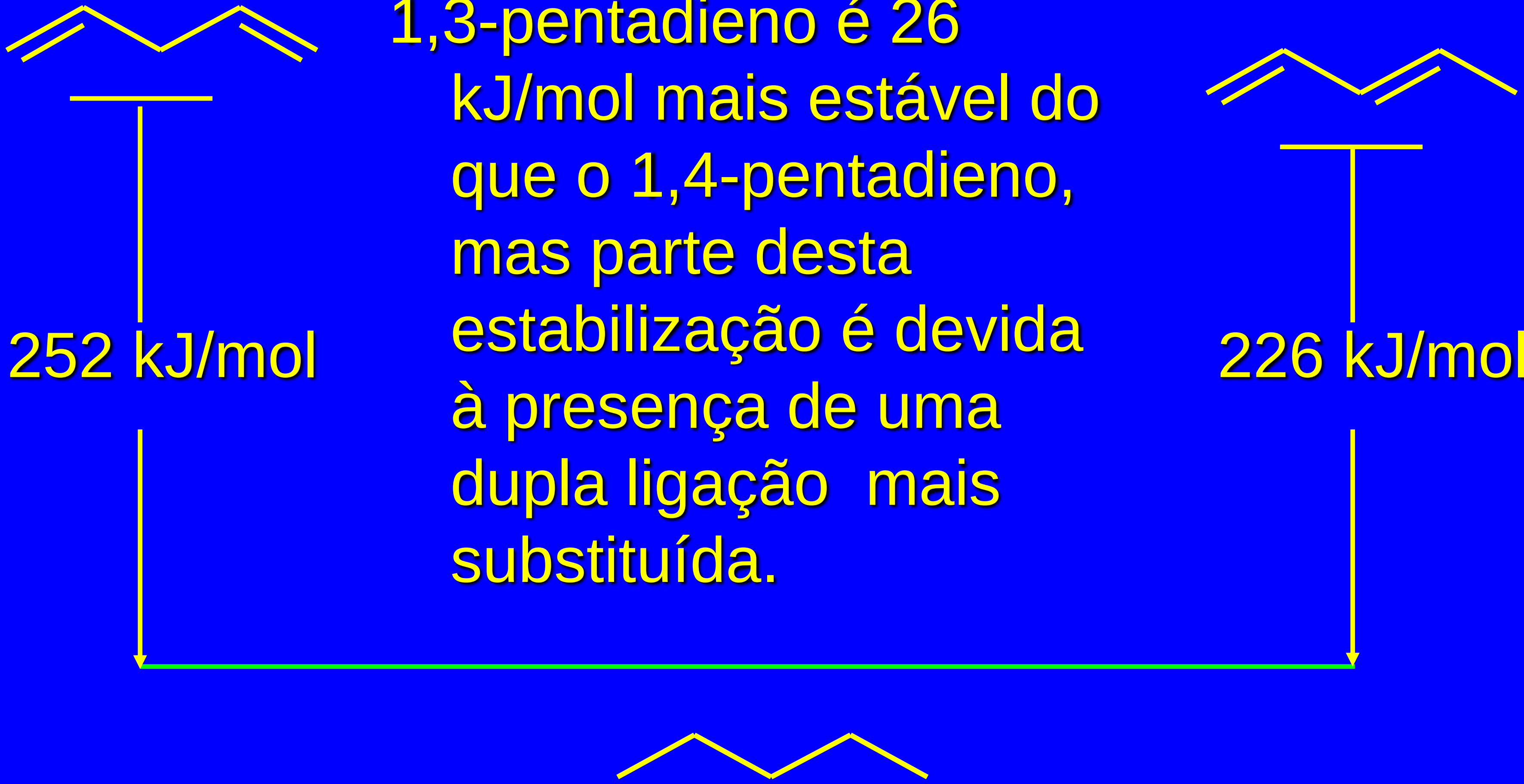
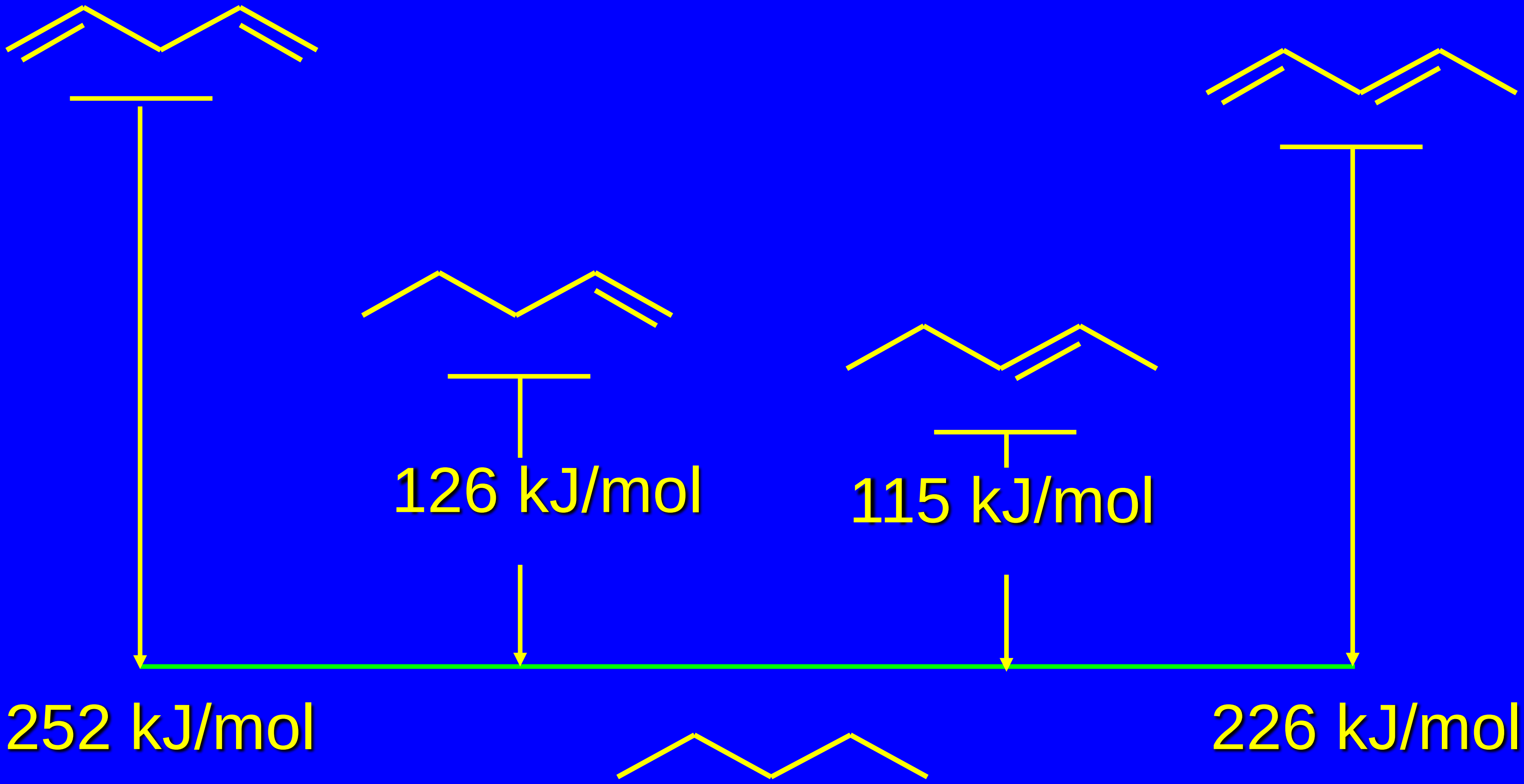
Estabilidade Relativa dos Dienos

Calor de Hidrogenação



1,3-pentadieno é 26 kJ/mol mais estável do que o 1,4-pentadieno, mas parte desta estabilização é devida à presença de uma dupla ligação mais substituída.

Calor de Hidrogenação



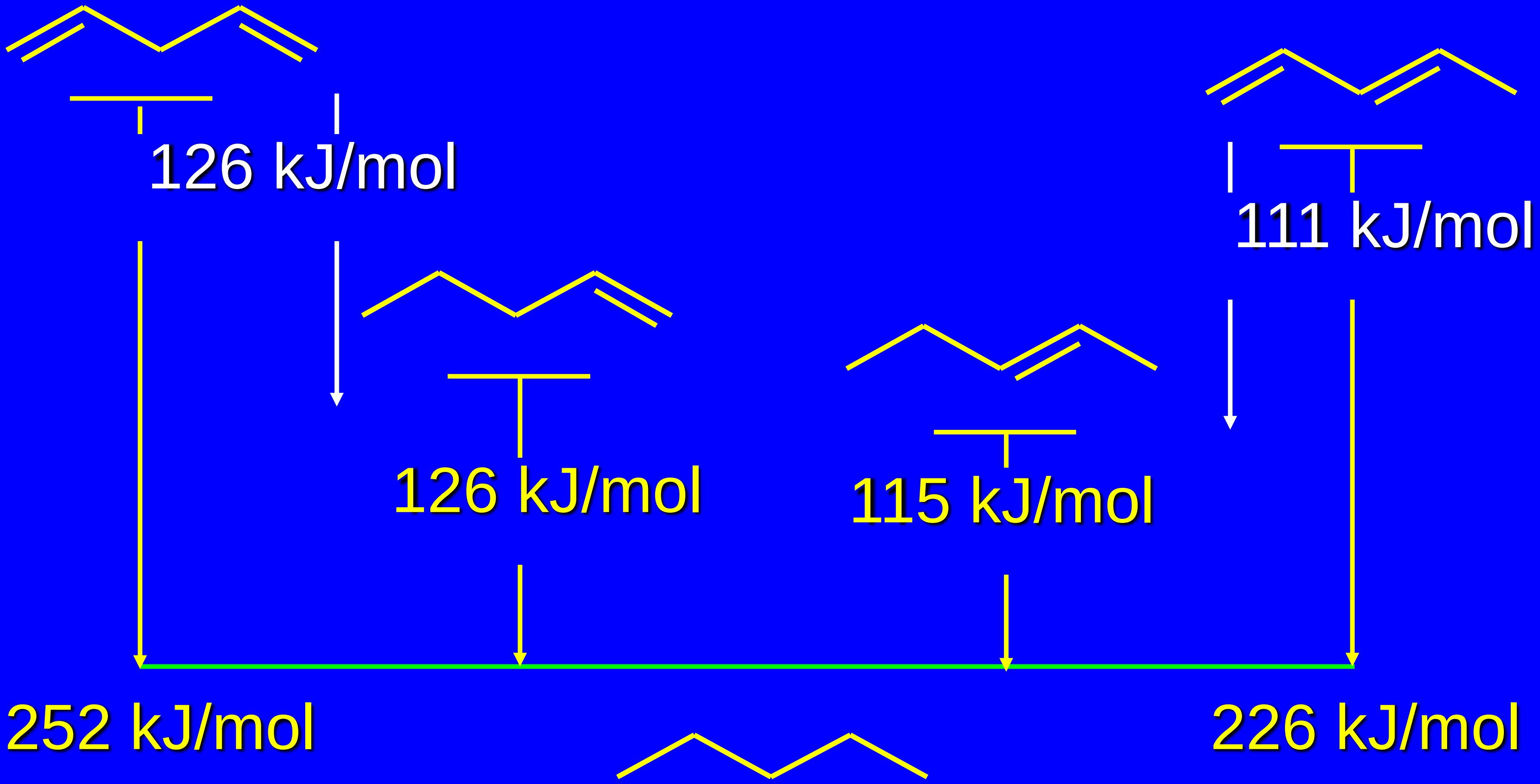
126 kJ/mol

115 kJ/mol

252 kJ/mol

226 kJ/mol

Calor de Hidrogenação



126 kJ/mol

111 kJ/mol

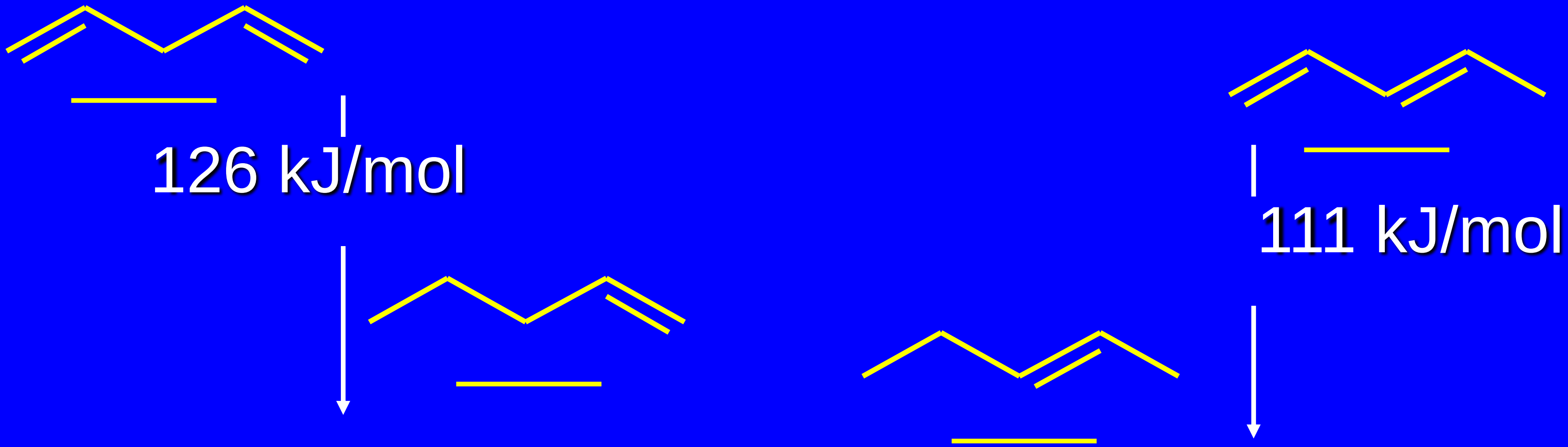
126 kJ/mol

115 kJ/mol

252 kJ/mol

226 kJ/mol

Calor de Hidrogenação



126 kJ/mol

111 kJ/mol

este adicional de 15 kJ/mol é conhecido por nomes diferentes:

Energia de estabilização
Energia de deslocalização
Energia de Ressoância

Heats of Hydrogenation

Cumulated double bonds have relatively high heats of hydrogenation

$$H_2C{=}C{=}CH_2 \quad + \quad 2H_2 \longrightarrow CH_3CH_2CH_3$$

$\Delta H° = -295$ kJ

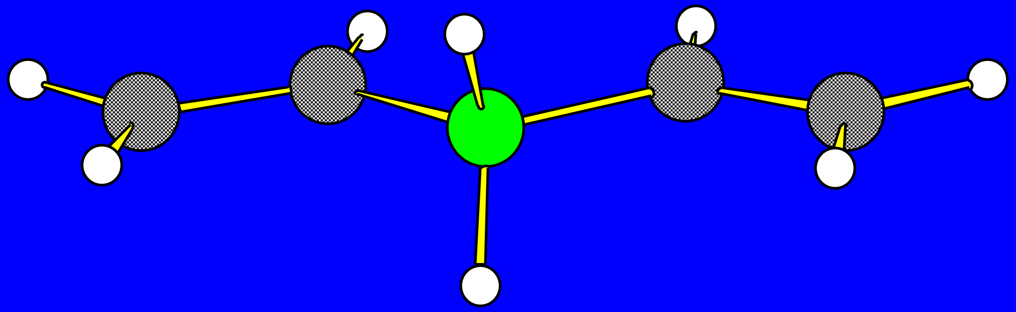
$$H_2C{=}CH_2CH_3 \quad + \quad H_2 \longrightarrow CH_3CH_2CH_3$$

$\Delta H° = -125$ kJ

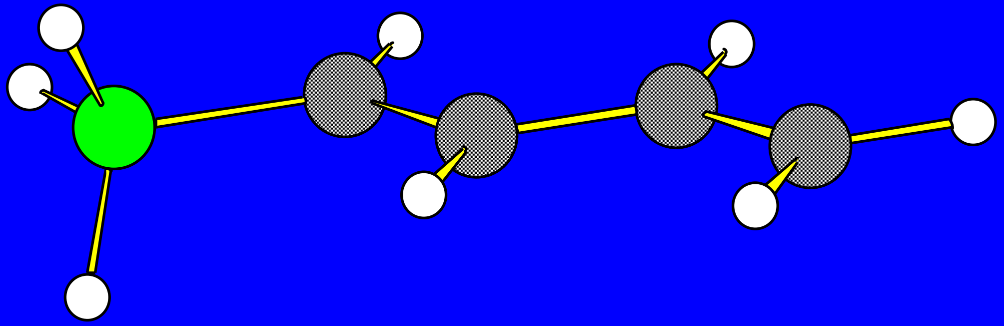
10.7

Bonding in Conjugated Dienes

Dieno isolado



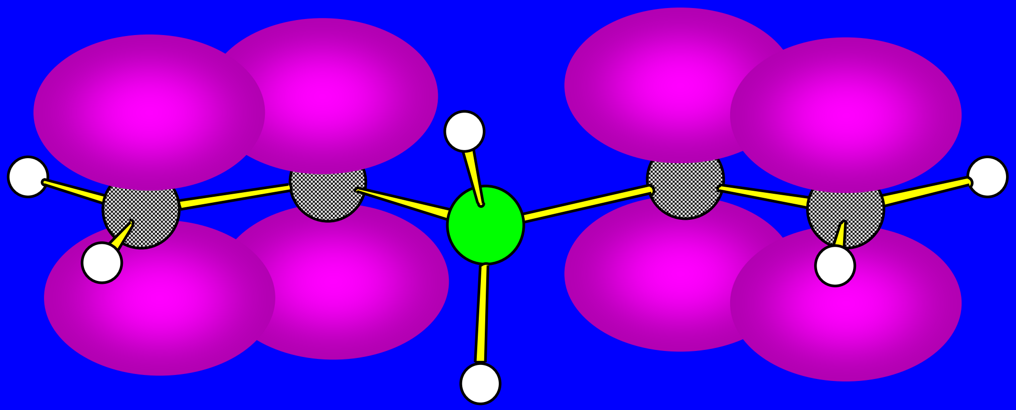
1,4-pentadieno



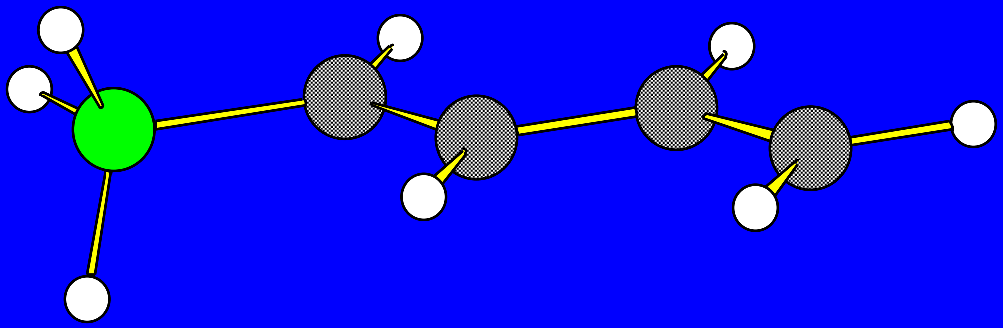
1,3-pentadieno

Dieno conjugado

Dieno isolado



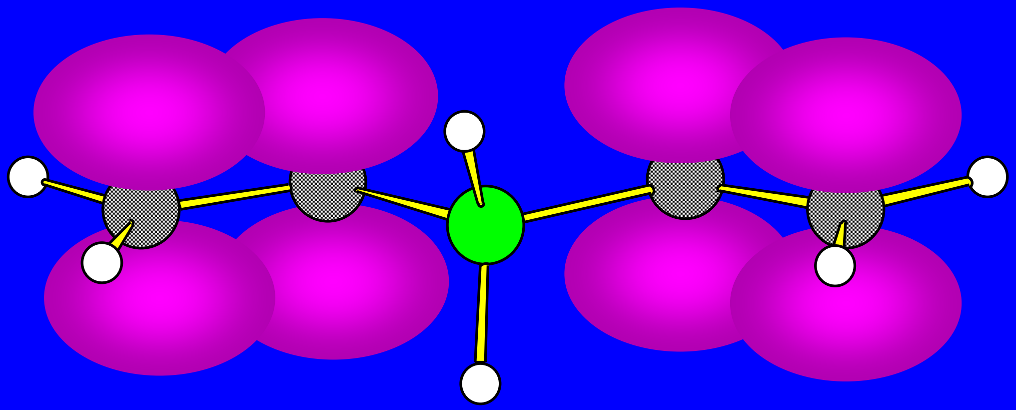
Ligações π são independentes uma da outra



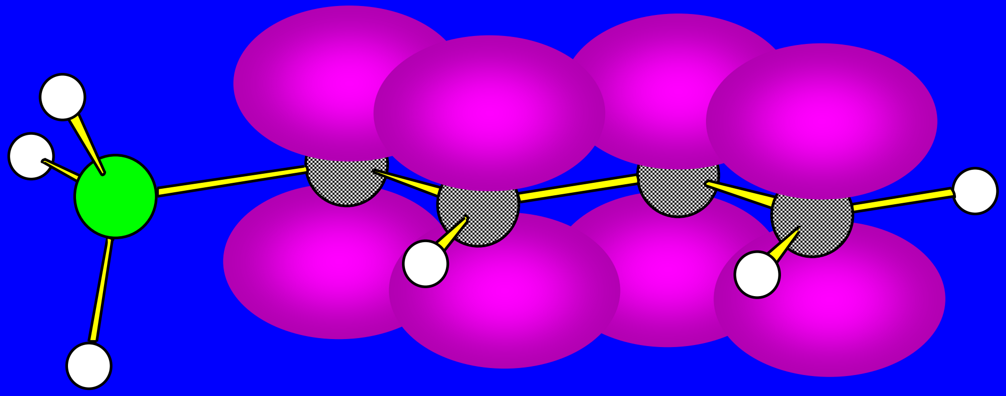
1,3-pentadiene

Dieno conjugado

Dieno isolado



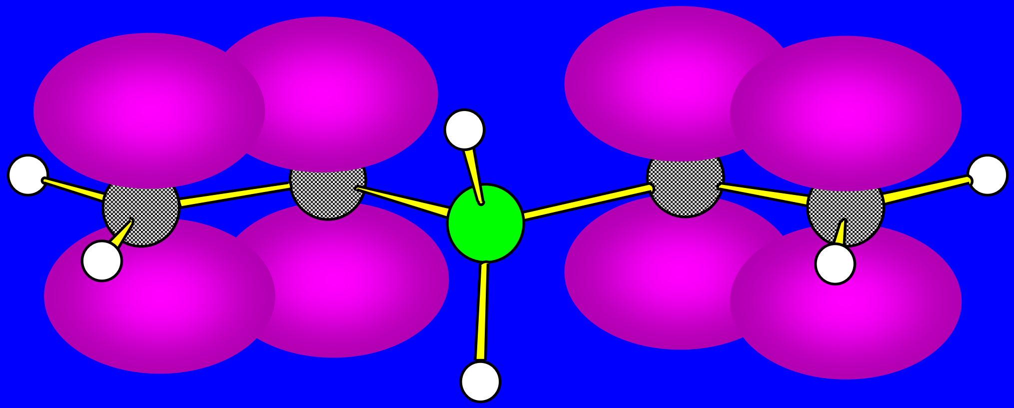
Ligações π são
independentes
uma da outra



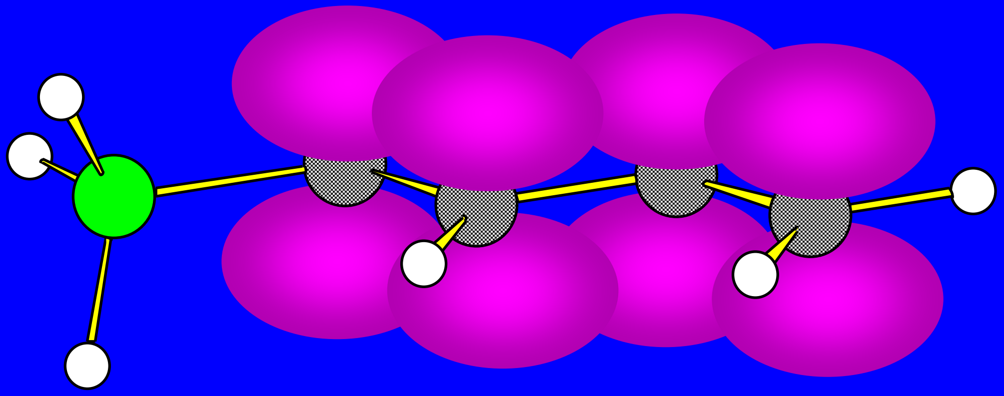
Orbitais *p* se
sobrepõem,
estendendo a
Ligãção π , a qual
passa a envolver
quatro carbonos

Dieno conjugado

Dieno isolado



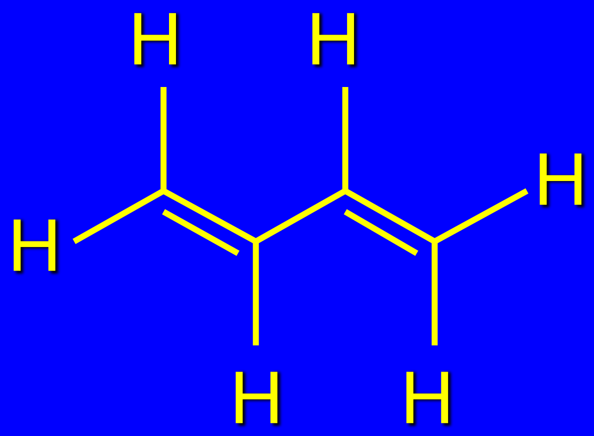
Menor deslocaização dos elétrons; Menos estável



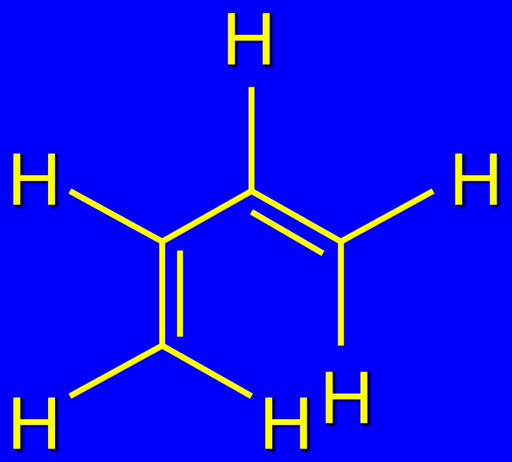
Maior deslocalização dos elétrons; mais estável

Dieno conjugado

Conformations of Dienes



s-trans

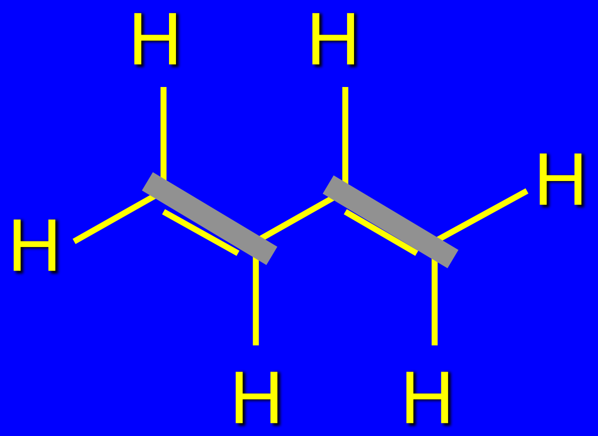


s-cis

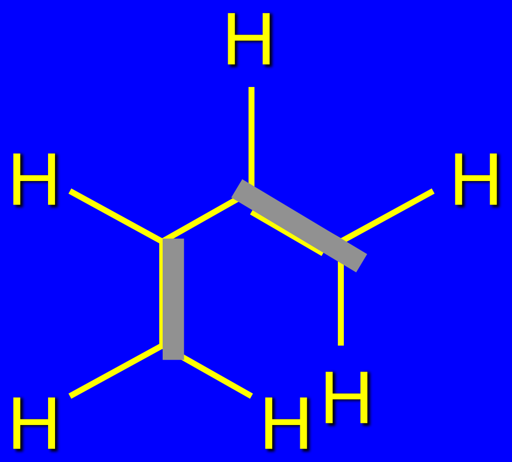
s prefix designates conformation around single bond

s prefix is lower case (different from Cahn-Ingold-Prelog *S* which designates configuration and is upper case)

Conformations of Dienes



s-trans

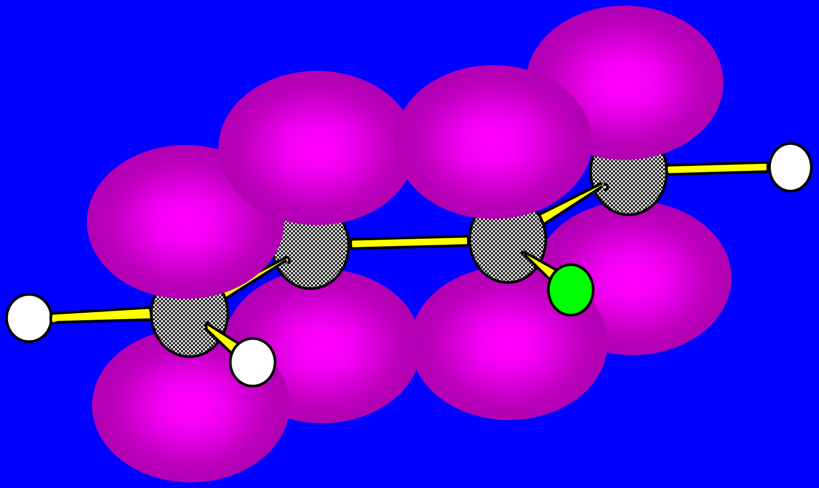


s-cis

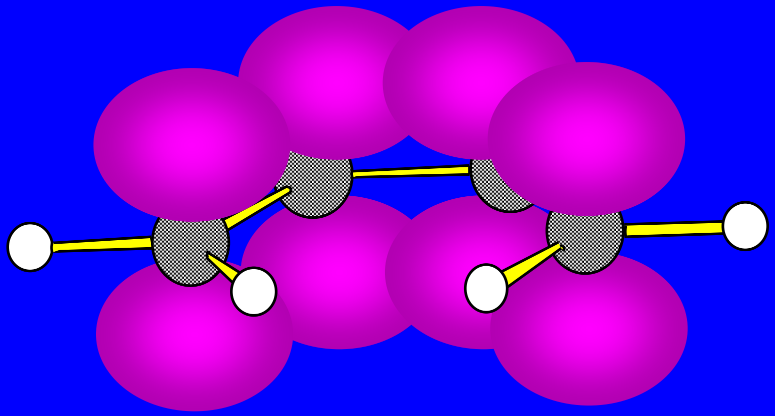
s prefix designates <u>conformation</u> around single bond

s prefix is lower case (different from Cahn-Ingold-Prelog *S* which designates <u>configuration</u> and is upper case)

Conformations of Dienes



s-trans

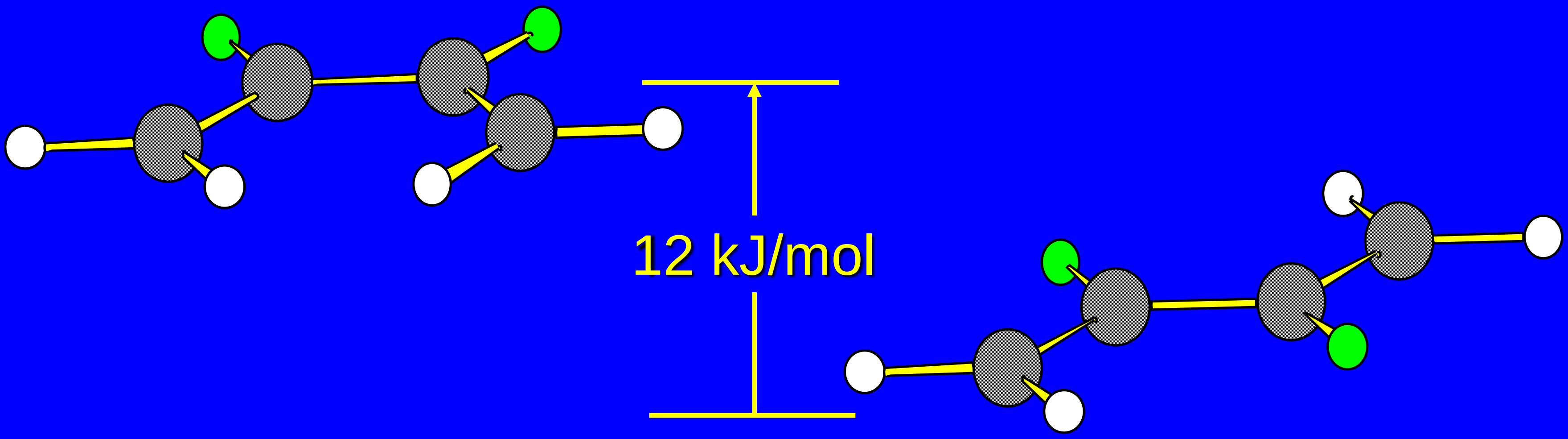


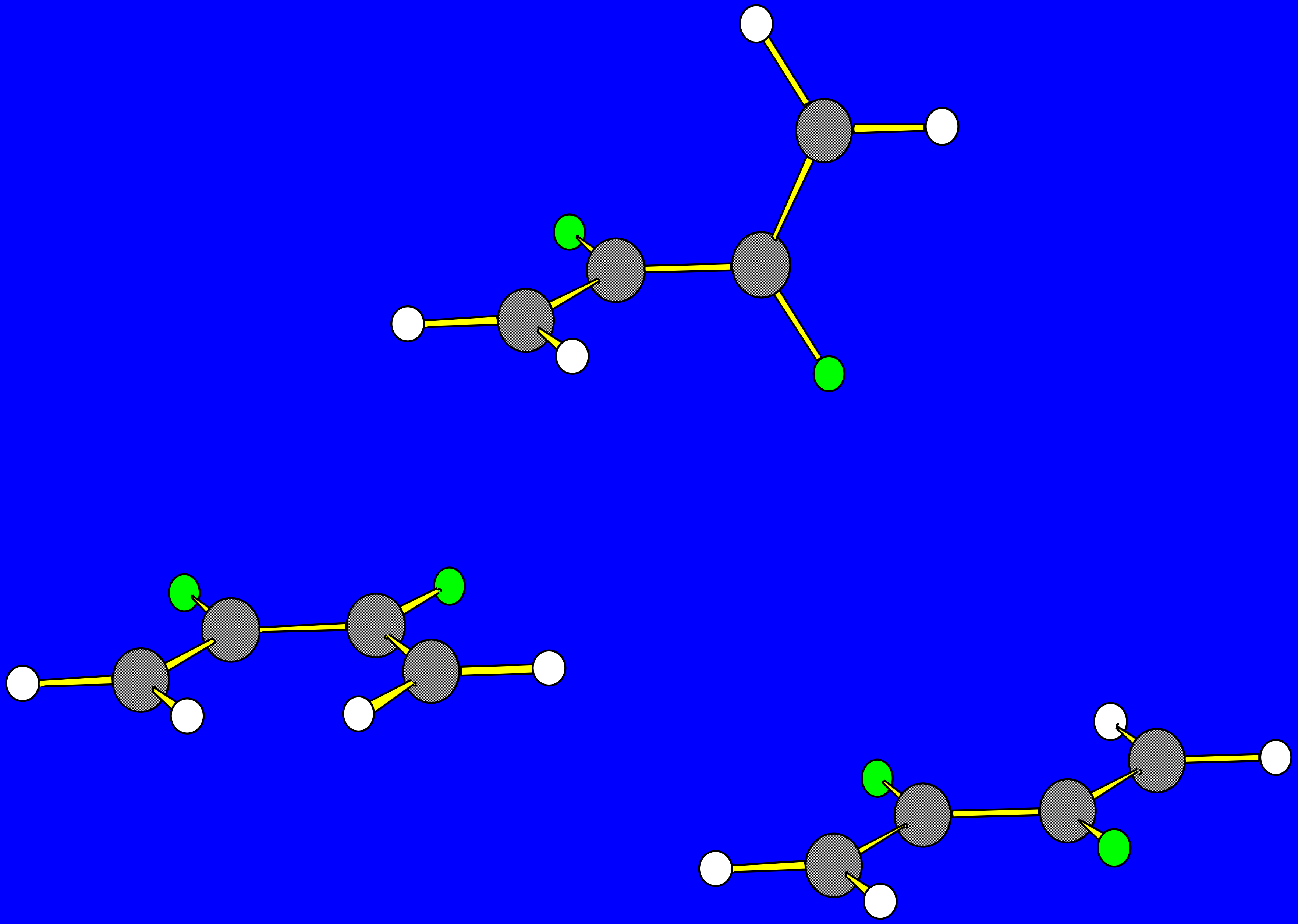
s-cis

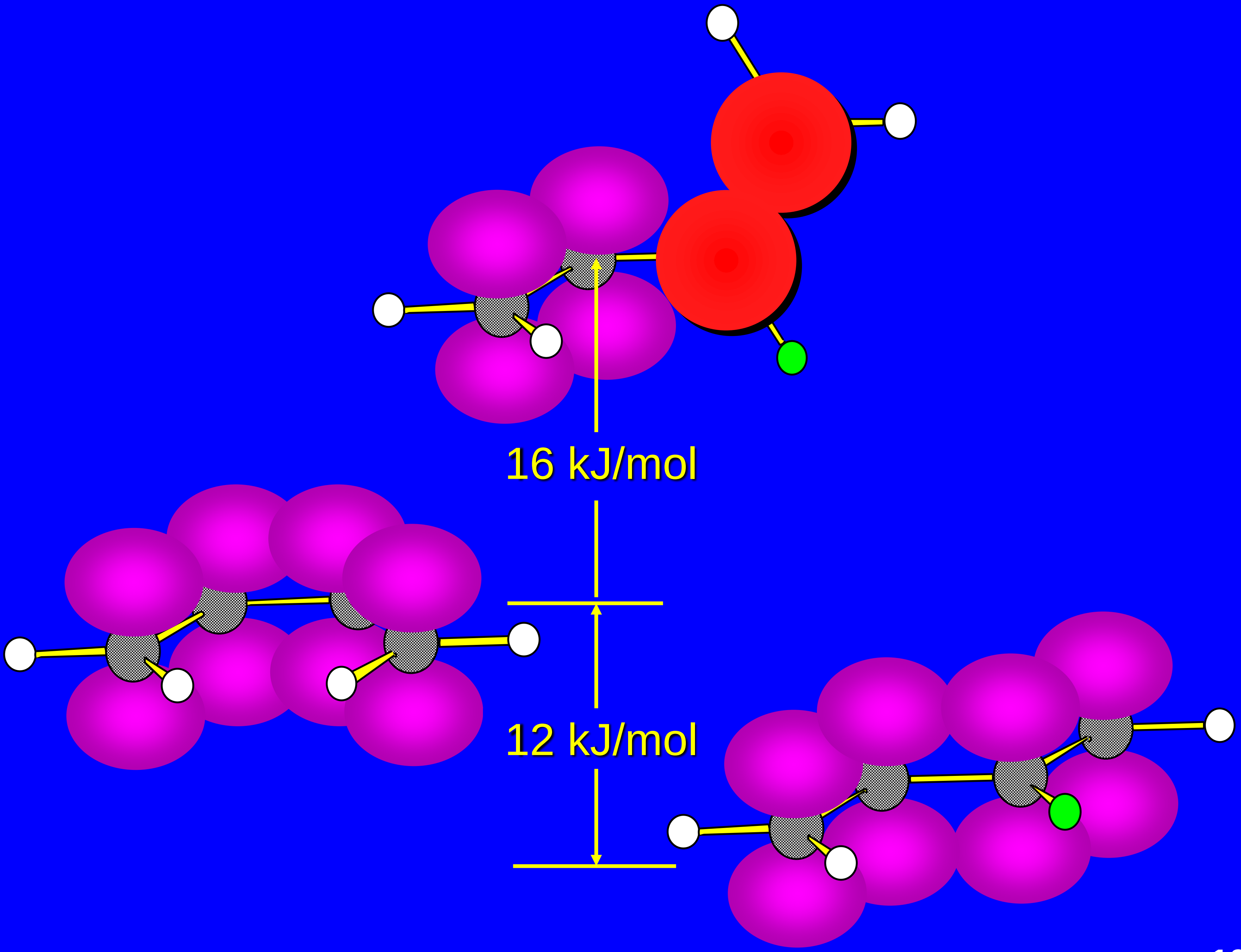
Both conformations allow electron delocalization via overlap of *p* orbitals to give extended π system

s-trans is more stable than s-cis

Interconversion of conformations requires two π bonds to be at right angles to each other and prevents conjugation






16 kJ/mol
12 kJ/mol

1,3-Butadiene

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{chromia-alumina}]{590\text{-}675°C} H_2C{=}CHCH{=}CH_2 + 2H_2$$

More than 4 billion pounds of 1,3-butadiene prepared by this method in U.S. each year

used to prepare synthetic rubber (See "Diene Polymers" box)

Reactions of Dienes

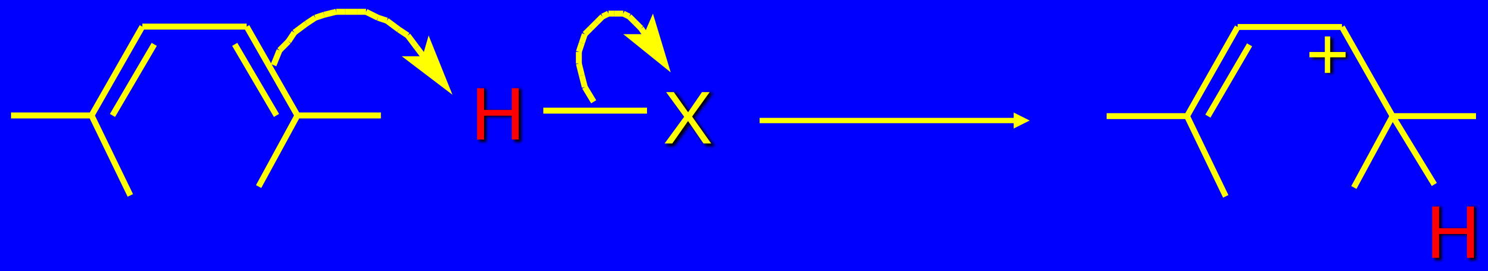
isolated dienes: double bonds react independently of one another

cumulated dienes: specialized topic

conjugated dienes: reactivity pattern requires us to think of conjugated diene system as a functional group of its own

<u>Addition</u> of Hydrogen Halides
to
Conjugated Dienes

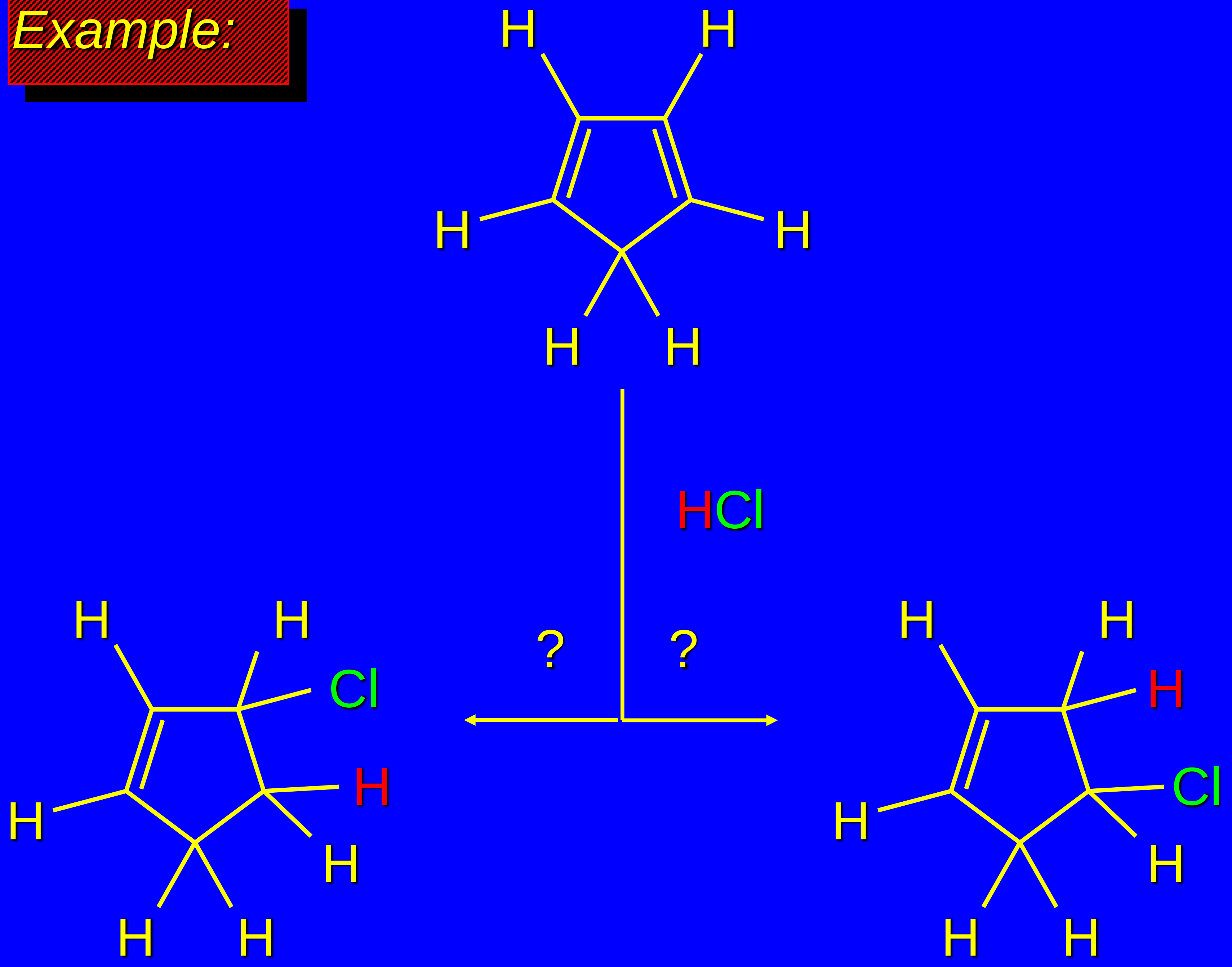
Electrophilic Addition to Conjugated Dienes



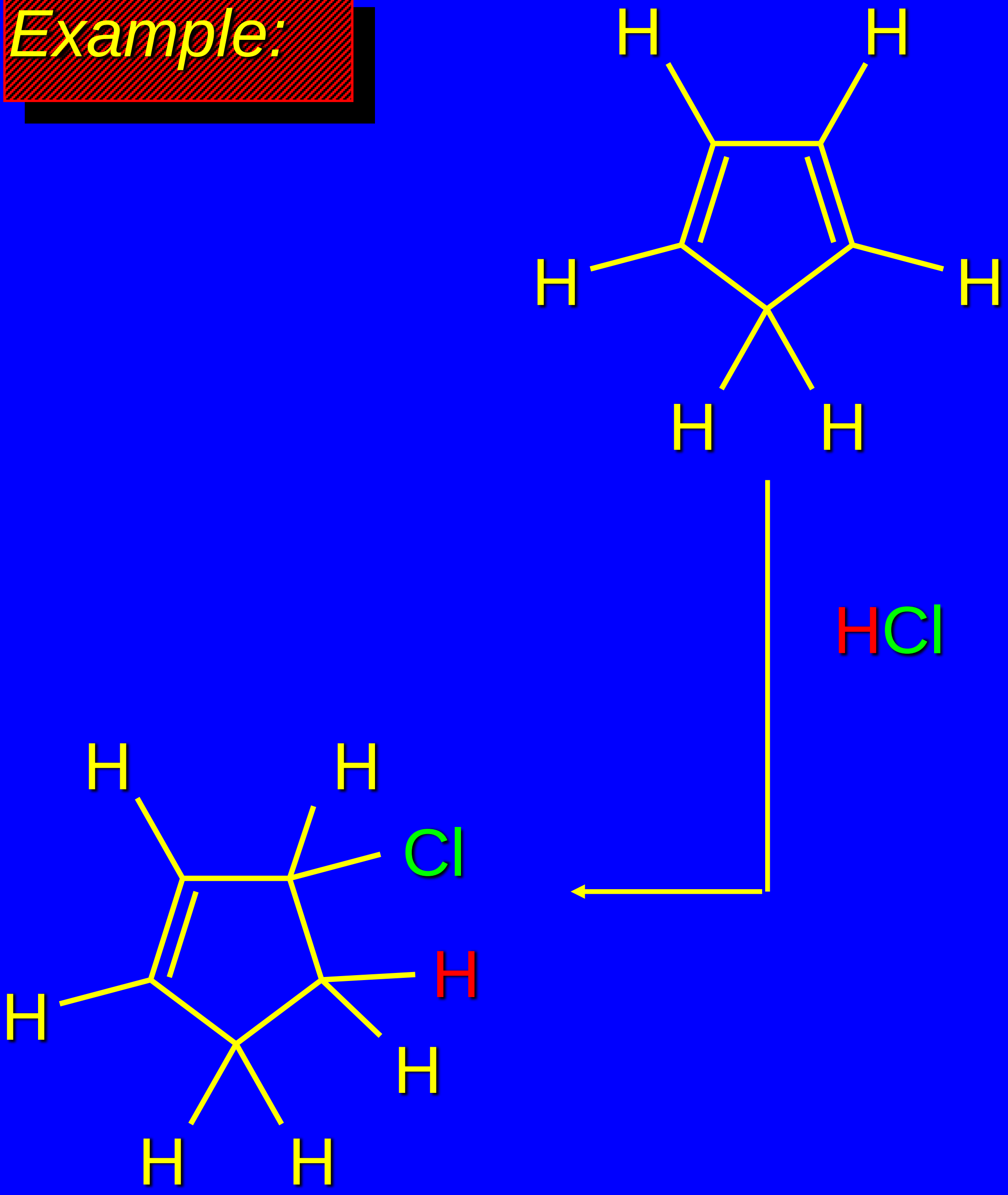
Proton adds to end of diene system

Carbocation formed is allylic

Example:



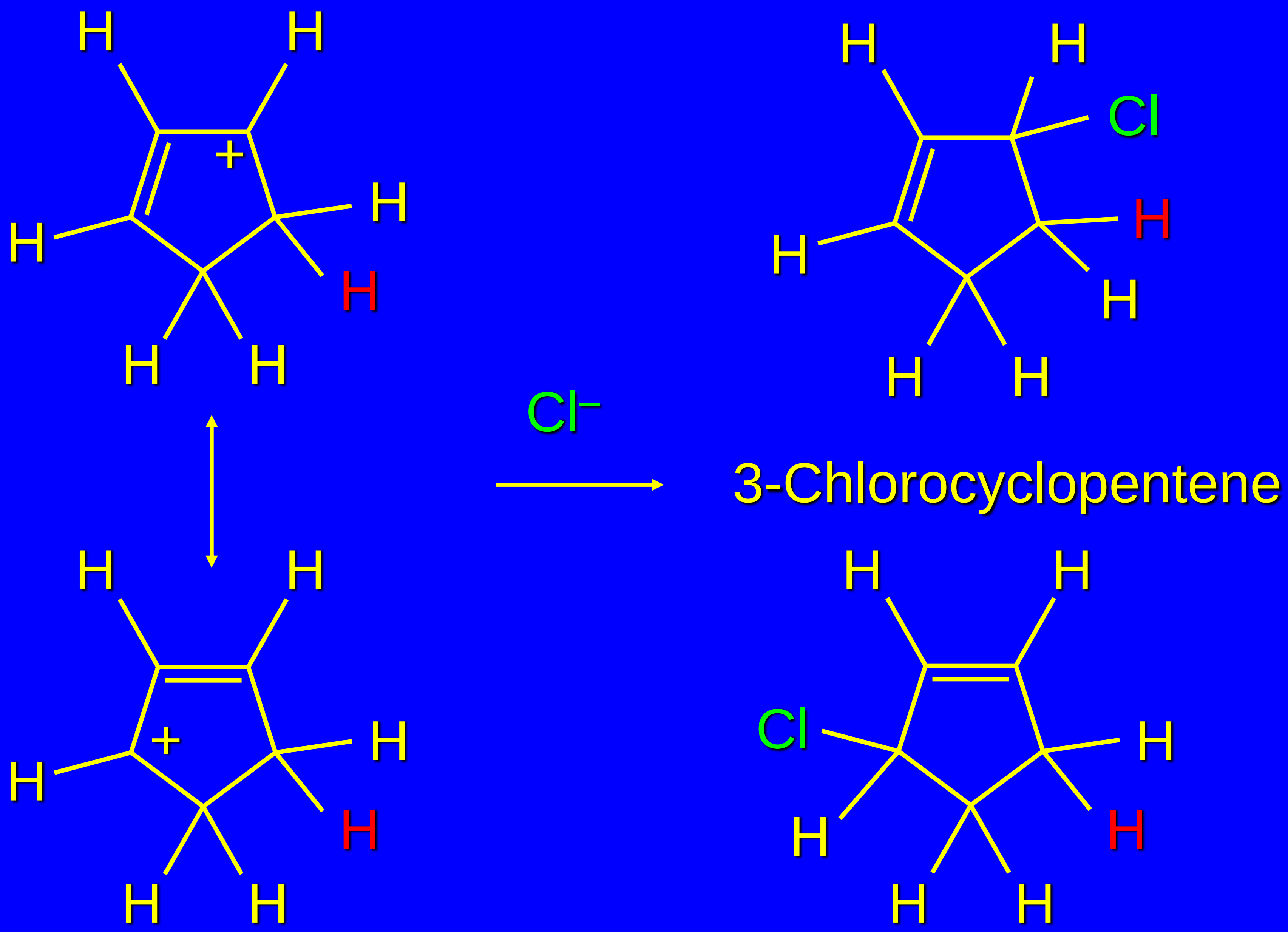
Example:



via:

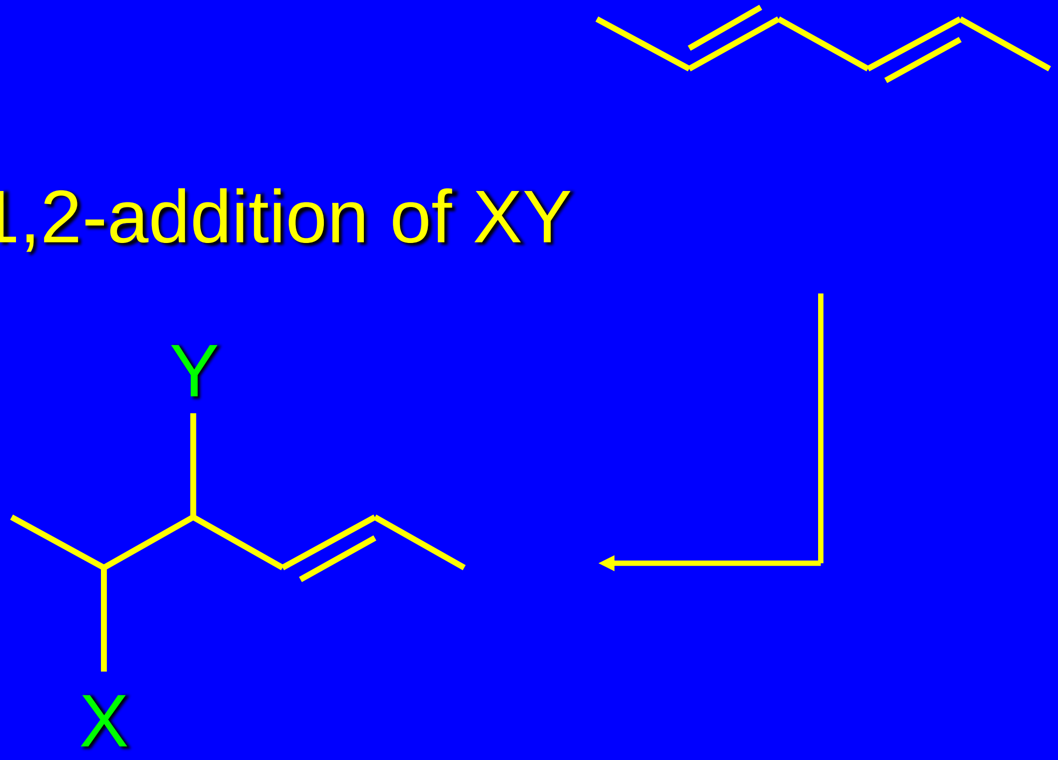
Estabilização por ressonância

Segundo passo: ataque do nucleófilo



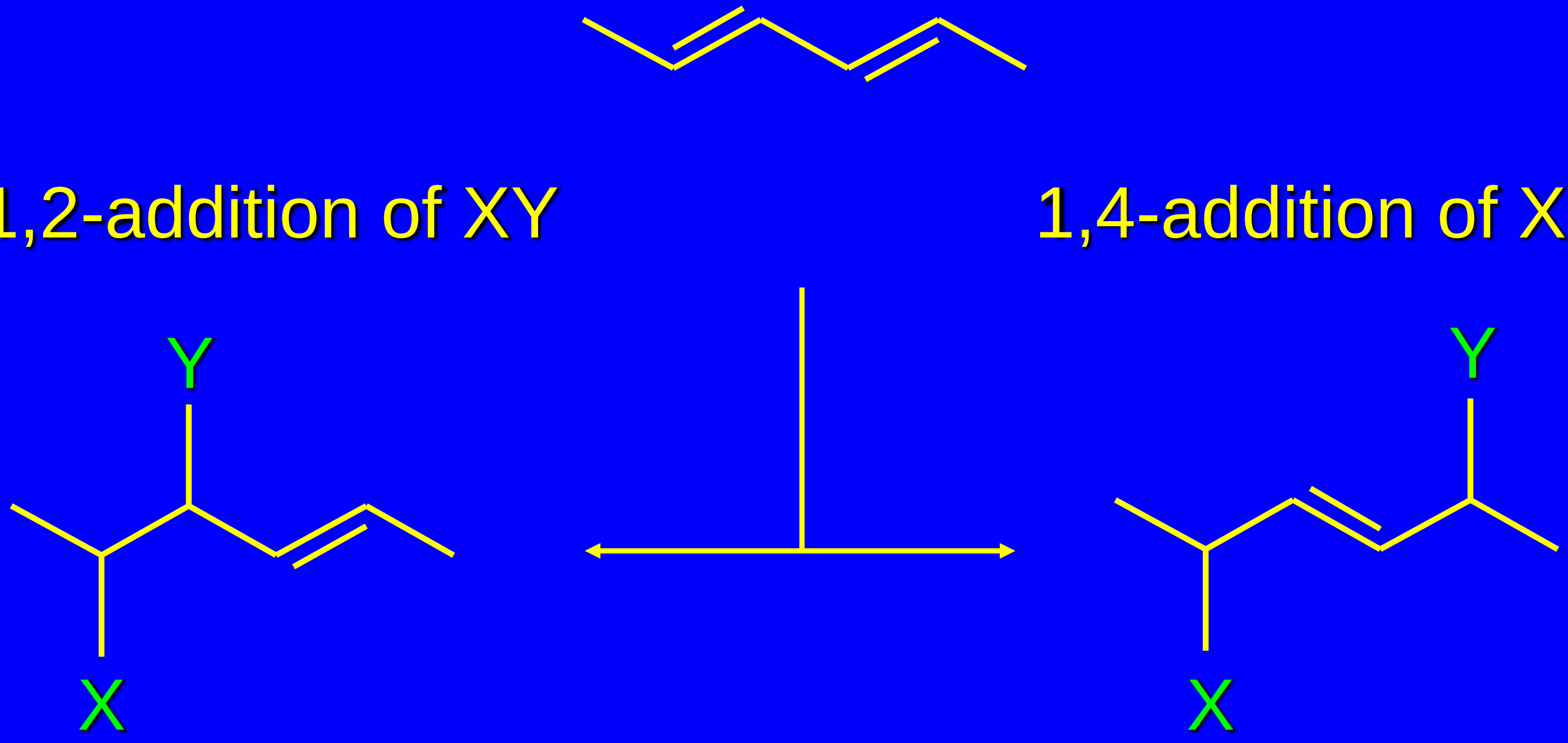
3-Chlorocyclopentene

1,2-Addition versus 1,4-Addition



1,2-addition of XY

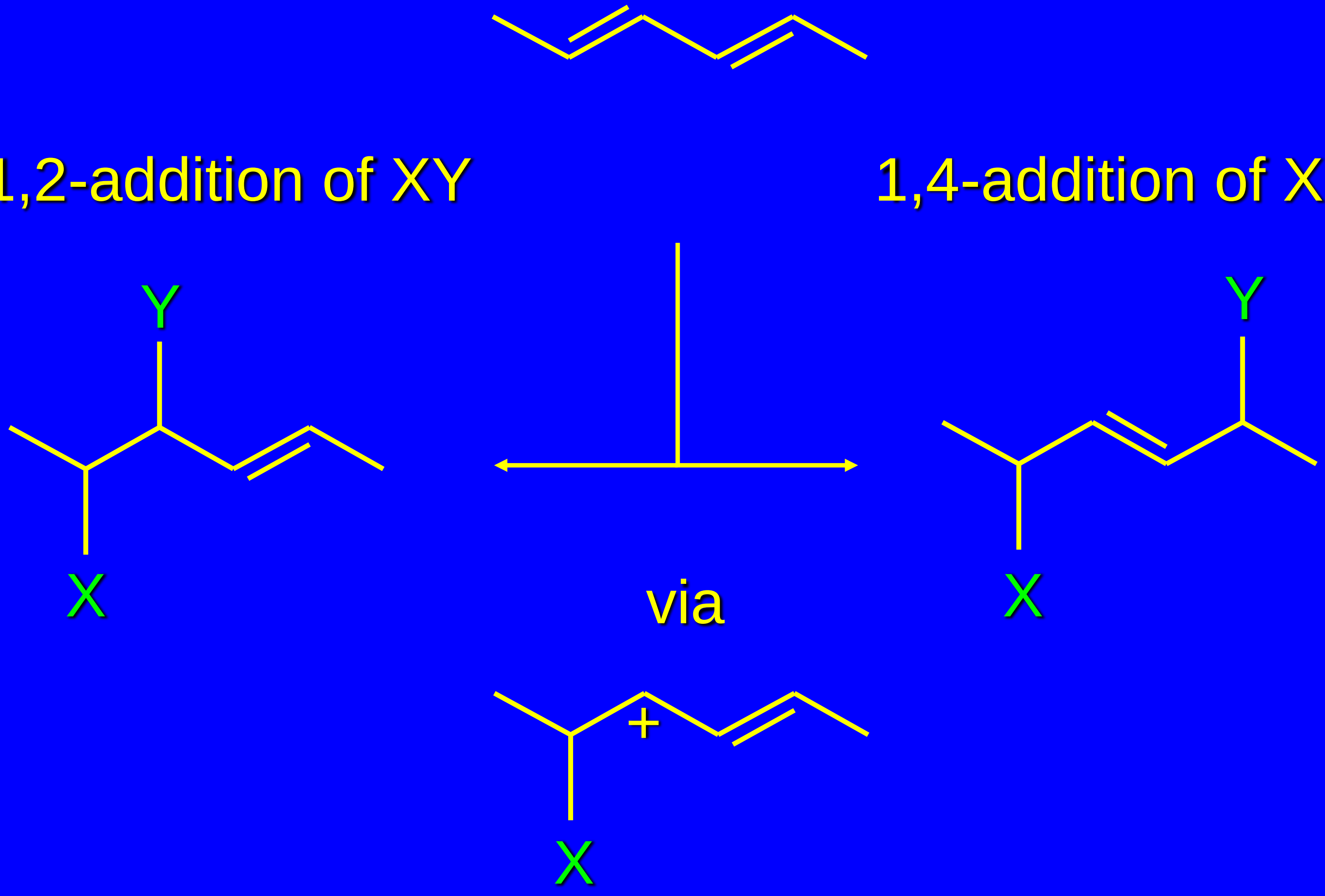
1,2-Addition versus 1,4-Addition



1,2-addition of XY

1,4-addition of XY

1,2-Addition versus 1,4-Addition

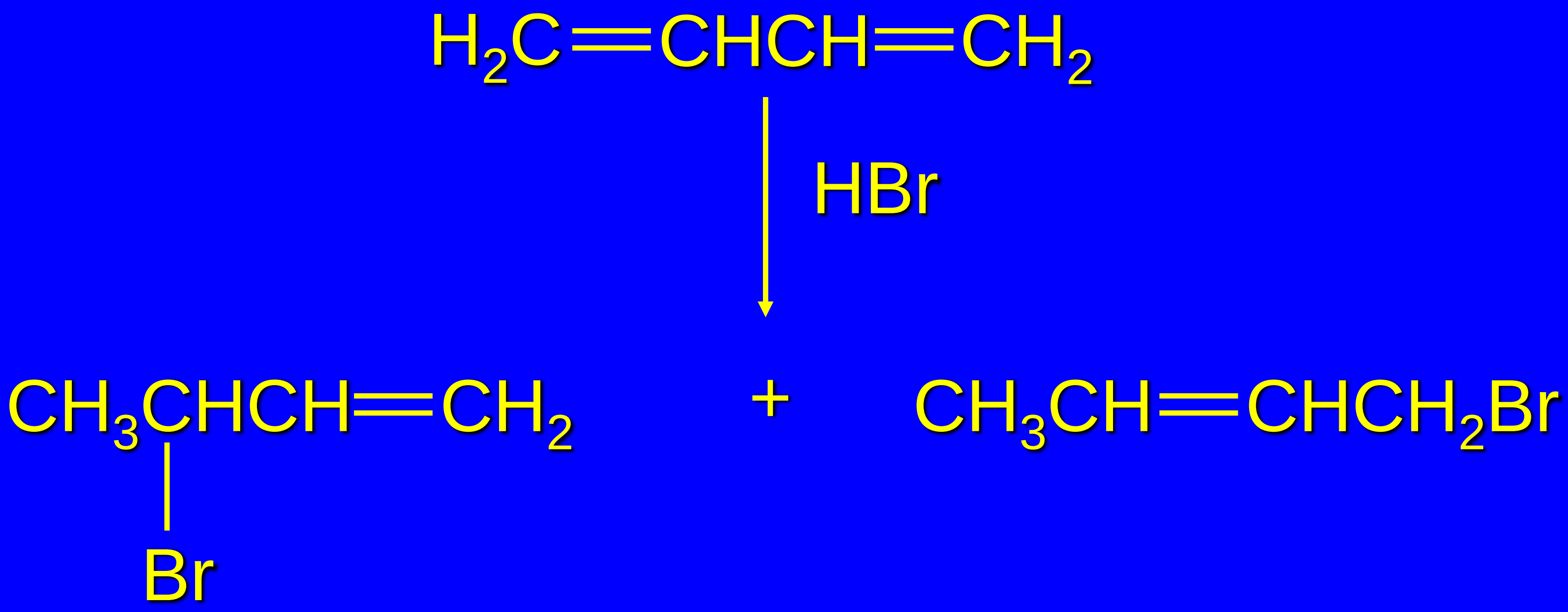


1,2-addition of XY

1,4-addition of XY

via

HBr Addition to 1,3-Butadiene



$$H_2C{=}CHCH{=}CH_2$$

$$\Big\downarrow\ \mathrm{HBr}$$

$$CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH{=}CH_2 \quad + \quad CH_3CH{=}CHCH_2Br$$

electrophilic addition

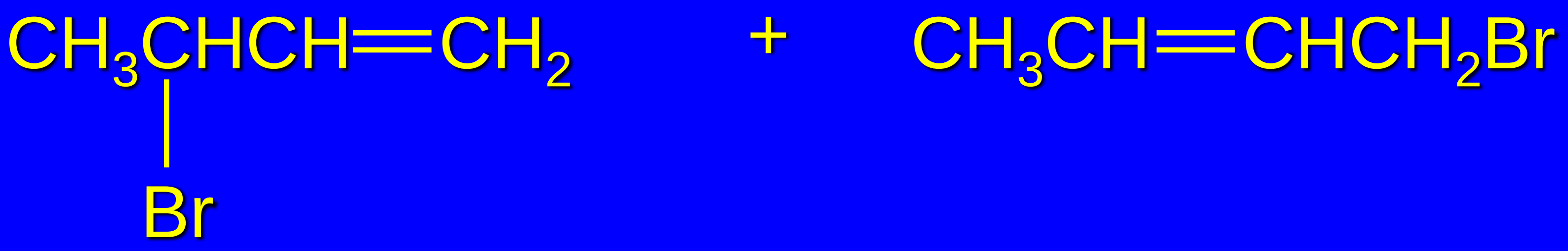
1,2 and 1,4-addition both observed

product ratio depends on temperature

Modelo explicativo

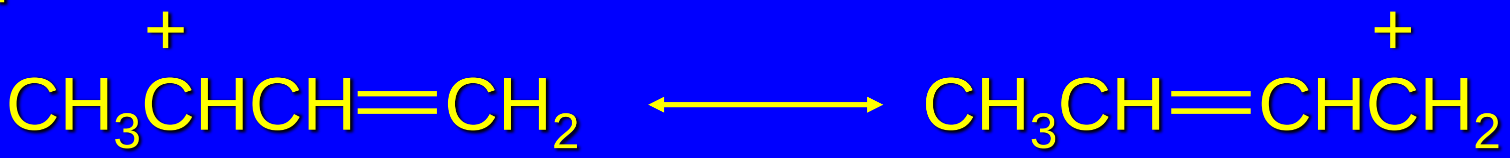
3-Bromo-1-butene is formed faster than 1-bromo-2-butene because allylic carbocations react with nucleophiles preferentially at the carbon that bears the greater share of positive charge.

Por que??????



$CH_3\underset{\displaystyle |\atop \displaystyle Br}{C}HCH{=}CH_2 \quad + \quad CH_3CH{=}CHCH_2Br$

via:



$CH_3\overset{+}{C}HCH{=}CH_2 \longleftrightarrow CH_3CH{=}CH\overset{+}{C}H_2$

Modelo explicativo

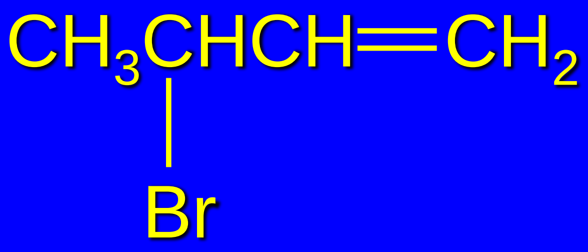
3-Bromo-1-butene is formed faster than 1-bromo-2-butene because allylic carbocations react with nucleophiles preferentially at the carbon that bears the greater share of positive charge.

$CH_3\underset{\underset{Br}{|}}{C}HCH{=}CH_2$ + $CH_3CH{=}CHCH_2Br$

formed faster

Modelo explicativo

1-Bromo-2-butene is more stable than 3-bromo-1-butene because it has a more highly substituted double bond.



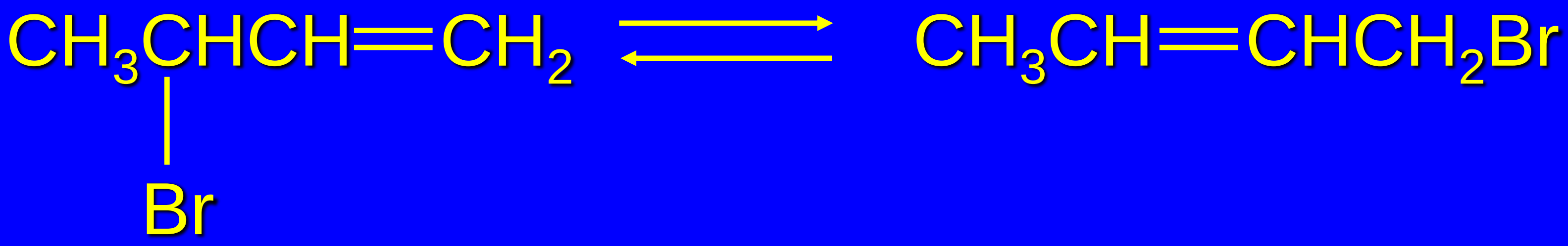
$CH_3\underset{\underset{\textstyle Br}{|}}{C}HCH{=}CH_2$ + $CH_3CH{=}CHCH_2Br$

1-Bromo-2-butene

more stable

Modelo explicativo

The two products equilibrate at 25°C.
Once equilibrium is established, the more stable isomer predominates.



$$CH_3\underset{\displaystyle Br}{\underset{|}{C}H}CH{=}CH_2 \rightleftharpoons CH_3CH{=}CHCH_2Br$$

major product at -80°C

(formed faster)

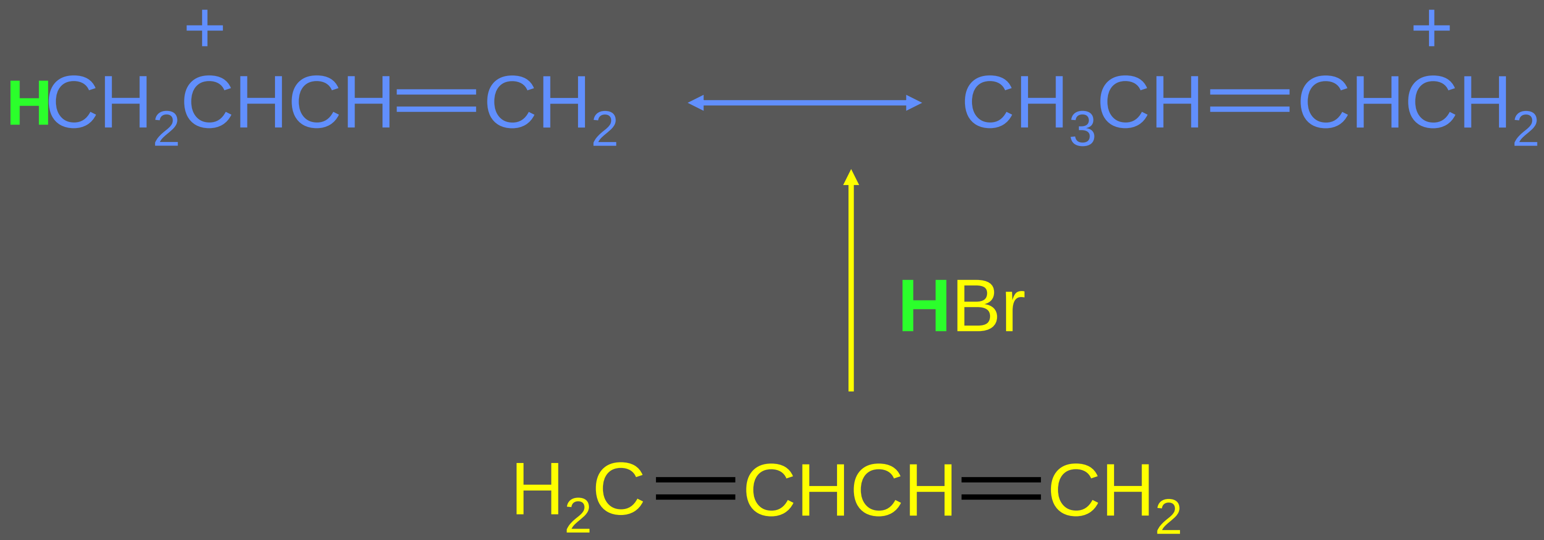
major product at 25°C

(more stable)

Kinetic Control versus Thermodynamic Control

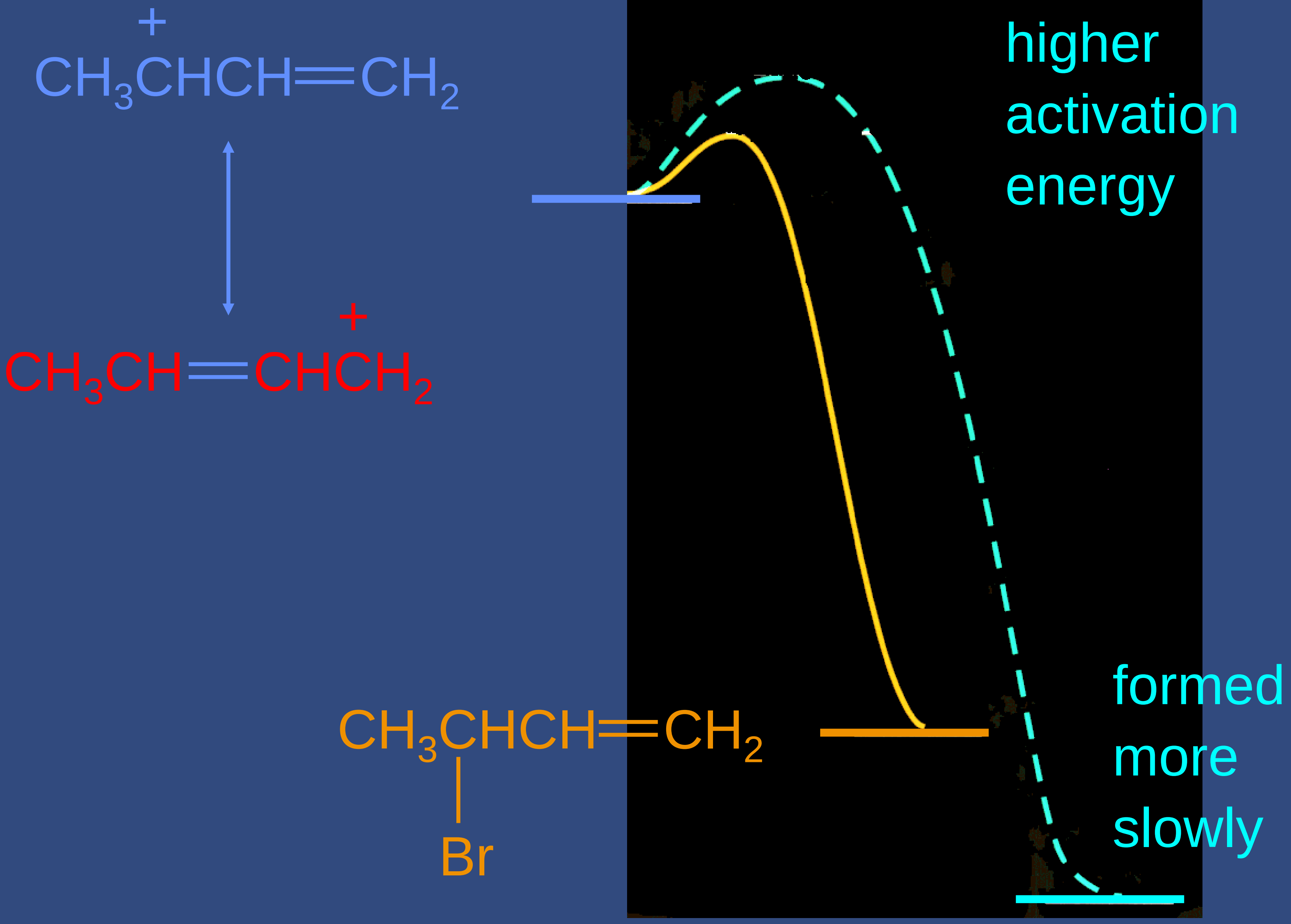
- **Kinetic control: major product is the one formed at the fastest rate**

- **Thermodynamic control: major product is the one that is the most stable**



$$\mathbf{H}CH_2\overset{+}{C}HCH{=}CH_2 \longleftrightarrow CH_3CH{=}CH\overset{+}{C}H_2$$

$$H_2C{=}CHCH{=}CH_2 \xrightarrow{\mathbf{H}Br}$$



$$CH_3\overset{+}{C}HCH{=}CH_2$$

$$\updownarrow$$

$$CH_3CH{=}CH\overset{+}{C}H_2$$

$$CH_3\underset{Br}{\underset{|}{C}}HCH{=}CH_2$$

higher
activation
energy

formed
more
slowly

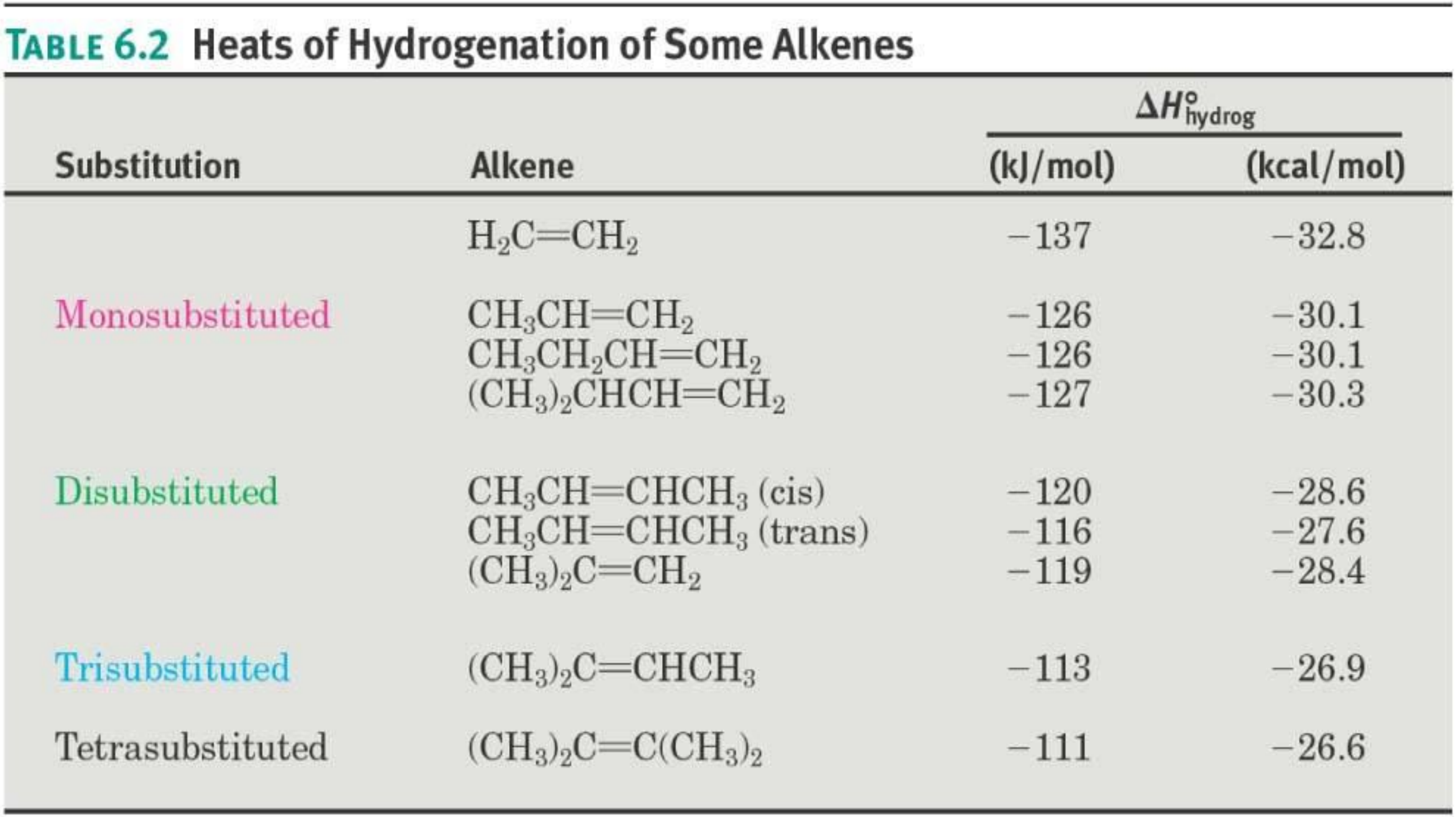
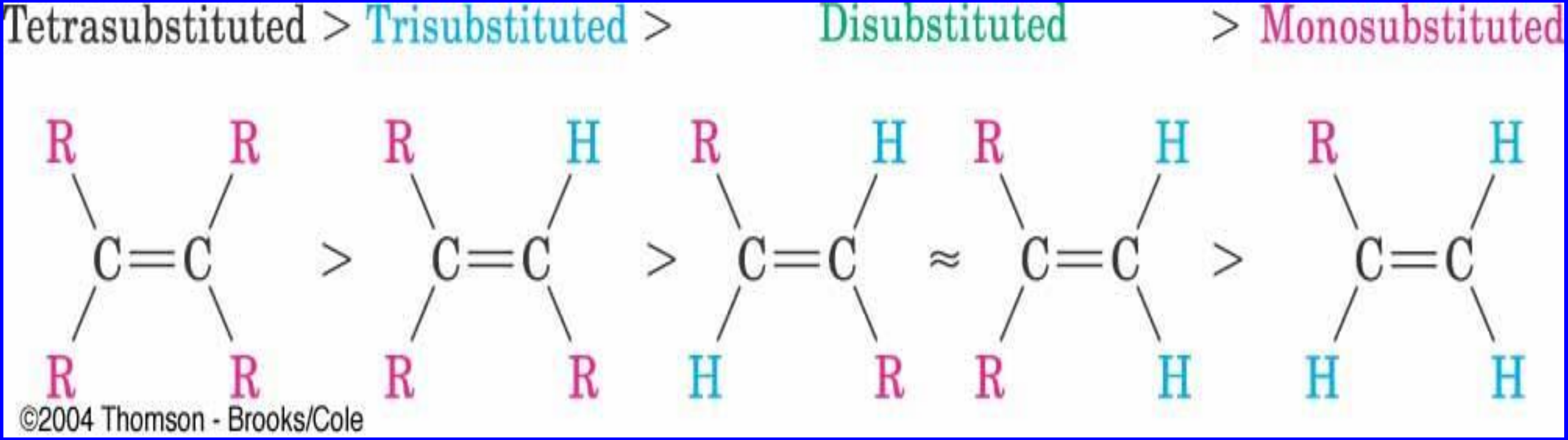


TABLE 6.2 Heats of Hydrogenation of Some Alkenes

Substitution	Alkene	$\Delta H^\circ_{\text{hydrog}}$ (kJ/mol)	$\Delta H^\circ_{\text{hydrog}}$ (kcal/mol)
	$H_2C{=}CH_2$	−137	−32.8
Monosubstituted	$CH_3CH{=}CH_2$	−126	−30.1
	$CH_3CH_2CH{=}CH_2$	−126	−30.1
	$(CH_3)_2CHCH{=}CH_2$	−127	−30.3
Disubstituted	$CH_3CH{=}CHCH_3$ (cis)	−120	−28.6
	$CH_3CH{=}CHCH_3$ (trans)	−116	−27.6
	$(CH_3)_2C{=}CH_2$	−119	−28.4
Trisubstituted	$(CH_3)_2C{=}CHCH_3$	−113	−26.9
Tetrasubstituted	$(CH_3)_2C{=}C(CH_3)_2$	−111	−26.6

Alkene Stabilities from ΔH's:

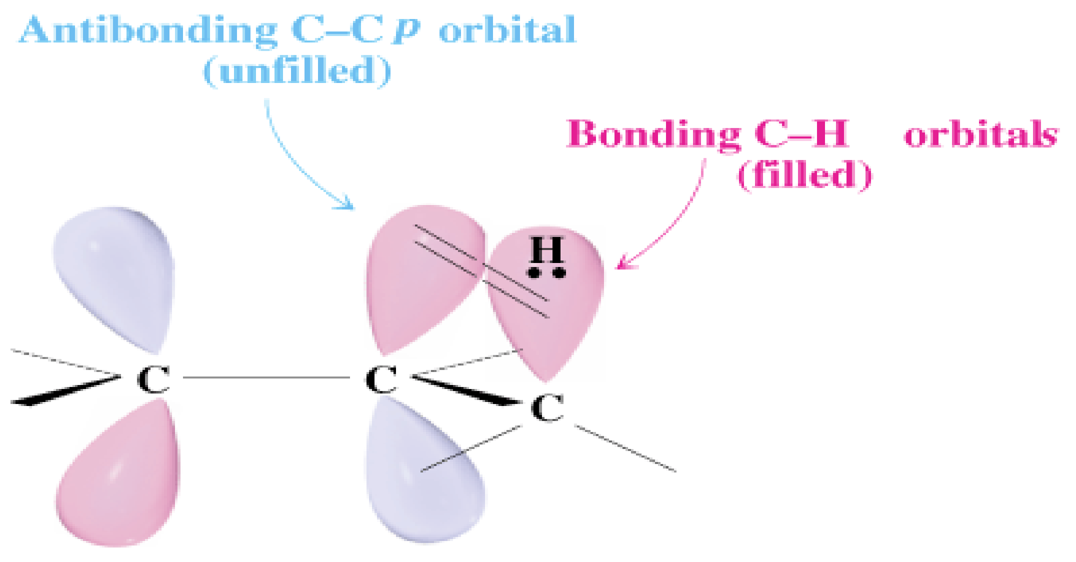


©2004 Thomson - Brooks/Cole

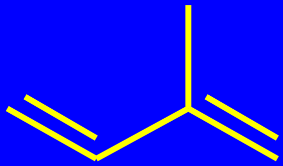
Diminui

Hiperconjugação

- Elétrons no orbital vizinho σ (lig. C-H) estabiliza o orbital antiligante π vazio – Interação com efeito líquido positivo interaction
- Grupos Alquila interagem melhor que H

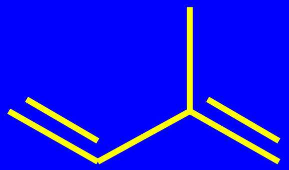


Addition of hydrogen chloride to 2-methyl-1,3-butadiene is a kinetically controlled reaction and gives one product in much greater amounts than any isomers. What is this product?



$+ \quad HCl \longrightarrow \quad ?$

Think mechanistically.



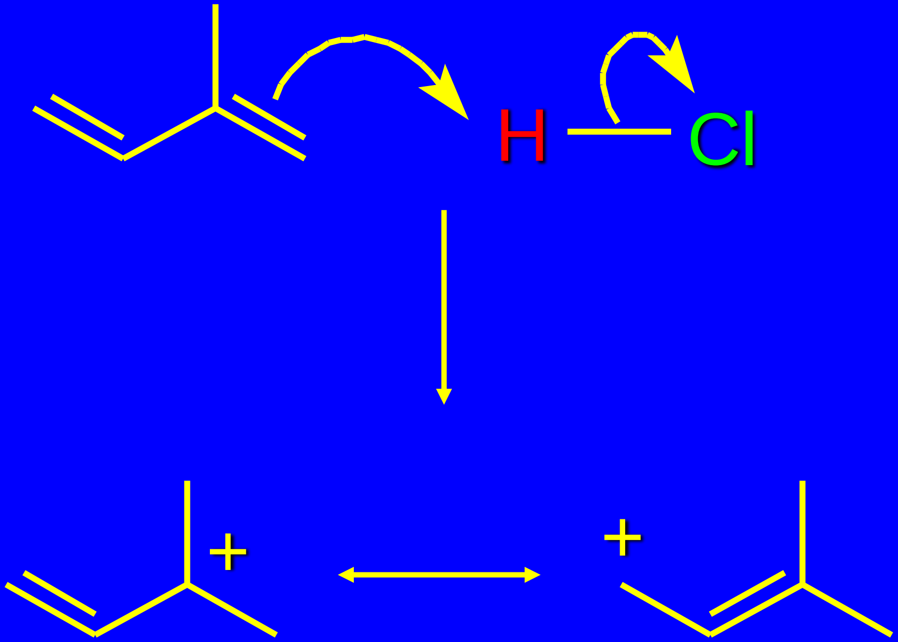
\+ HCl

Protonation occurs:

- at end of diene system
- in direction that gives most stable carbocation

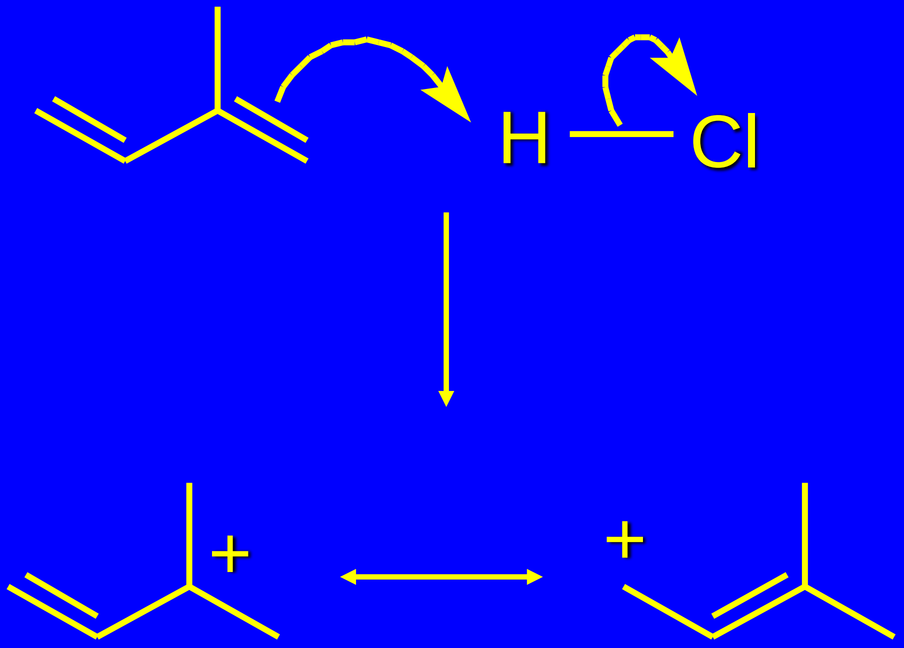
Kinetically controlled product corresponds to attack by chloride ion at carbon that has the greatest share of positive charge in the carbocation

Think mechanistically

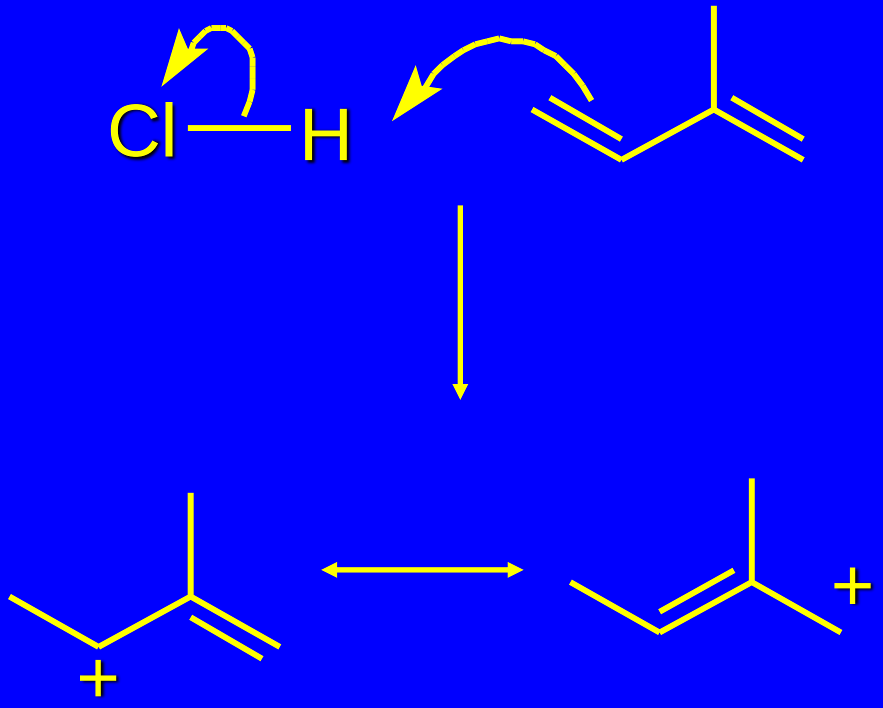


one resonance form is
tertiary carbocation;
other is primary

Think mechanistically

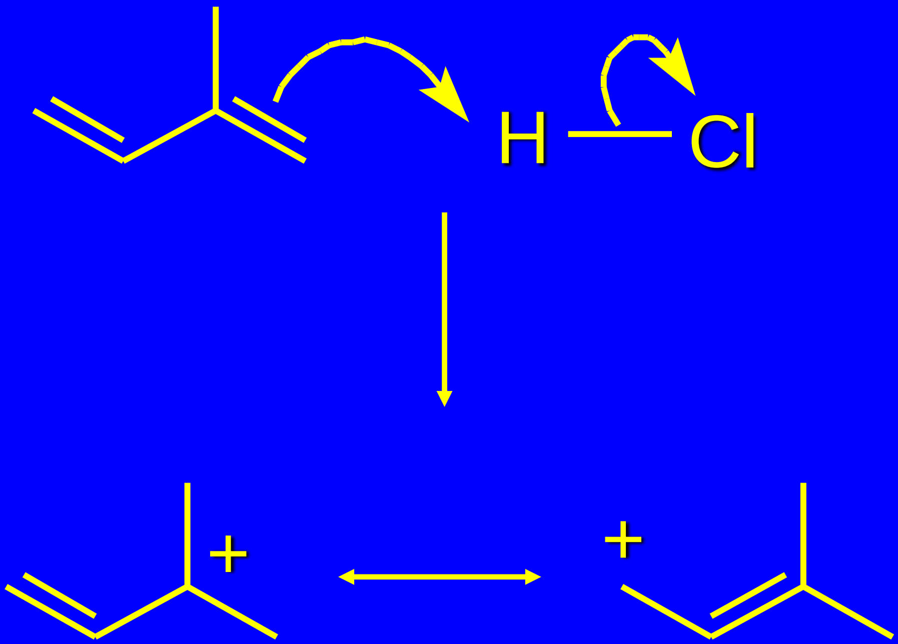


one resonance form is
tertiary carbocation;
other is primary



one resonance form is
secondary carbocation;
other is primary

Think mechanistically

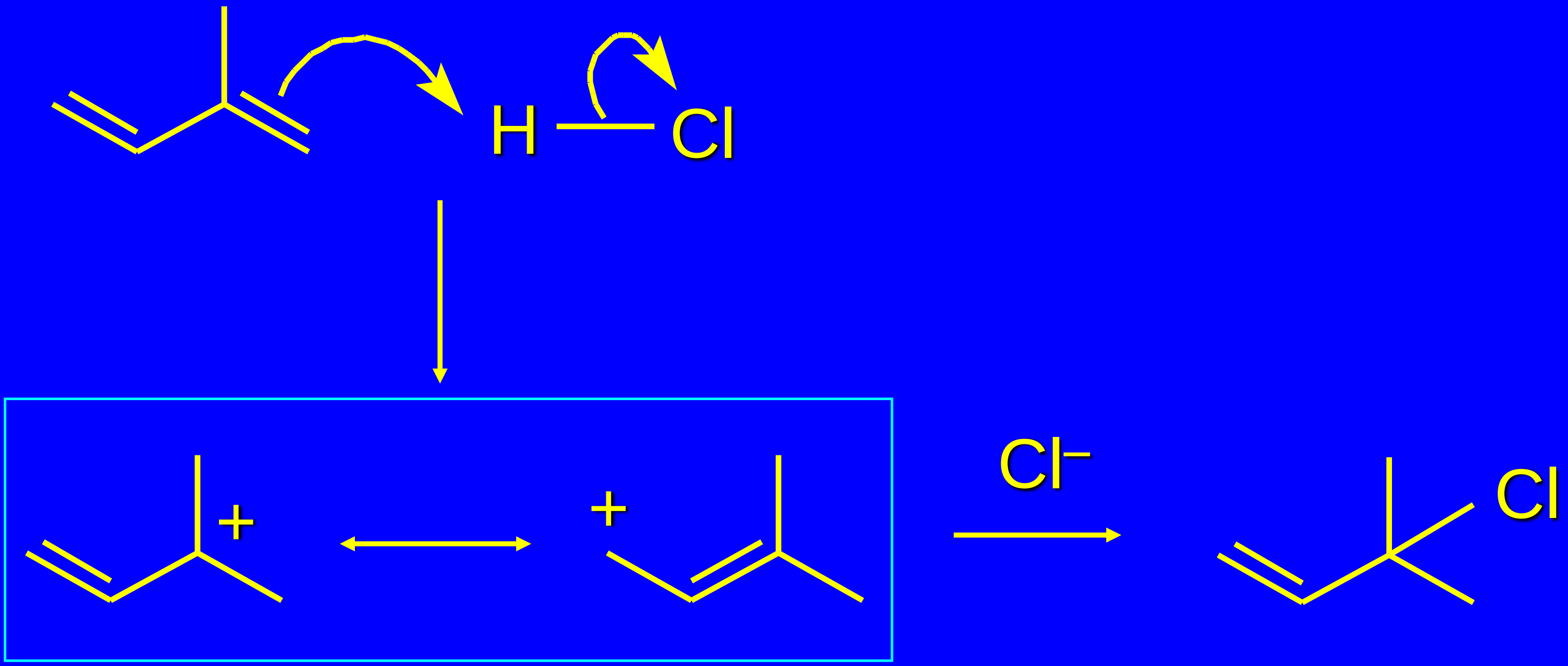


one resonance form is
tertiary carbocation;
other is primary

More stable carbocation

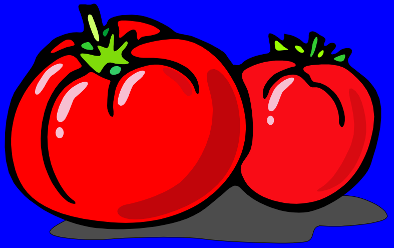
Is attacked by chloride ion at carbon that bears greater share of positive charge

Think mechanistically

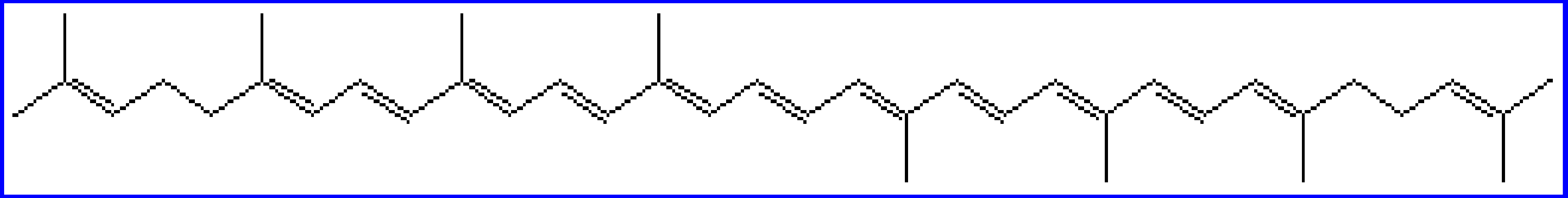


one resonance form is tertiary carbocation; other is primary

major product

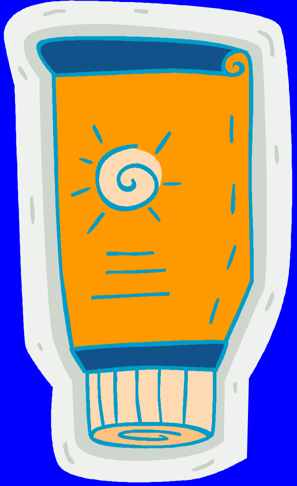


Tomates

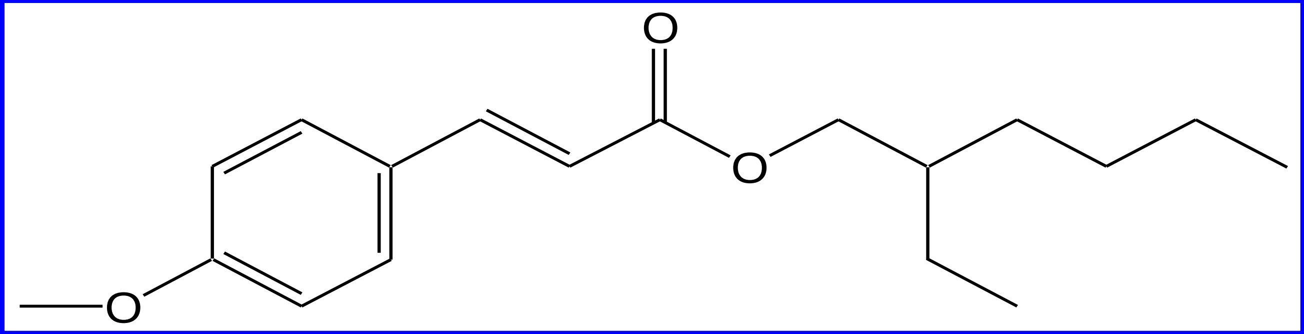


Licopeno

- Pigmento vermelho dos tomates
- Polieno Conjugado
- Antioxidante, neutraliza radicais Livres



Sunscreen



Octyl methoxycinnamate

- Conjugated cinnamate ester
- Found in Coppertone Sport, Bullfrog Sunblock, Hawaiian Tropic Water Sport
- Absorbs radiation, preventing skin damage