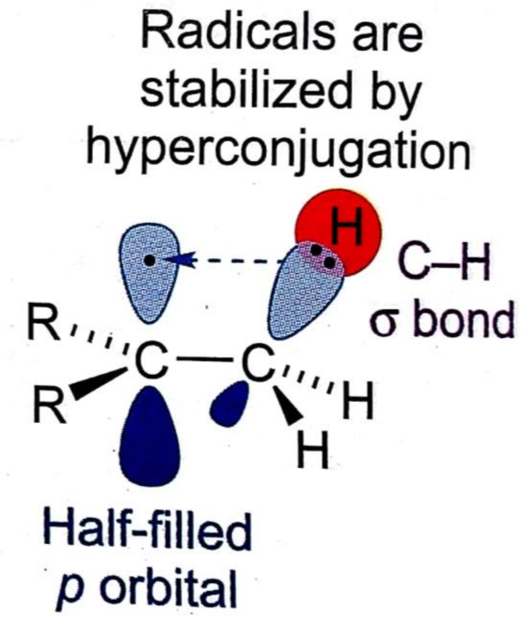


Delocalization of the positive charge in the *tert*-butyl cation

Stabilization of carbocations and radicals by **hyperconjugation**

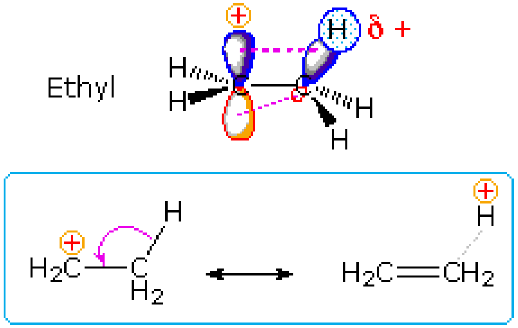


carbocations

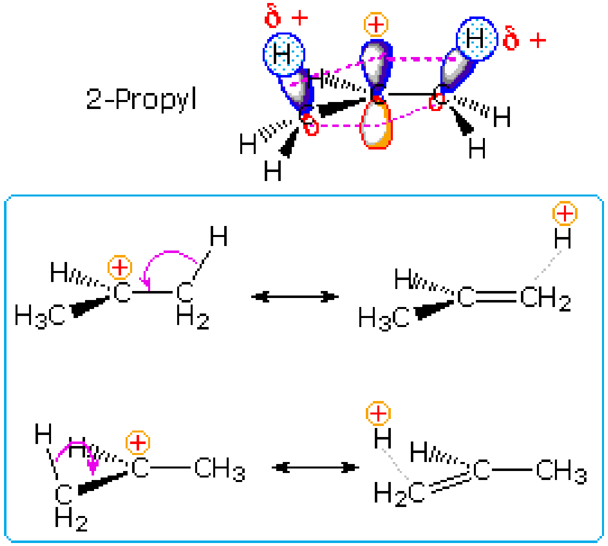


radicals

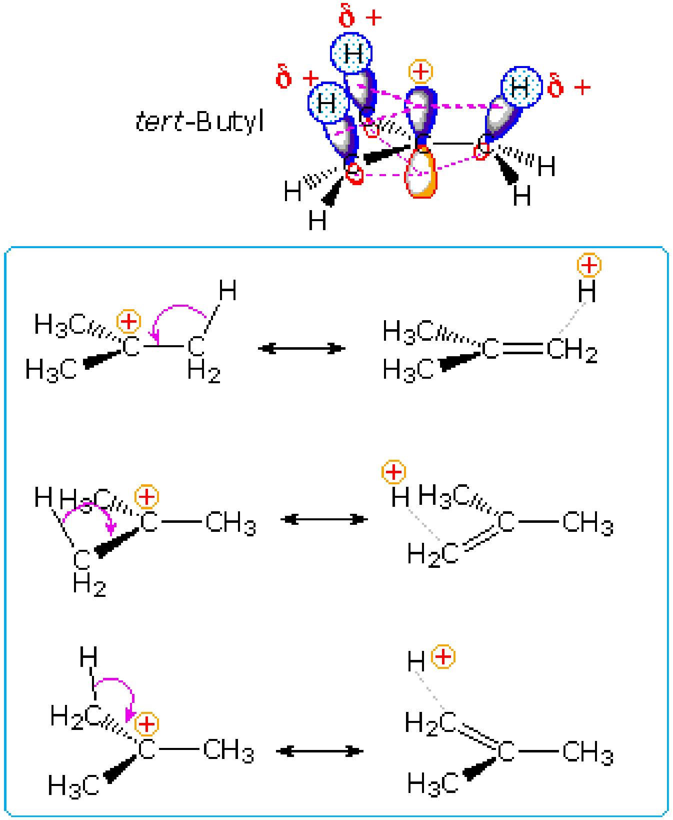
Stabilization of carbocations by **hyperconjugation**



one alkyl group



two alkyl groups



three alkyl groups

Causes for stabilization of carbocations :

1) **+ I** (inductive effects) (but not **–I**)

2) Hyperconjugation

3) Mesomeric effect (+M) (but not **–M**)
(or resonance)

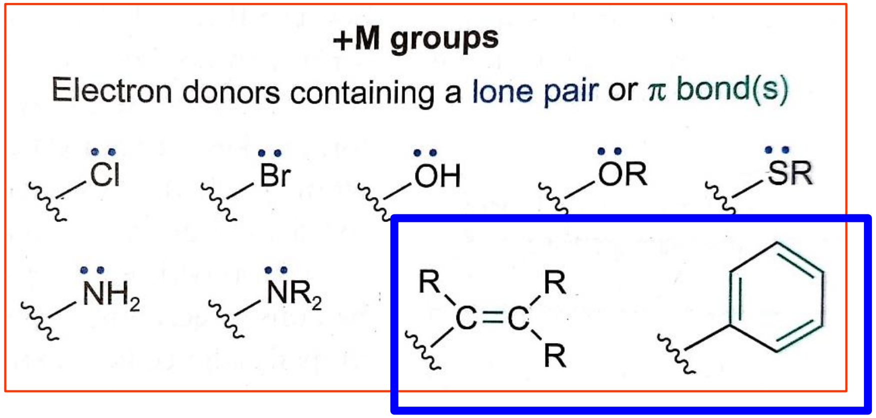
"Mesomerism" t is often encountered in German and French literature.
"Resonance" dominates in English literature.

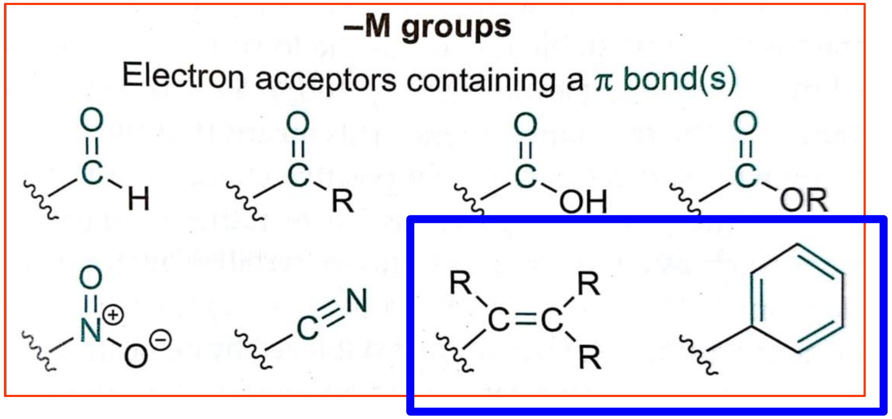
Greek *mésos* middle, in the middle; akin to Latin *medius*;

Mesomeric effect (or resonance effect)

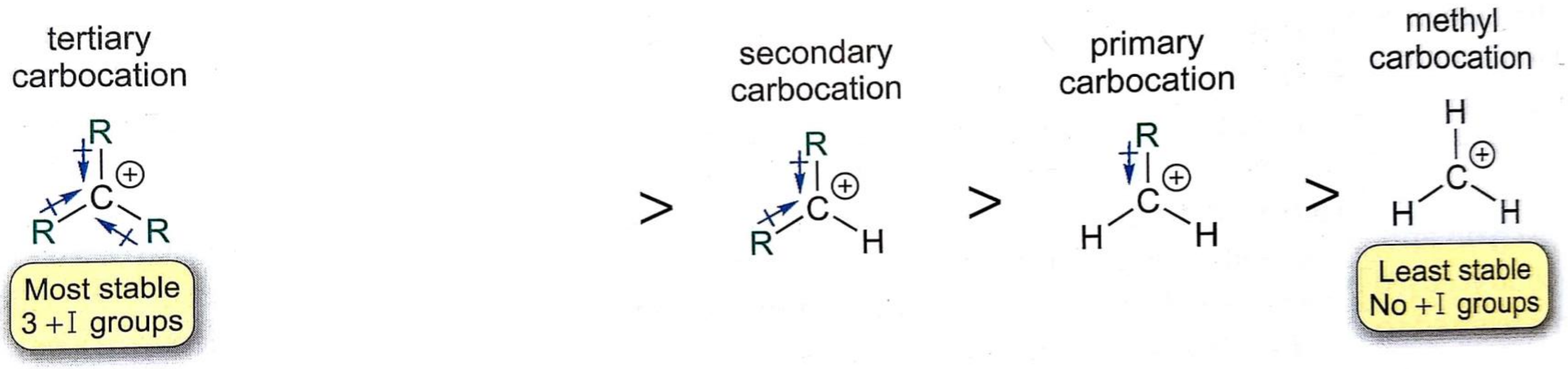
Inductive effects: push and pull electrons in the bonds of organic molecules and are associated to electronegative properties of the atoms connected to the double bonds, carbocations, radical and carbanion under consideration.

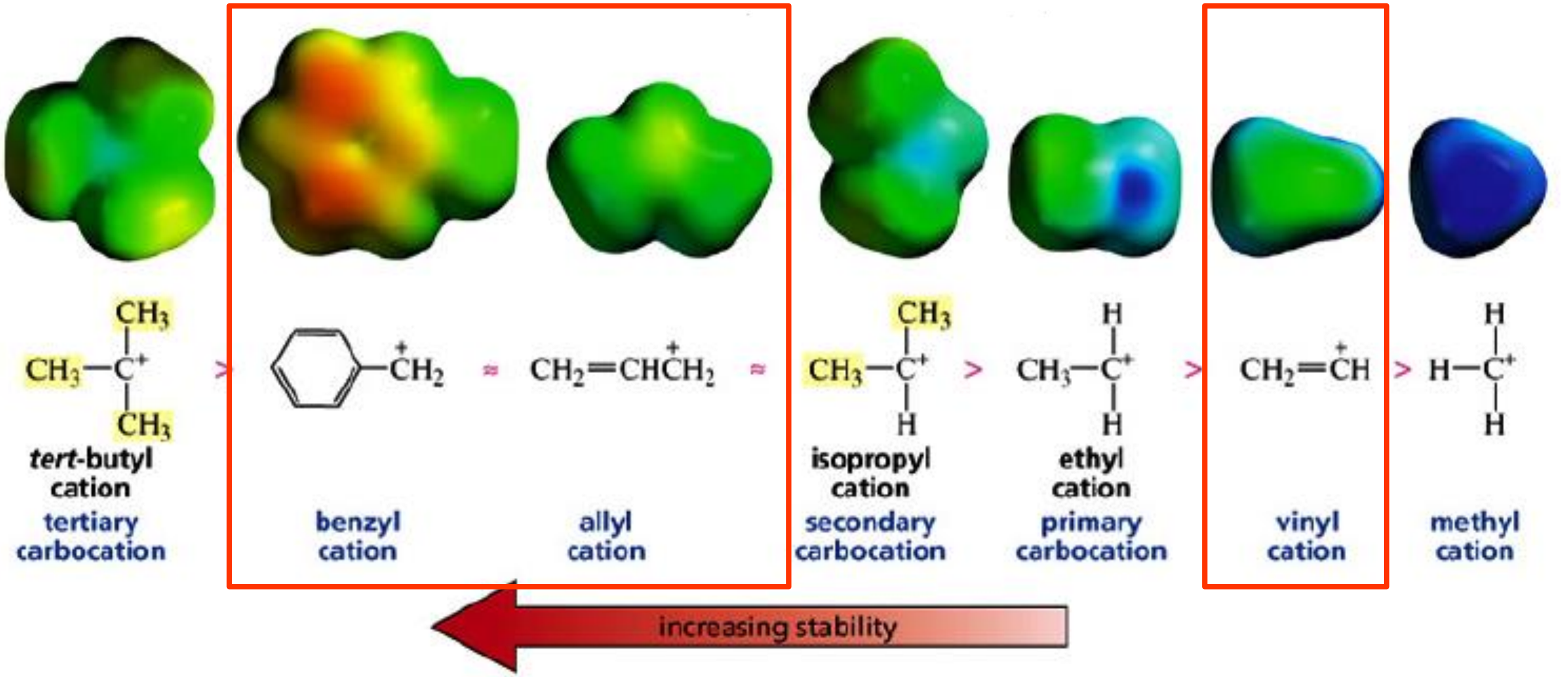
Mesomeric effects: involve delocalization of electron density through π bonds



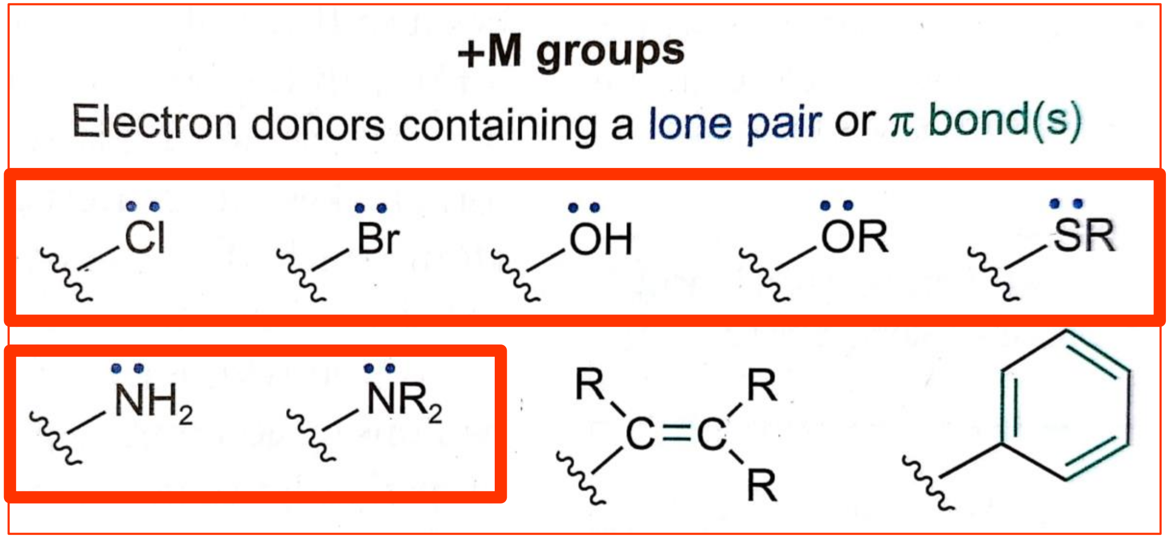


The relative stability of carbocations can be extended Including vinyl, allyl, and benzyl cations





Stabilization of a carbocation by **mesomeric** effect +M



+M groups

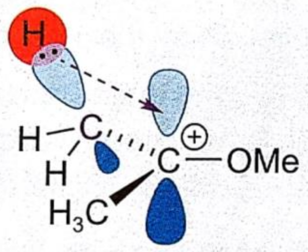
Electron donors containing a lone pair or π bond(s)

What about their electronegative effects
(inductive effect -I) ???

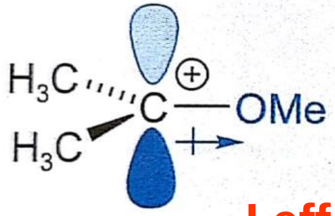
The hyperconjugation contributes to the stabilization of carbocation,

but the inductive effect **–I** of -OMe (with electron-withdrawing properties) destabilizes the carbocation.

Hyperconjugation



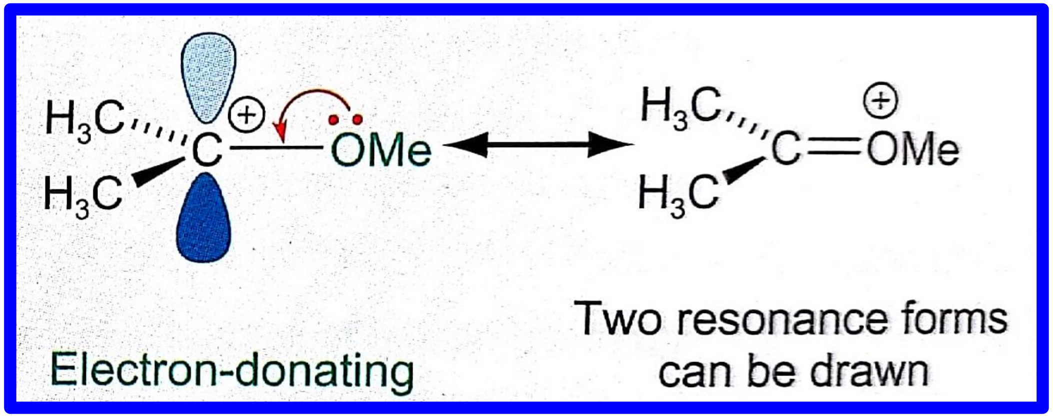
Electron-donating



–I effect of OMe

Electron-withdrawing

The +M (electron-donating properties) of –OR group stabilizes the carbocation.



Electron-donating

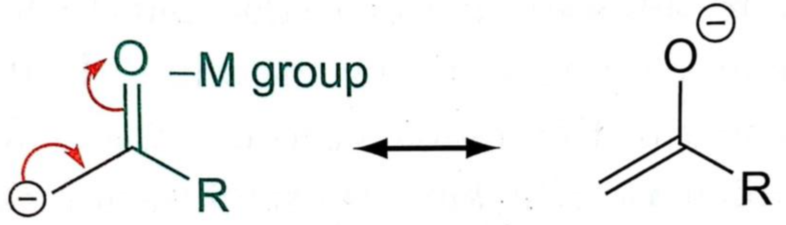
Two resonance forms can be drawn

Overall,
the **+M** effect is
more important
than -I

Efeito do haletos (efeito **–I** mas **+M**) em SEAr (QFL-0342)

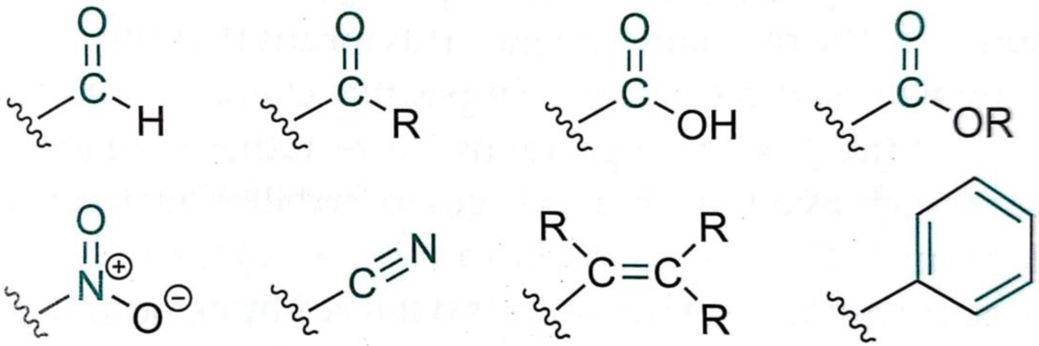
Stabilization of a <u>carbanions</u> by mesomeric effect -M

Stabilization of a carbanion by C=O



Major resonance form.
A negative charge on
oxygen is more stable
than a negative
charge on carbon.

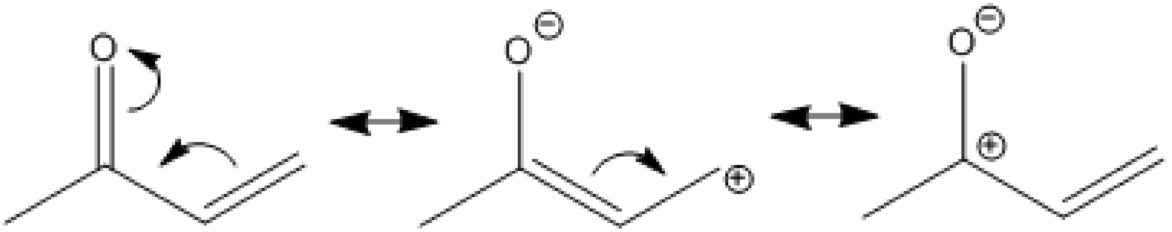
Química de enolatos
(QFL-0342)



–M groups

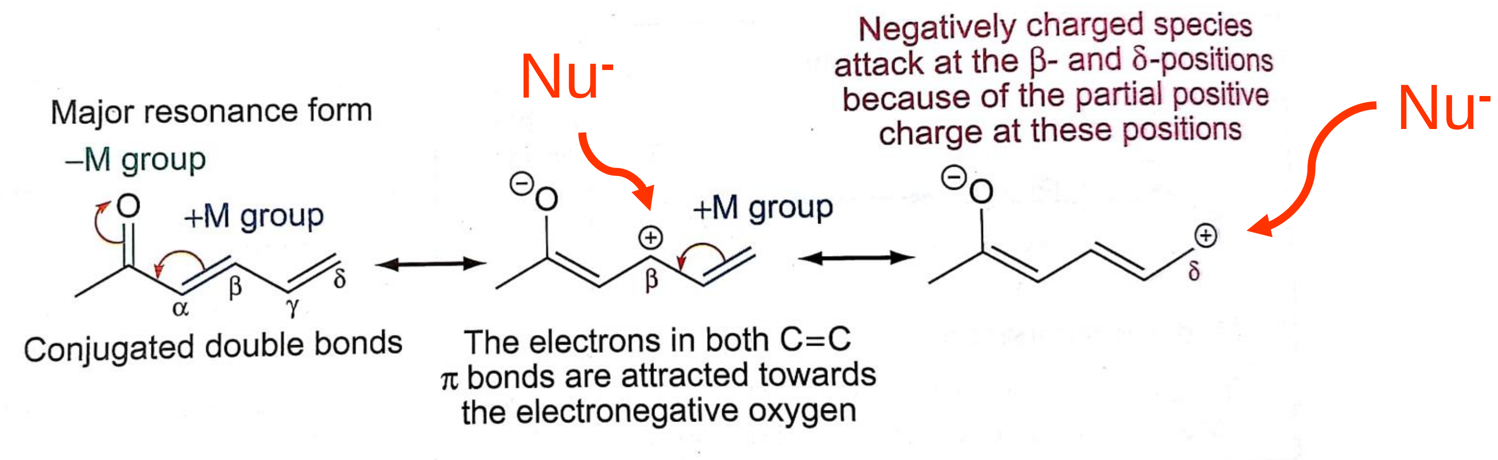
Electron acceptors containing a π bond(s)

The mesomeric effect **–M** can affect electron density at β–position in α,β-unsaturated carbonyl compounds



resonance structures of the beta unsaturated carbonyl

…and also affects γ position in α,β,γ,δ-unsaturated carbonyl compounds



Negatively charged species attack at the β- and δ-positions because of the partial positive charge at these positions

Major resonance form

–M group

+M group

+M group

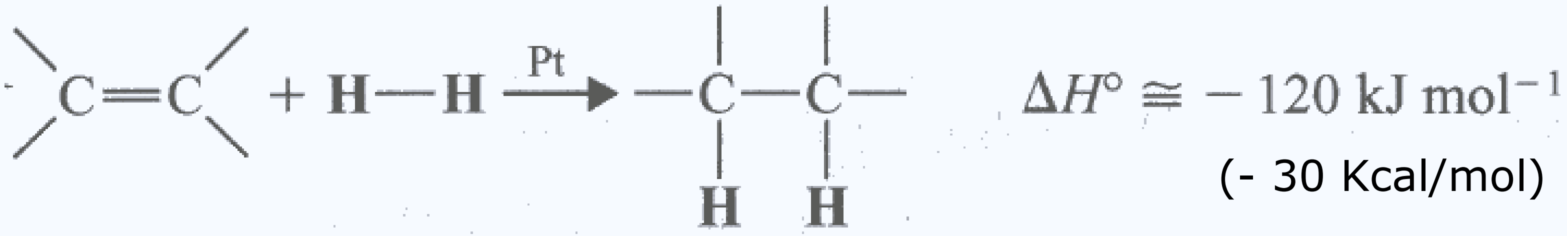
Conjugated double bonds

The electrons in both C=C π bonds are attracted towards the electronegative oxygen

Estabilidade Relativa de Ligações Duplas

Diferença na estabilidade relativa dos diferentes arranjos de substituição de uma ligação dupla.

Energia liberada na hidrogenação da ligação dupla.



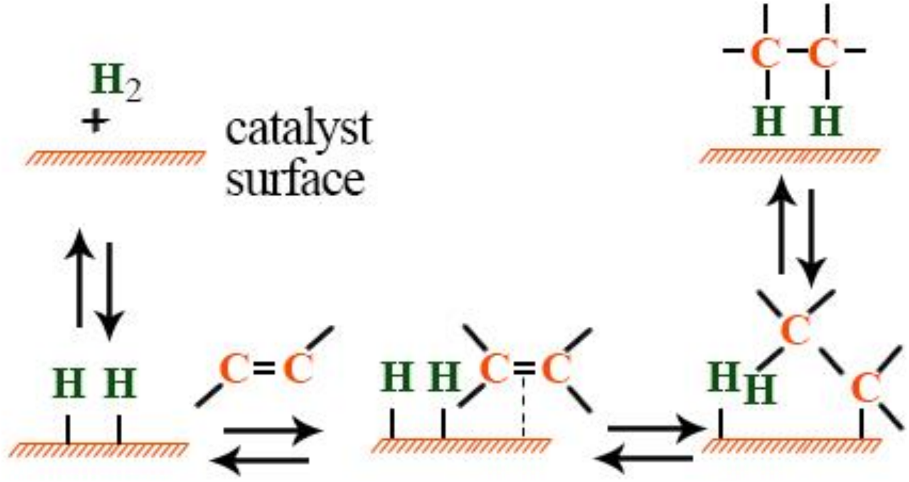
$$\mathrm{C{=}C} + \mathrm{H{-}H} \xrightarrow{\mathrm{Pt}} \mathrm{-\underset{H}{C}-\underset{H}{C}-} \qquad \Delta H^\circ \cong -120\ \mathrm{kJ\ mol^{-1}}$$

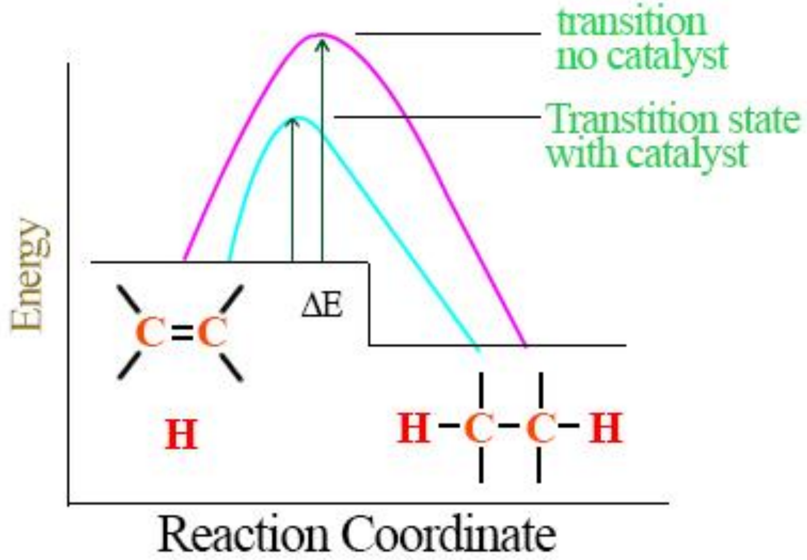
(- 30 Kcal/mol)

i) Quanto maior a energia contida em uma molécula, maior a energia liberada.

ii) Diferenças na energia liberada permitem a medida das estabilidades relativas de isômeros de alquenos quando a hidrogenação os converte no mesmo produto.

A estabilidade de sistemas conjugados pode ser medida através dos calores de hidrogenação





Stability of Conjugated Dienes

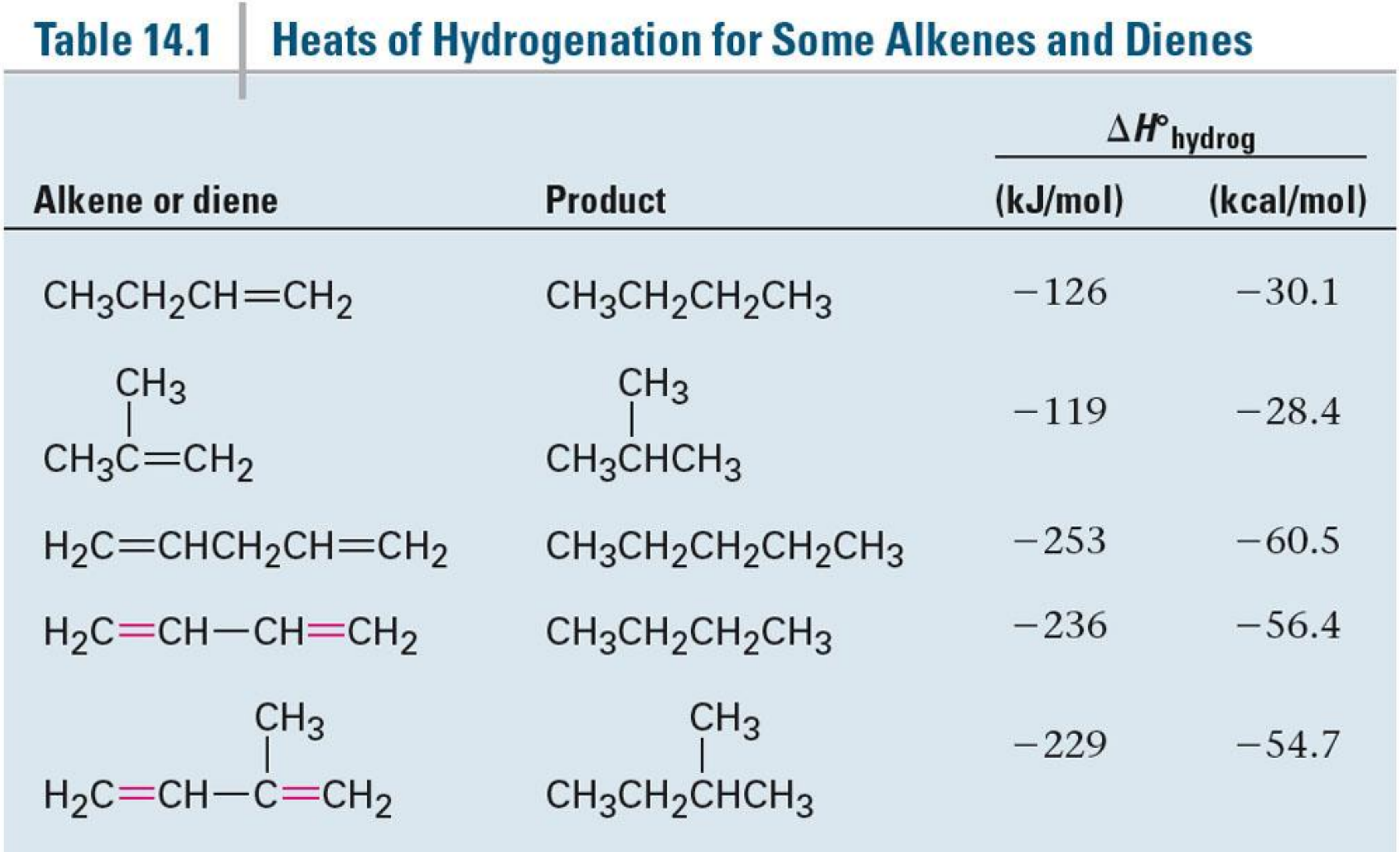


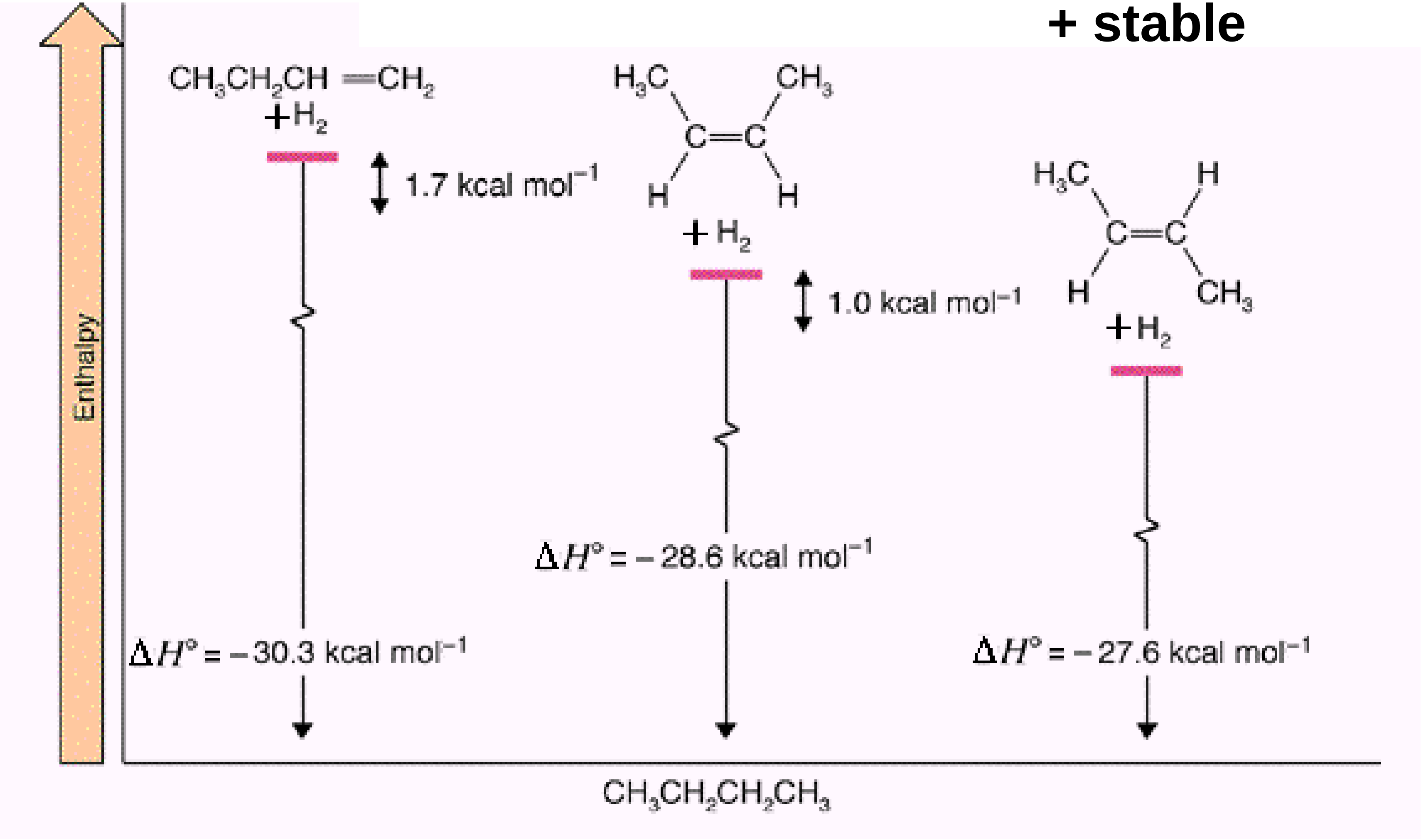
Table 14.1 **Heats of Hydrogenation for Some Alkenes and Dienes**

Alkene or diene	Product	$\Delta H^\circ_{\text{hydrog}}$ (kJ/mol)	$\Delta H^\circ_{\text{hydrog}}$ (kcal/mol)
$CH_3CH_2CH{=}CH_2$	$CH_3CH_2CH_2CH_3$	−126	−30.1
$CH_3\overset{CH_3}{\overset{\vert}{C}}{=}CH_2$	$CH_3\overset{CH_3}{\overset{\vert}{C}}HCH_3$	−119	−28.4
$H_2C{=}CHCH_2CH{=}CH_2$	$CH_3CH_2CH_2CH_2CH_3$	−253	−60.5
$H_2C{=}CH{-}CH{=}CH_2$	$CH_3CH_2CH_2CH_3$	−236	−56.4
$H_2C{=}CH{-}\overset{CH_3}{\overset{\vert}{C}}{=}CH_2$	$CH_3CH_2\overset{CH_3}{\overset{\vert}{C}}HCH_3$	−229	−54.7

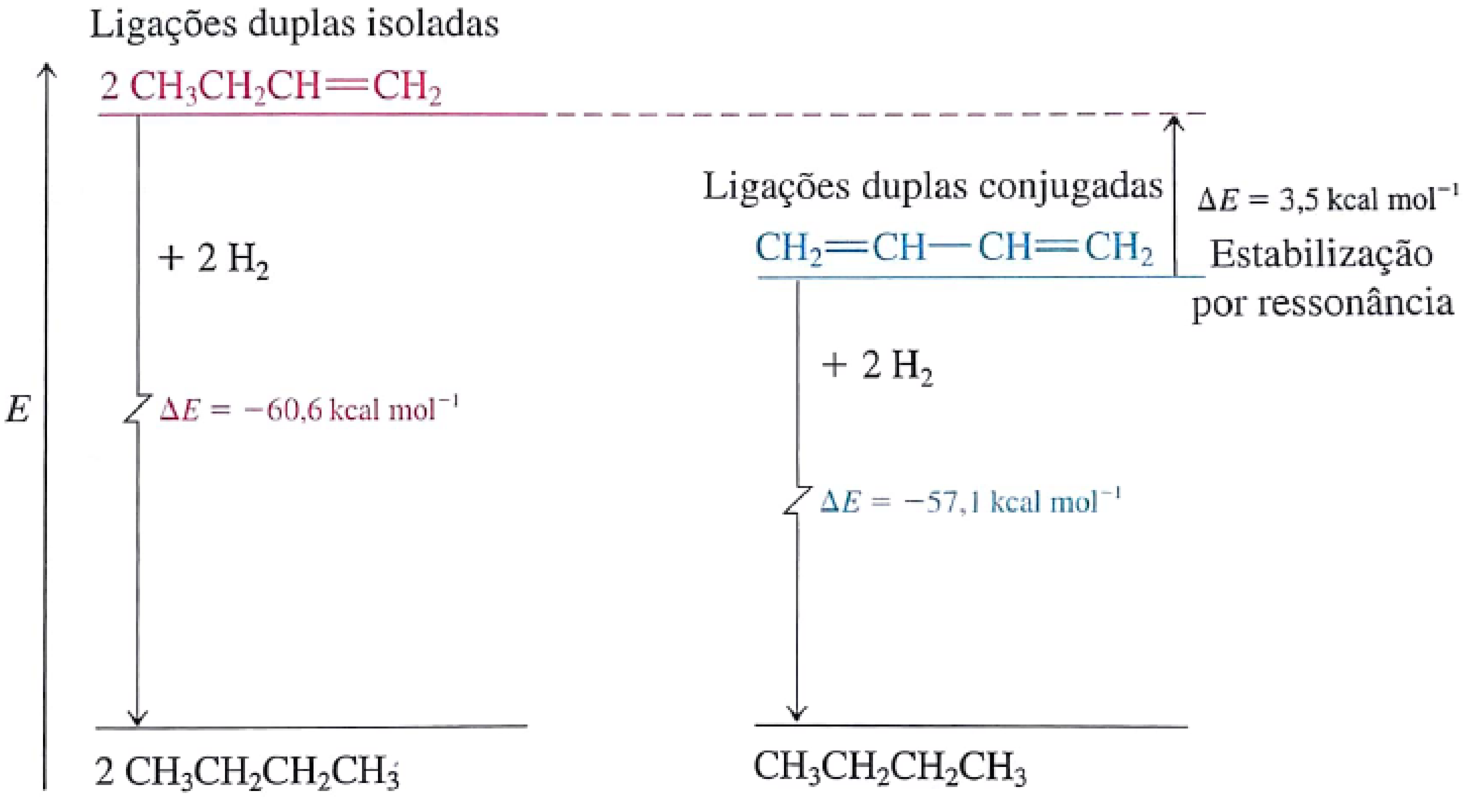
Relative stability of substituted alkenes

- stable

+ stable



Estabilidade relativa de dienos



Vollhardt (6a ed, p. 618)

Próximos Tópicos

Caracterização de sistemas deslocalizados por espectrofotometria no Ultravioleta

Literatura:
Bruice, p. 267 (3rd ed. 2001);
McMurry, p. 522 (5th ed, 2000);
Solomons, p. 549 (8a ed. 2004);
Volhard (6a ed): p. 28, 609;
Clayden, 151, 905.