

# Estabilidade Relativa dos Dienos

## Calor de Hidrogenação



252 kJ/mol

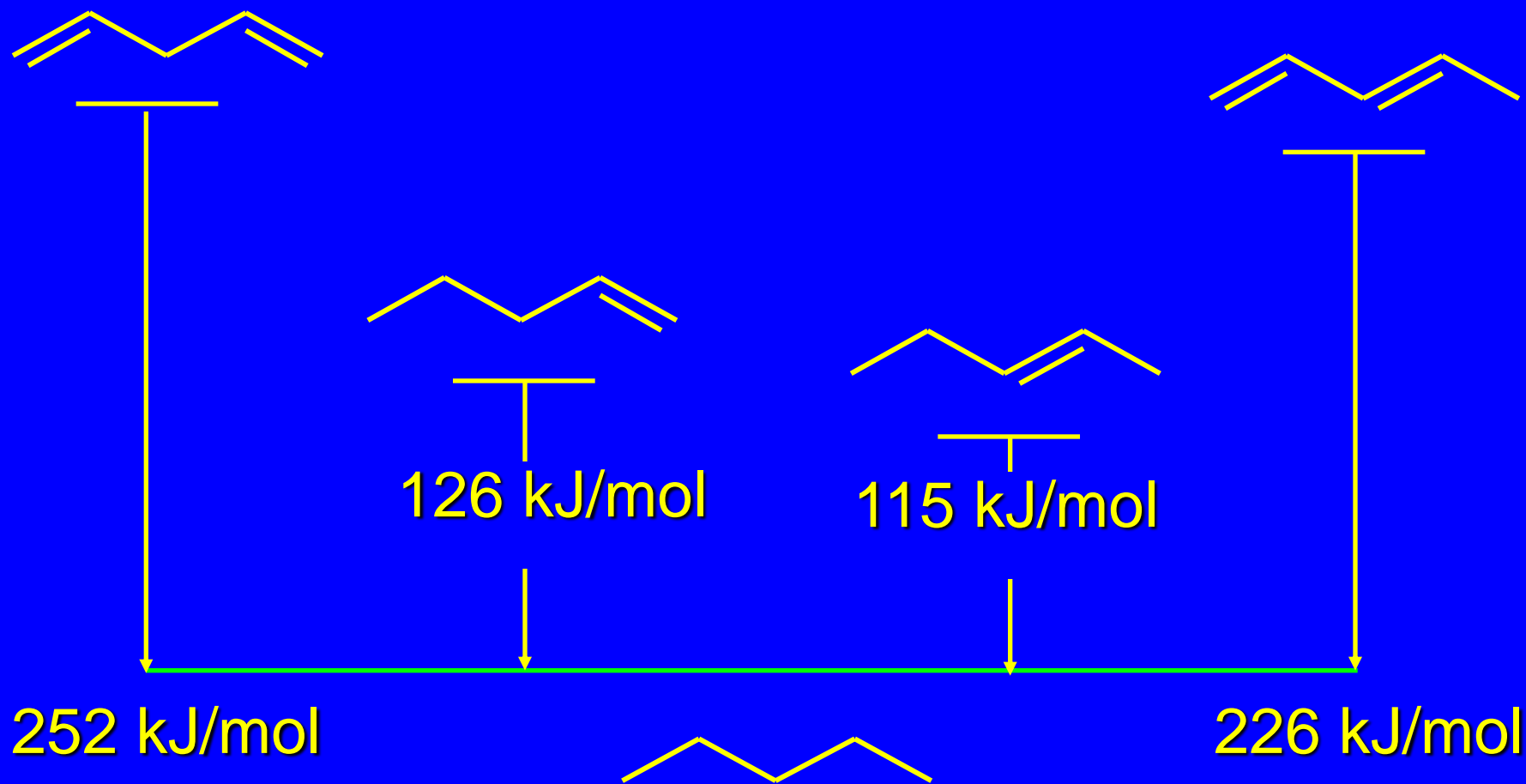
1,3-pentadieno é 26 kJ/mol mais estável do que o 1,4-pentadieno, mas parte desta estabilização é devida à presença de uma dupla ligação mais substituída.



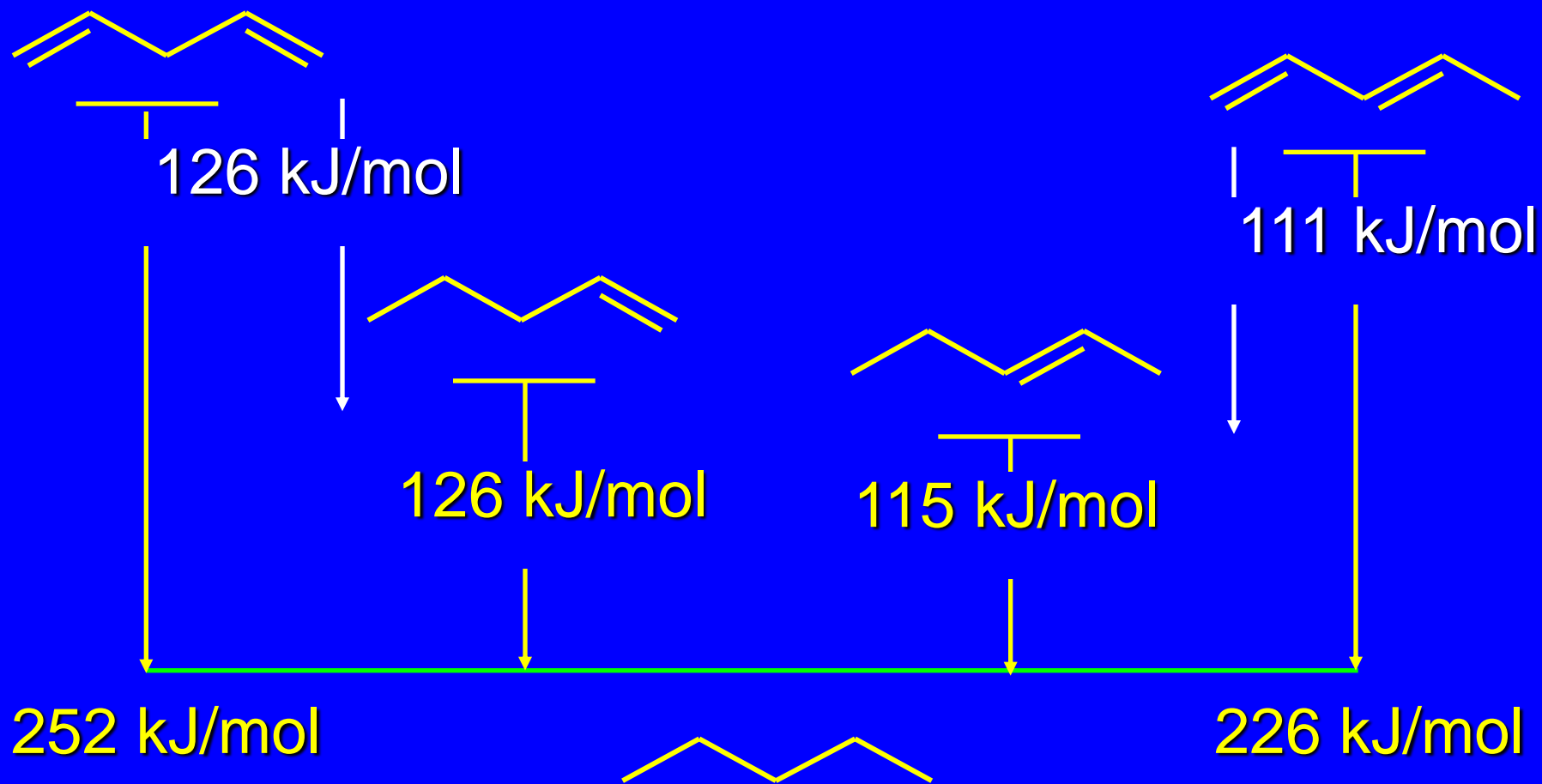
226 kJ/mol



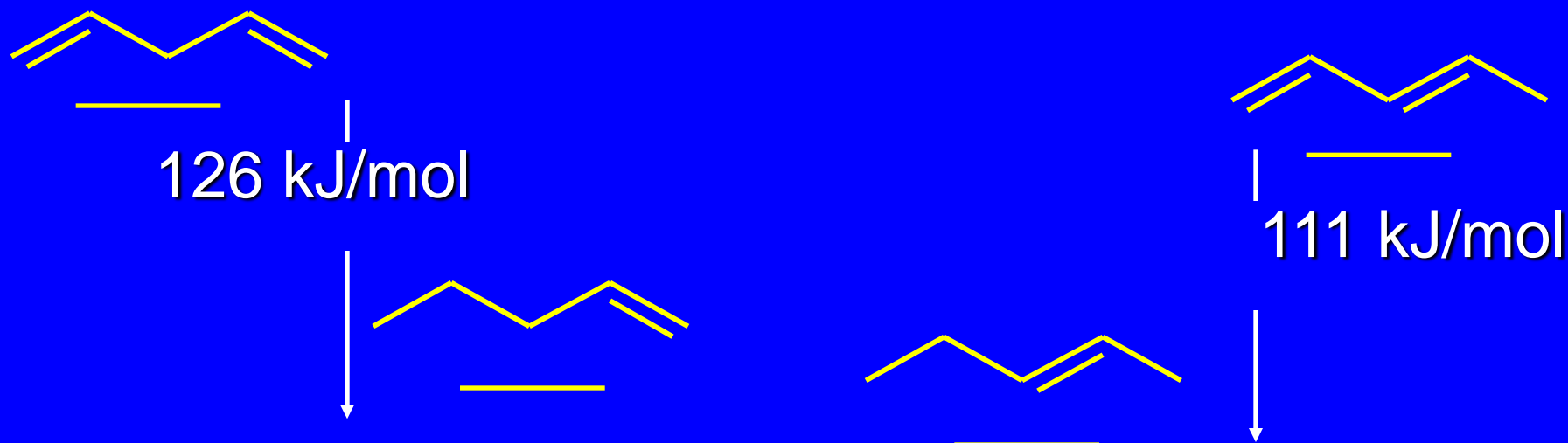
# Calor de Hidrogenação



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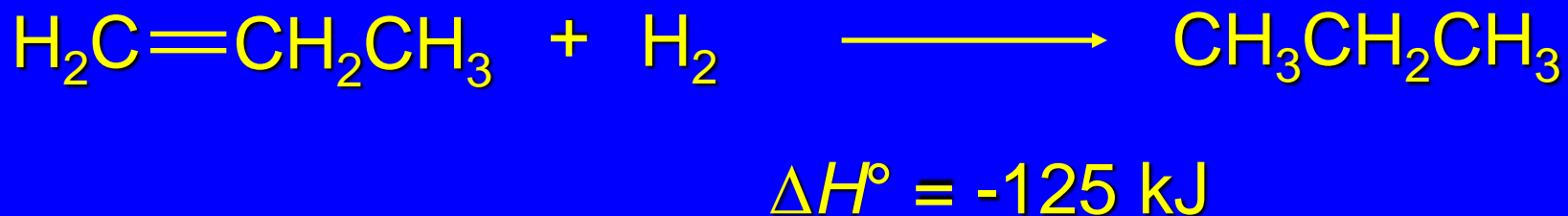
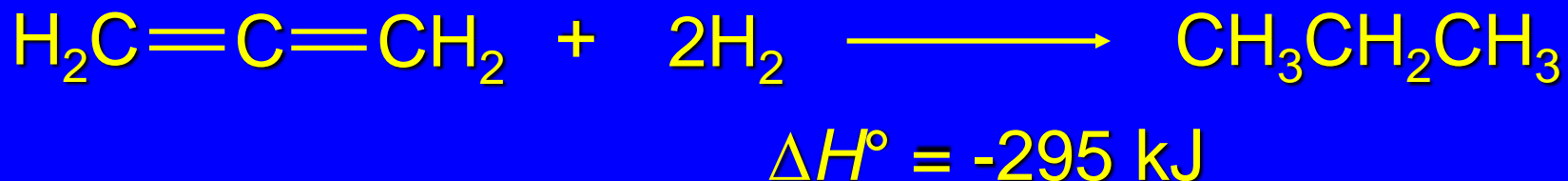


este adicional de 15 kJ/mol é conhecido por nomes diferentes:

Energia de estabilização  
Energia de deslocalização  
Energia de Ressonância

## Heats of Hydrogenation

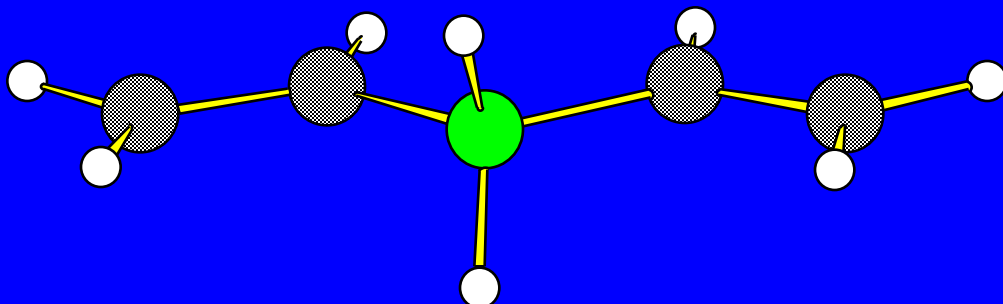
Cumulated double bonds have relatively high heats of hydrogenation



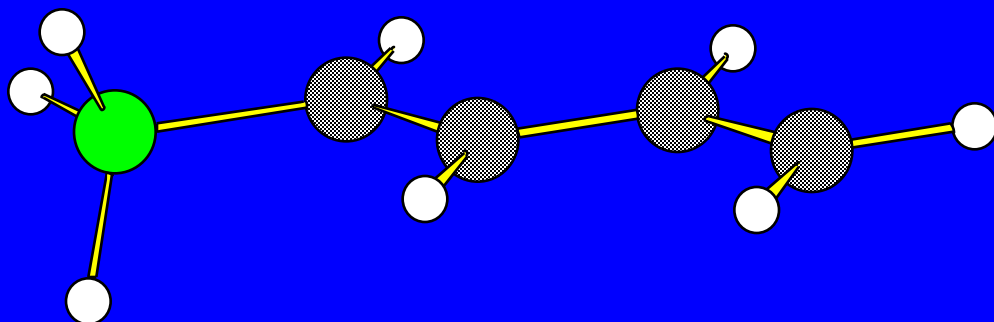
# 10.7

## Bonding in Conjugated Dienes

## Dieno aislado



1,4-pentadieno

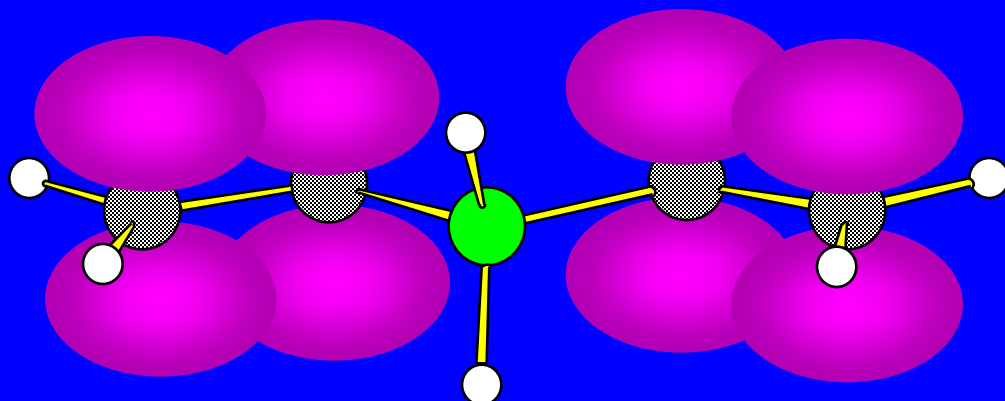


1,3-pentadieno

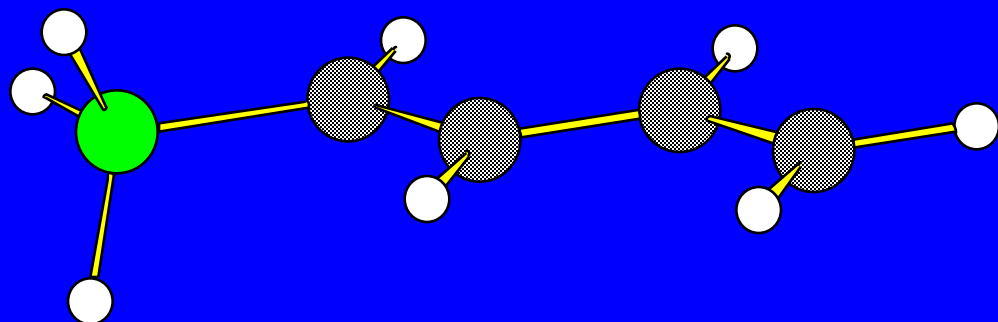
## Dieno conjugado



## Dieno isolado



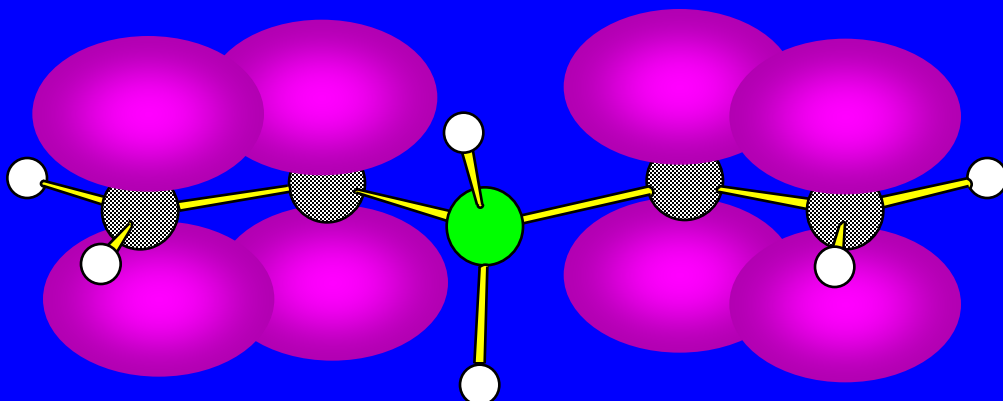
Ligações  $\pi$  são independentes uma da outra



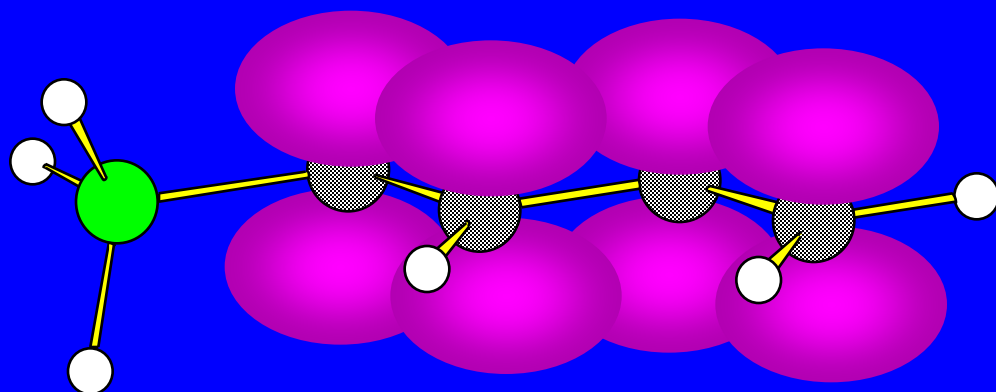
1,3-pentadiene

## Dieno conjugado

## Dieno isolado



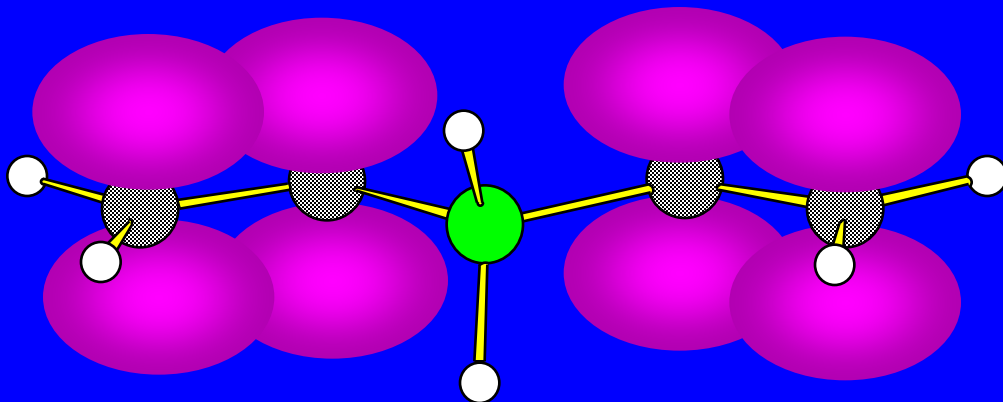
Ligações  $\pi$  são independentes uma da outra



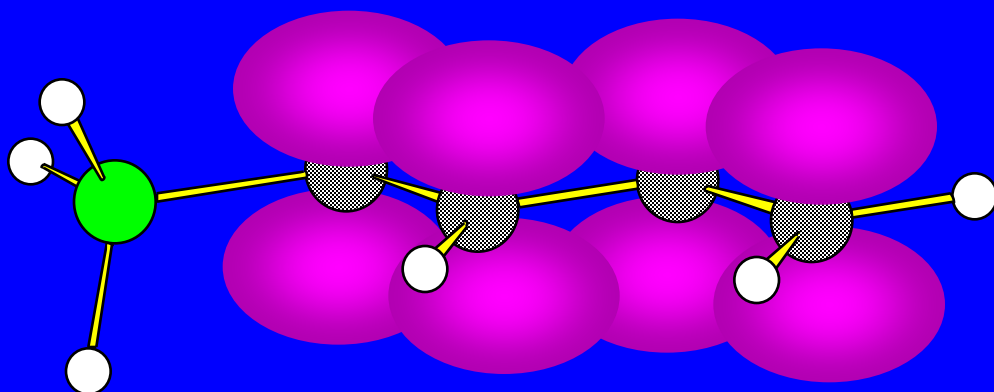
## Dieno conjugado

Orbitais  $p$  se sobrepõem, estendendo a Ligação  $\pi$ , a qual passa a envolver quatro carbonos

## Dieno isolado



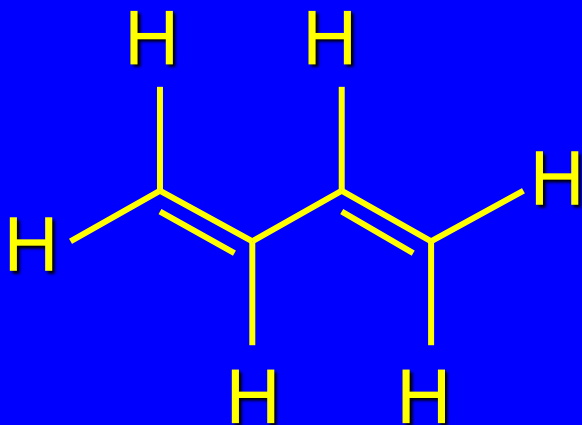
Menor  
deslocaização dos  
elétrons; Menos  
estável



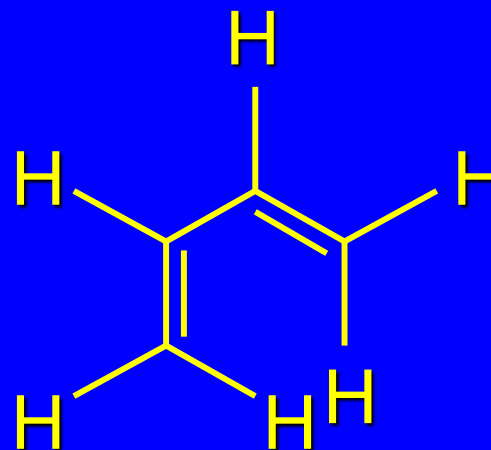
## Dieno conjugado

Maior  
deslocalização  
dos elétrons;  
mais estável

# Conformations of Dienes



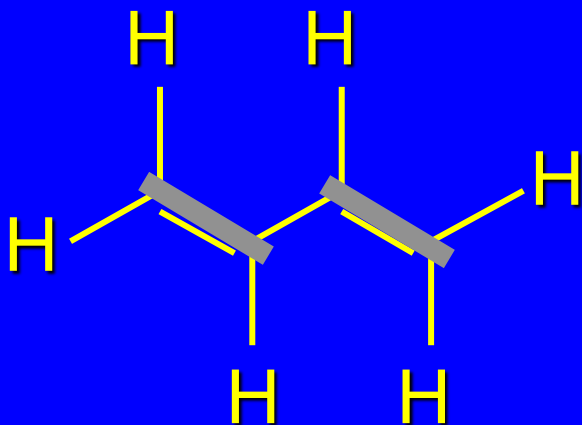
s-trans



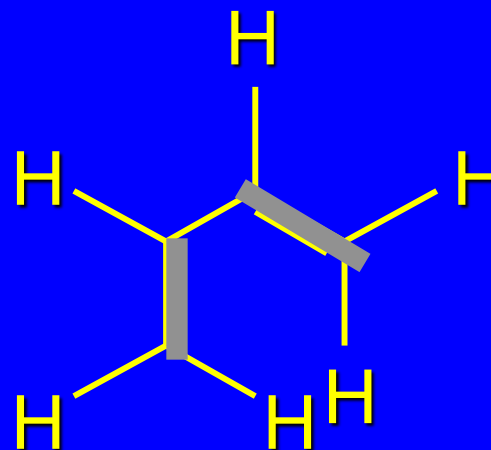
s-cis

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



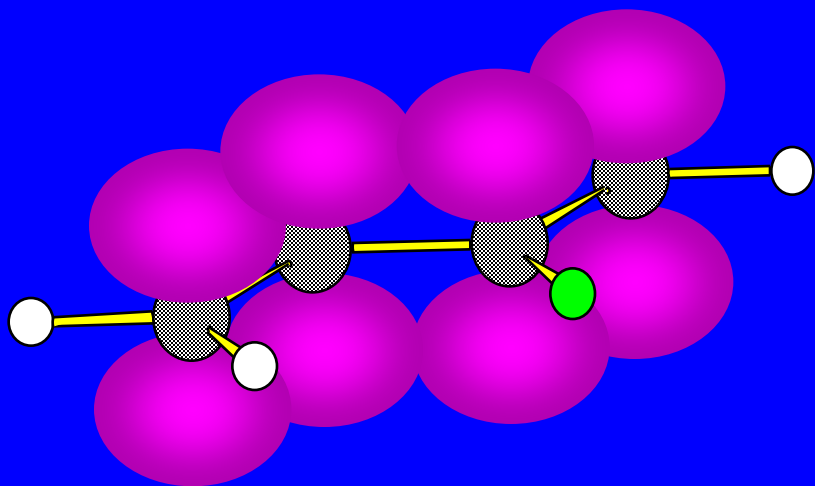
s-trans



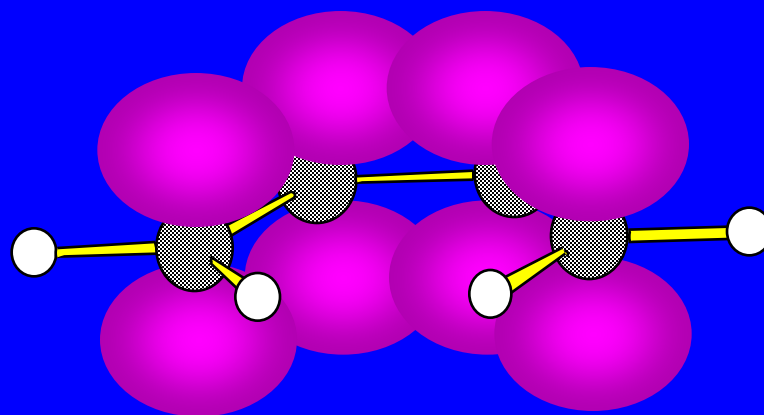
s-cis

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# Conformations of Dienes



s-trans

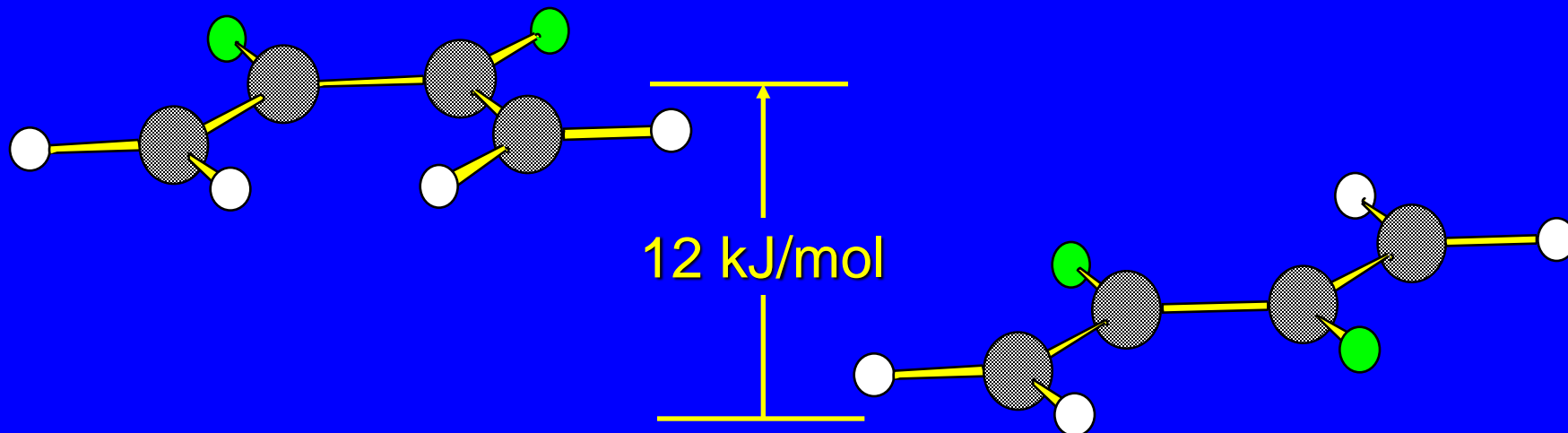


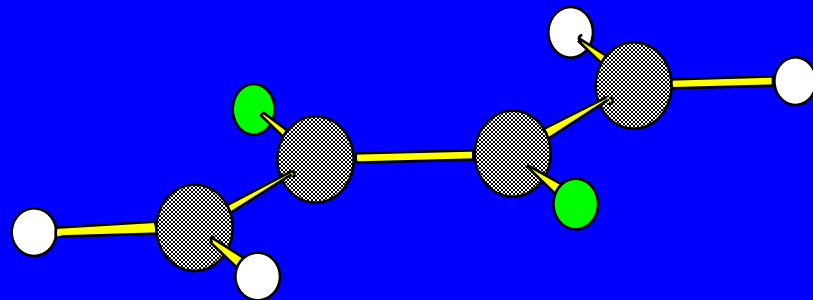
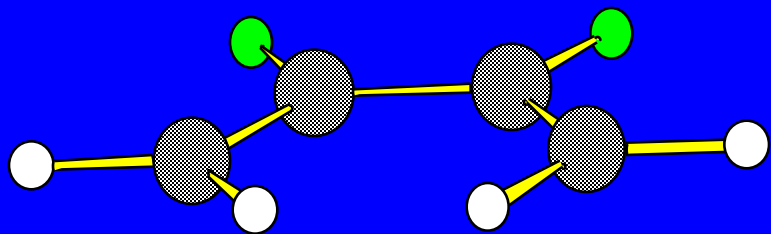
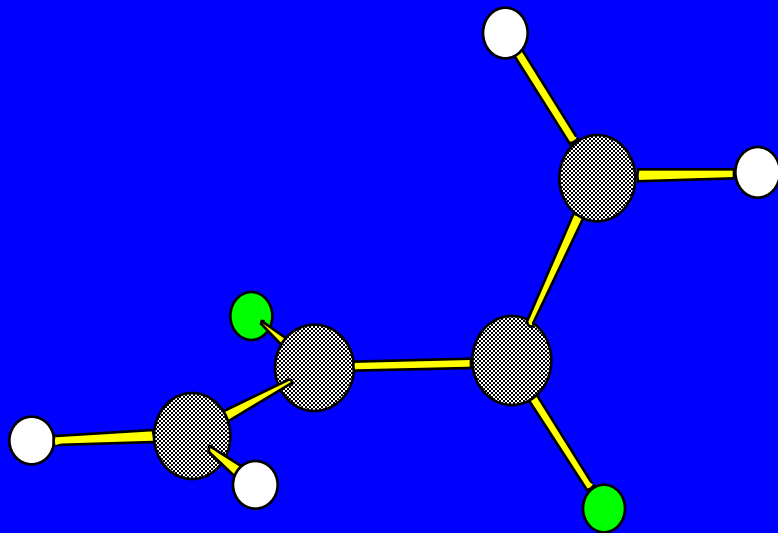
s-cis

Both conformations allow electron delocalization via overlap of  $p$  orbitals to give extended  $\pi$  system

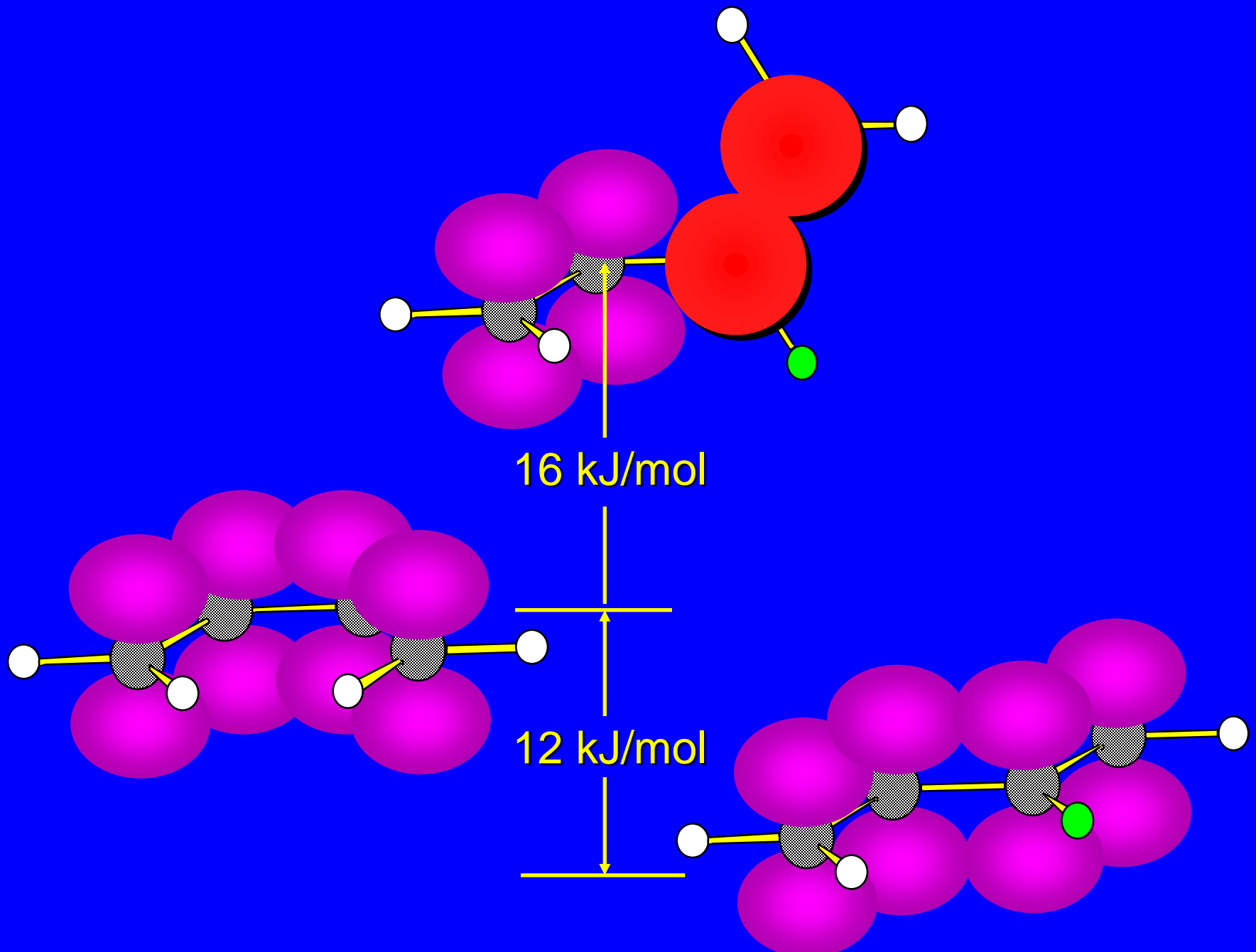
## *s-trans* is more stable than *s-cis*

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

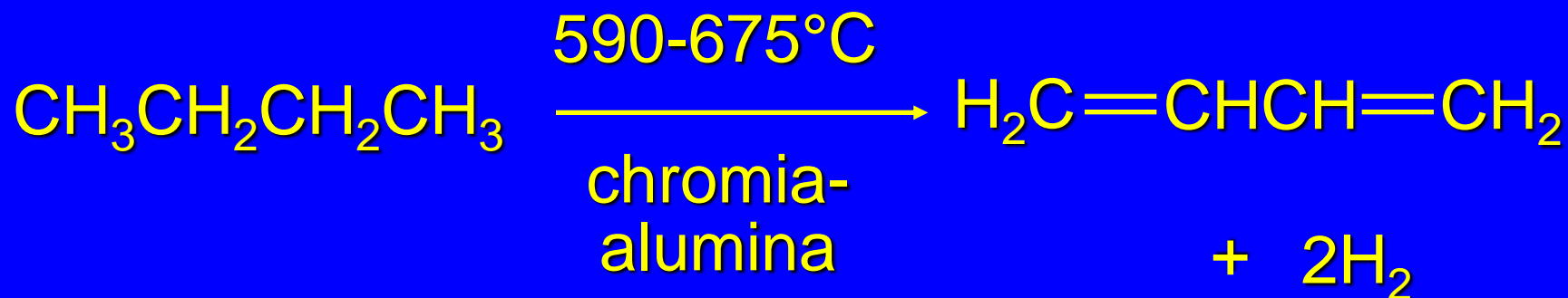








## 1,3-Butadiene



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

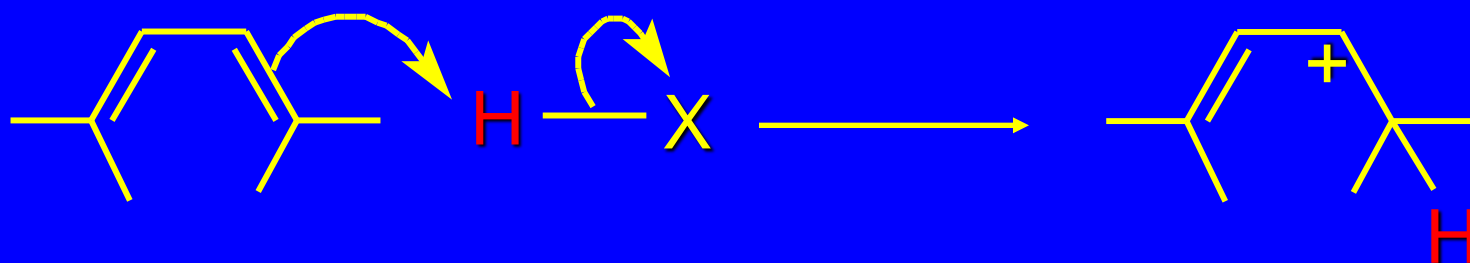
*isolated dienes:* double bonds react independently of one another

*cumulated dienes:* specialized topic

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

Addition of Hydrogen Halides  
to  
Conjugated Dienes

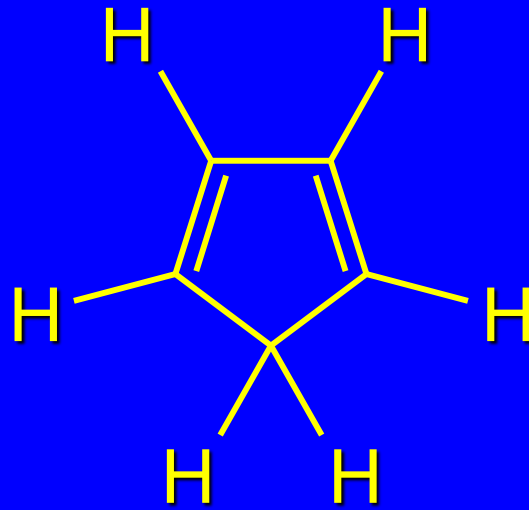
## *Electrophilic Addition to Conjugated Dienes*



**Proton** adds to end of diene system

Carbocation formed is allylic

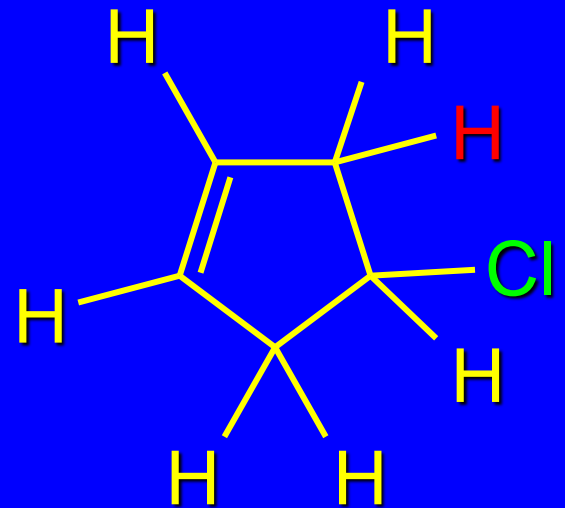
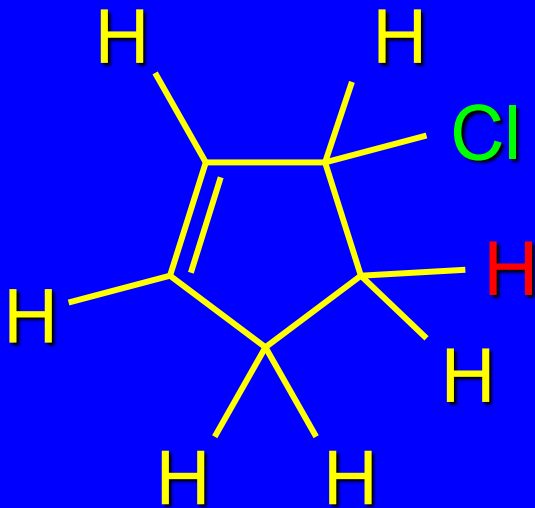
*Example:*



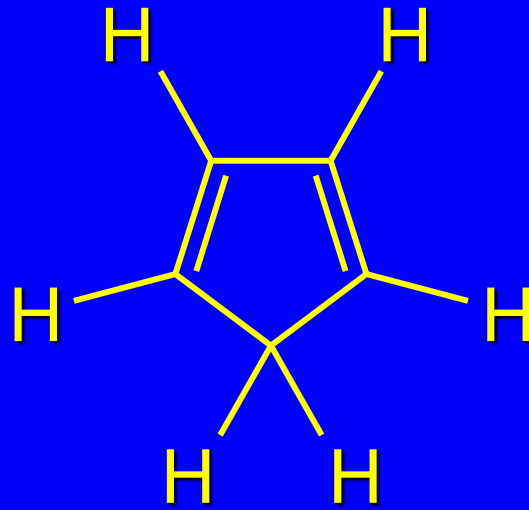
HCl

?

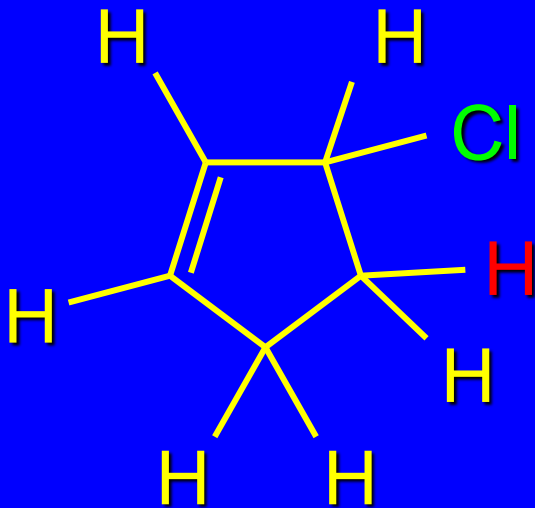
?



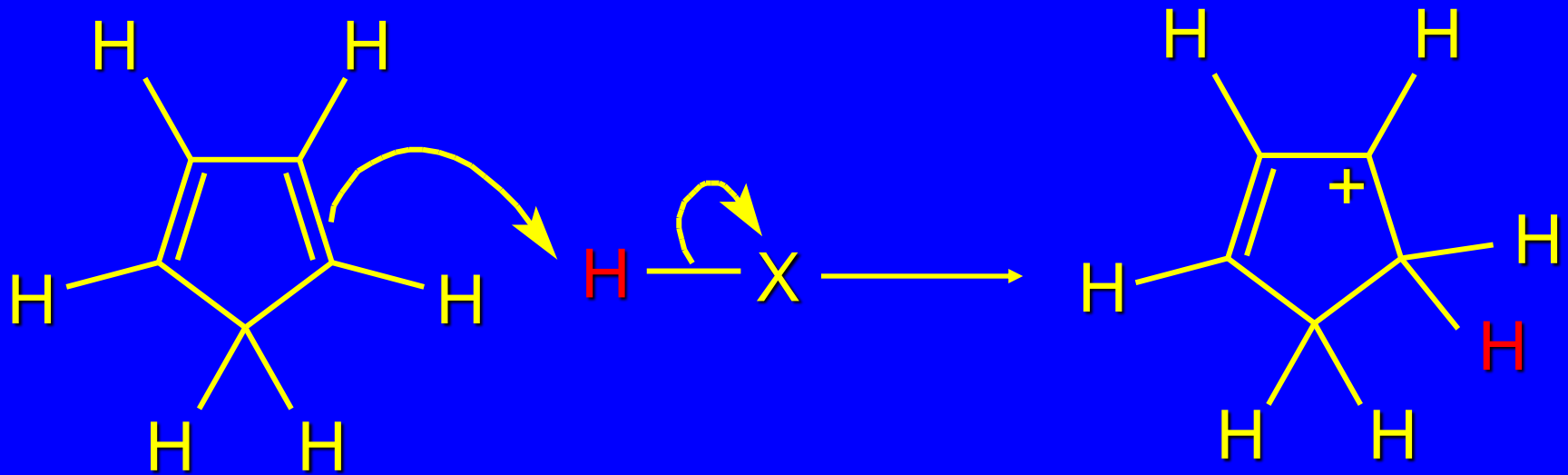
*Example:*



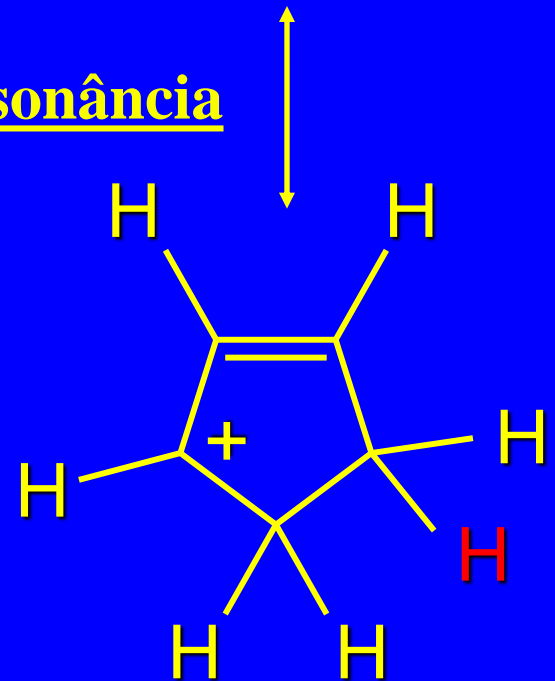
HCl



via:

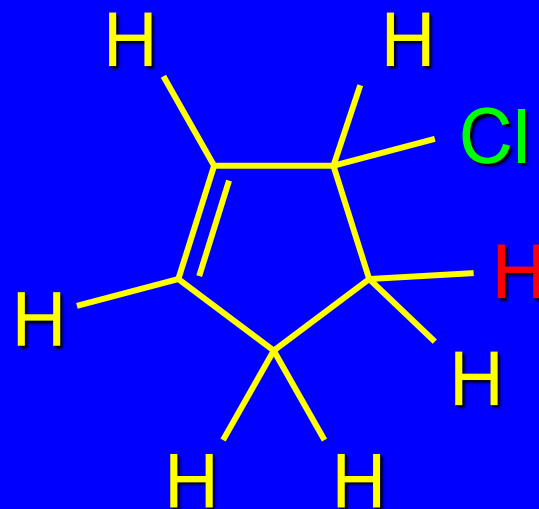
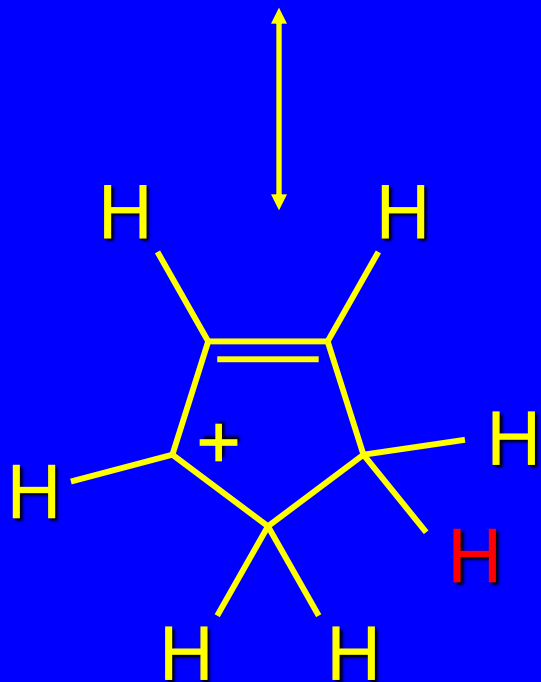
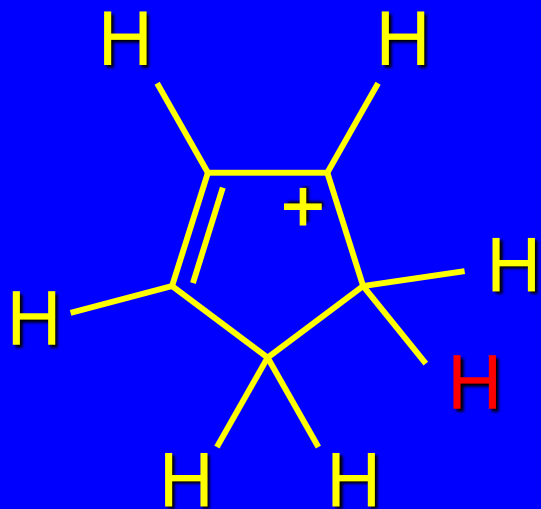


Estabilização por ressonância

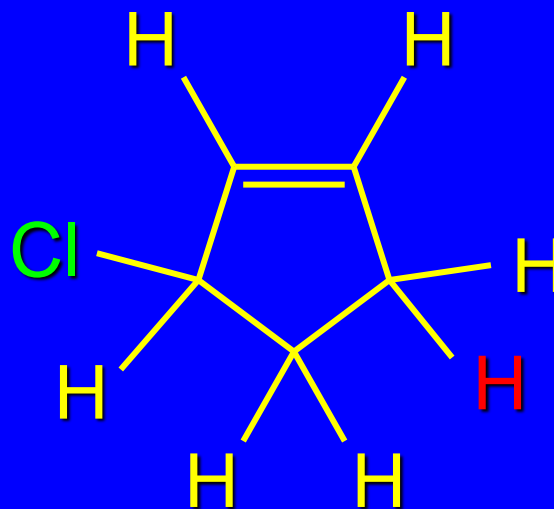




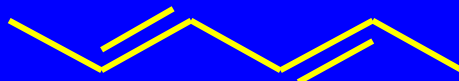
## Segundo passo: ataque do nucleófilo



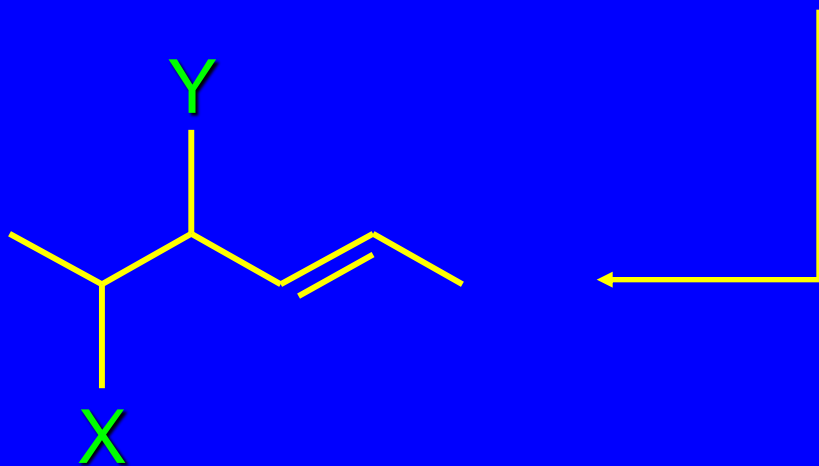
3-Chlorocyclopentene



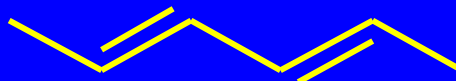
# 1,2-Addition versus 1,4-Addition



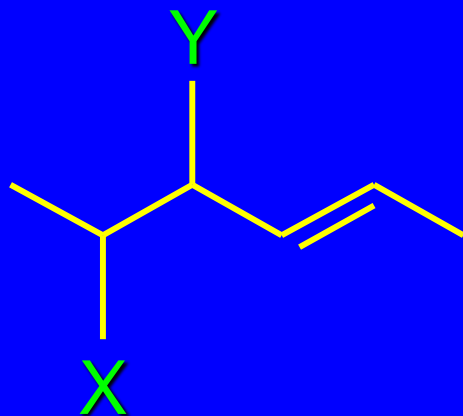
1,2-addition of XY



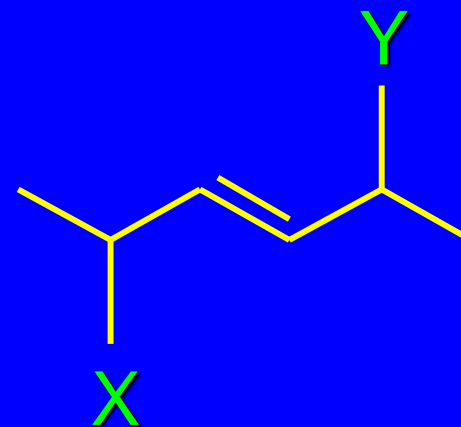
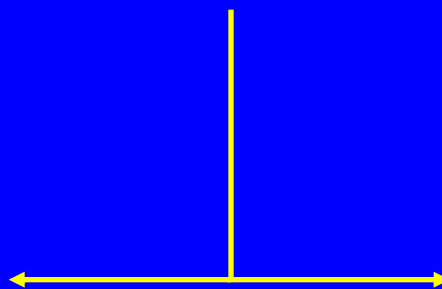
# 1,2-Addition versus 1,4-Addition



1,2-addition of XY



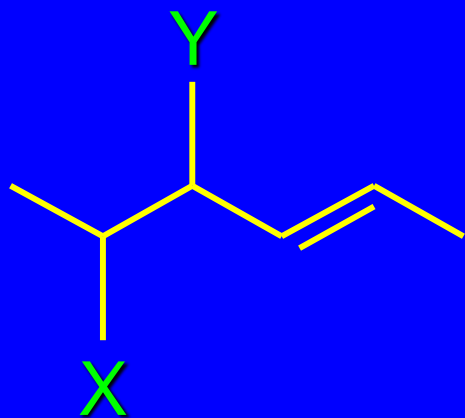
1,4-addition of XY



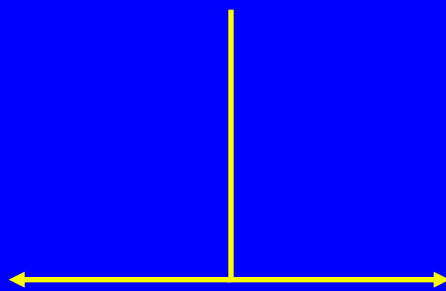
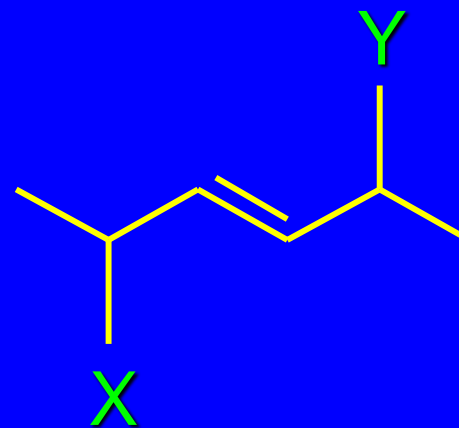
# 1,2-Addition versus 1,4-Addition



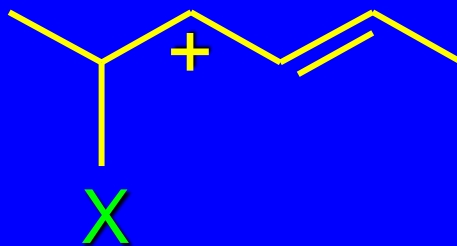
1,2-addition of XY



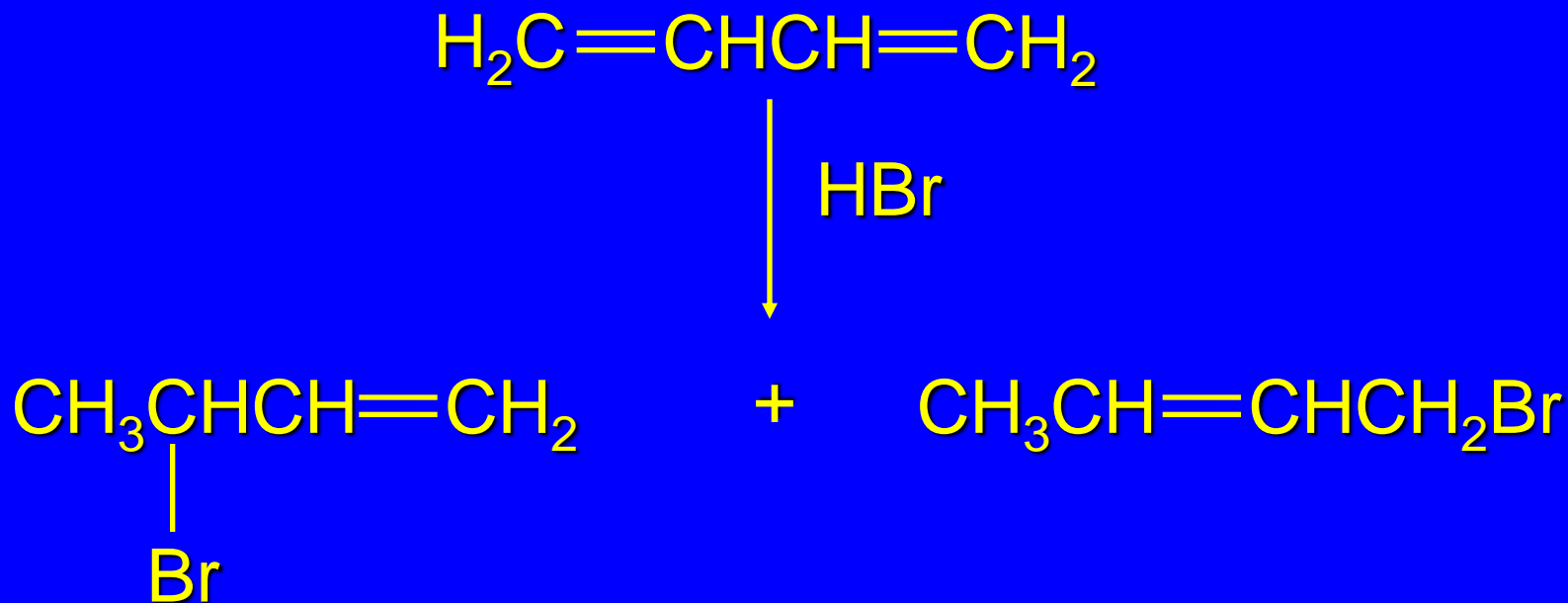
1,4-addition of XY



via



## HBr Addition to 1,3-Butadiene



electrophilic addition

1,2 and 1,4-addition both observed

product ratio depends on temperature

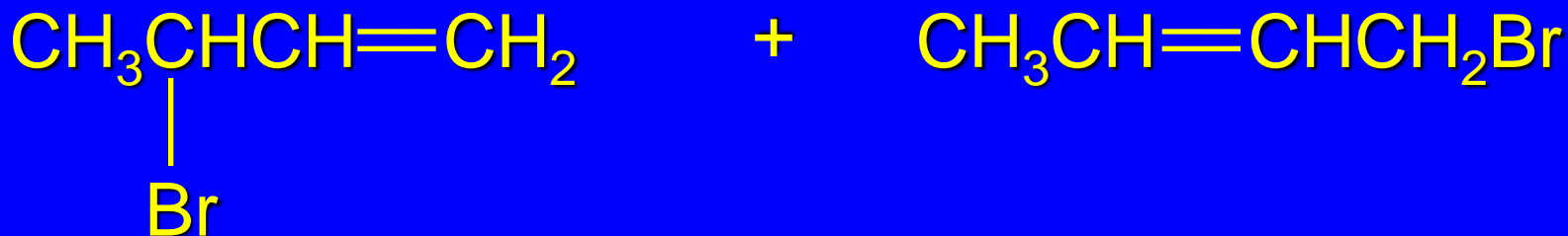
*Kinetic Control*  
*versus*  
*Thermodynamic Control*

- **Kinetic control:** major product is the one formed at the fastest rate
- **Thermodynamic control:** major product is the one that is the most stable

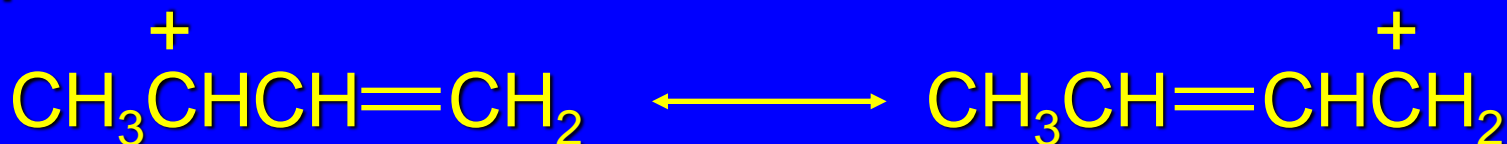
## Modelo explicativo

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??????

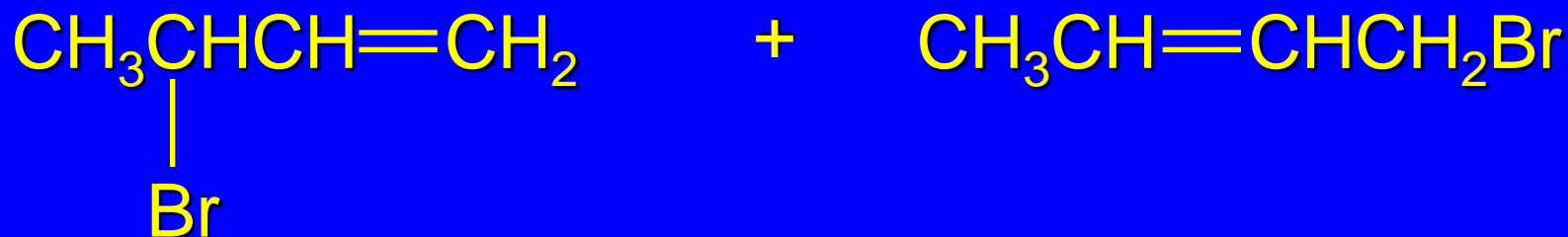


via:



## 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.

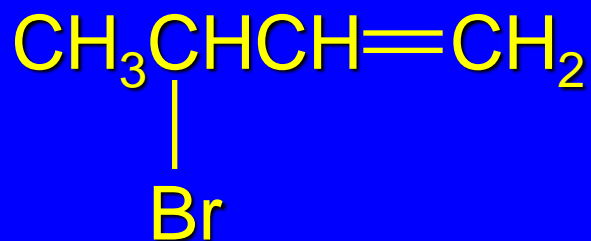


formed faster

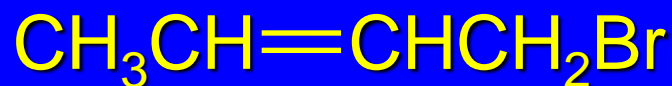


## Modelo explicativo

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



+

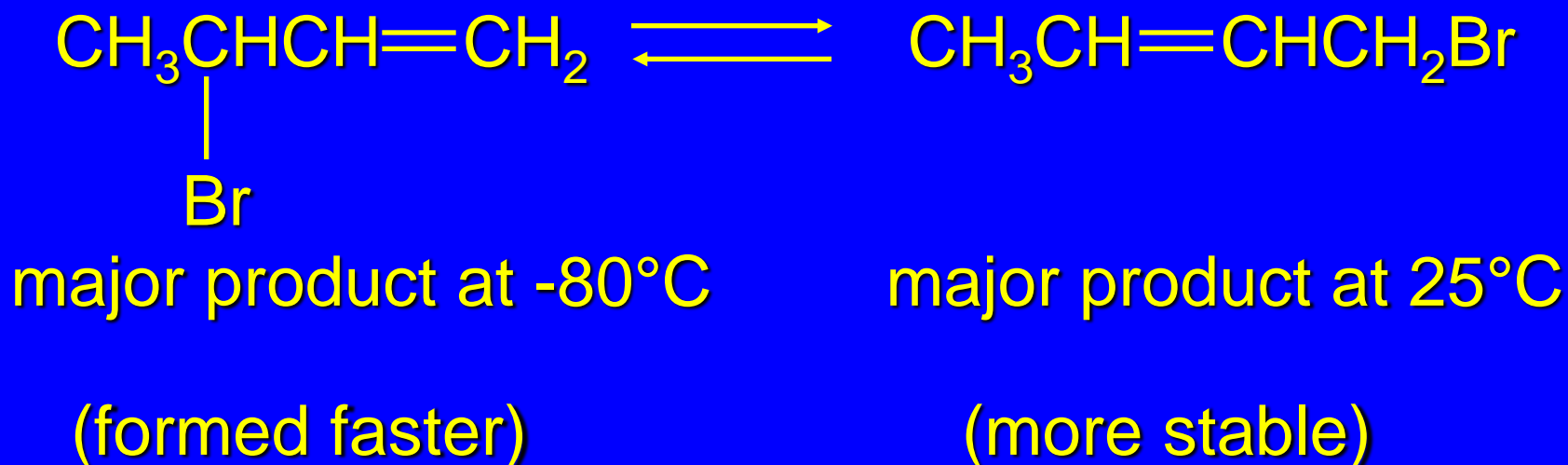


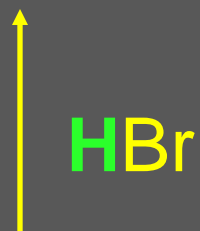
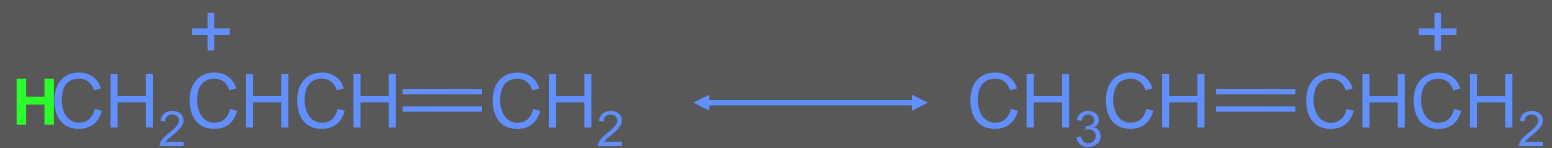
1-Bromo-2-butene

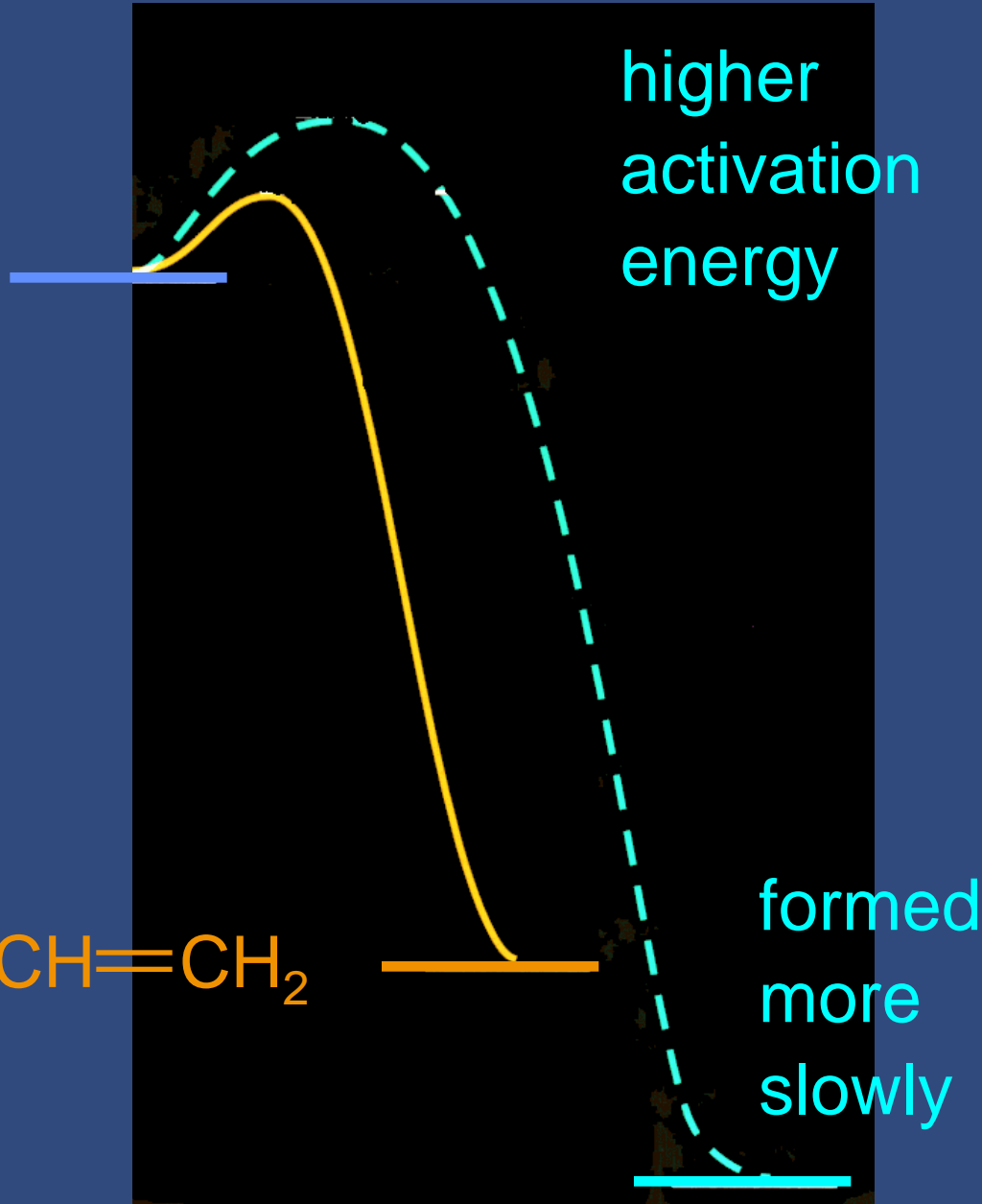
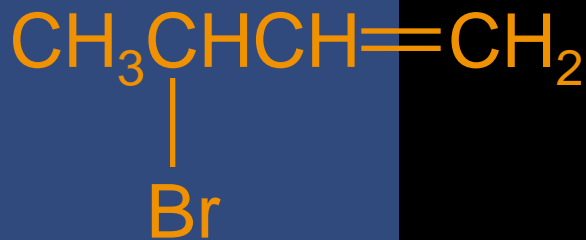
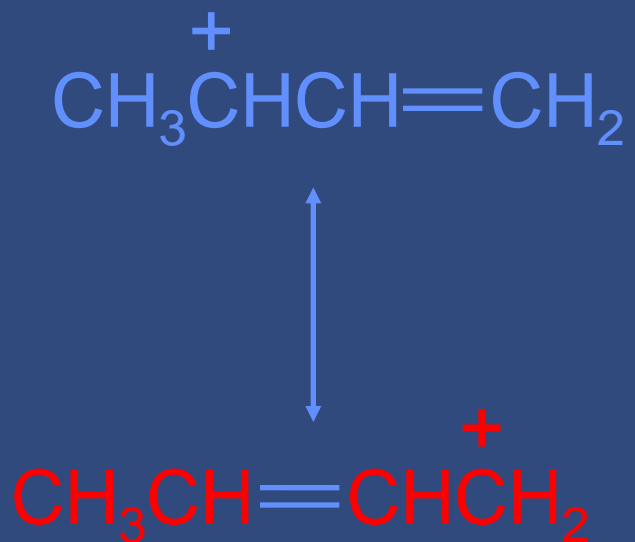
more stable

## Modelo explicativo

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



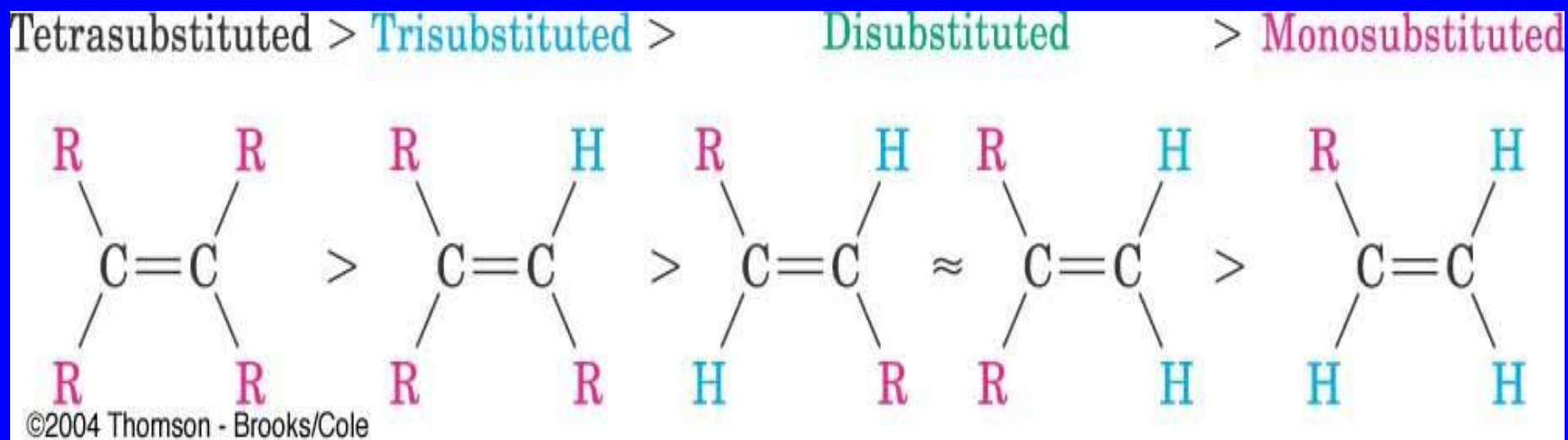




**TABLE 6.2** Heats of Hydrogenation of Some Alkenes

Substitution	Alkene	$\Delta H_{\text{hydrog}}^{\circ}$	
		(kJ/mol)	(kcal/mol)
	$\text{H}_2\text{C}=\text{CH}_2$	-137	-32.8
Monosubstituted	$\text{CH}_3\text{CH}=\text{CH}_2$	-126	-30.1
	$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	-126	-30.1
	$(\text{CH}_3)_2\text{CHCH}=\text{CH}_2$	-127	-30.3
Disubstituted	$\text{CH}_3\text{CH}=\text{CHCH}_3$ (cis)	-120	-28.6
	$\text{CH}_3\text{CH}=\text{CHCH}_3$ (trans)	-116	-27.6
	$(\text{CH}_3)_2\text{C}=\text{CH}_2$	-119	-28.4
Trisubstituted	$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	-113	-26.9
Tetrasubstituted	$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$	-111	-26.6

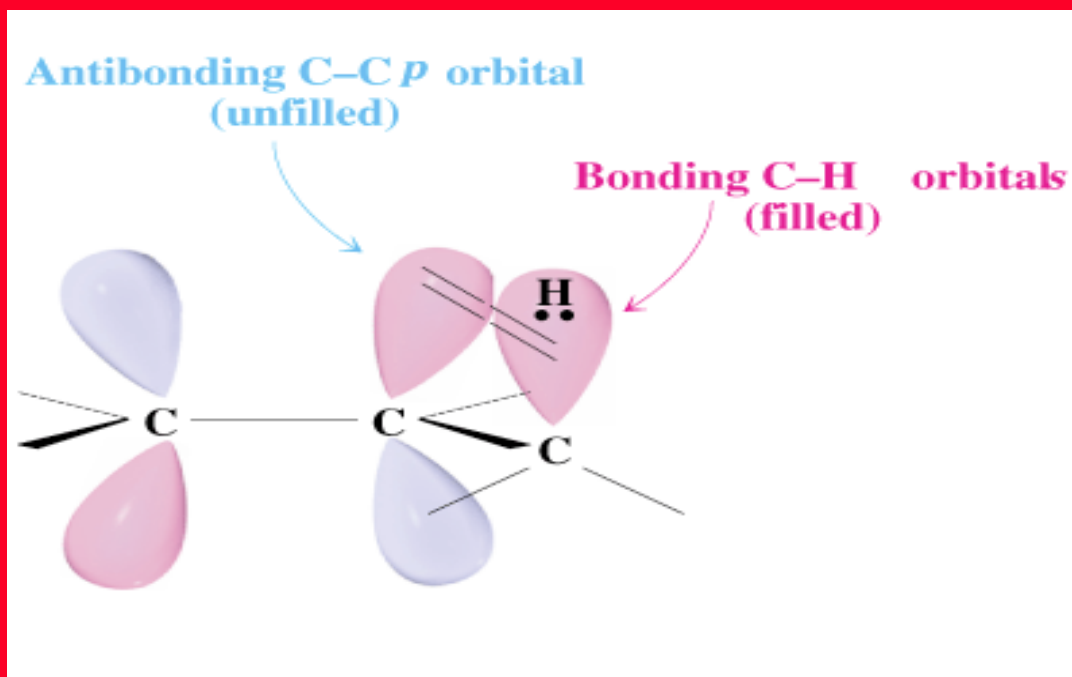
# Alkene Stabilities from $\Delta H$ 's:



**Diminui**

# Hiperconjugação

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



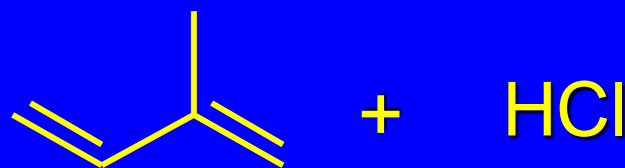
Addition of hydrogen chloride to 2-methyl-1,3-butadiene is a kinetically controlled reaction and gives one product in much greater amounts than any isomers. What is this product?





Think mechanistically.

Protonation occurs:

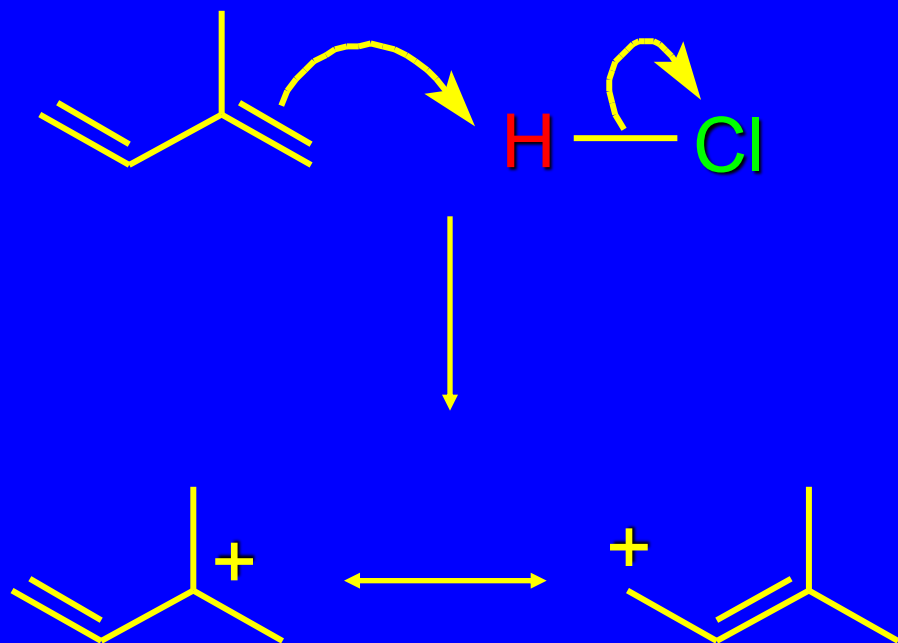


at end of diene system

in direction that gives most stable carbocation

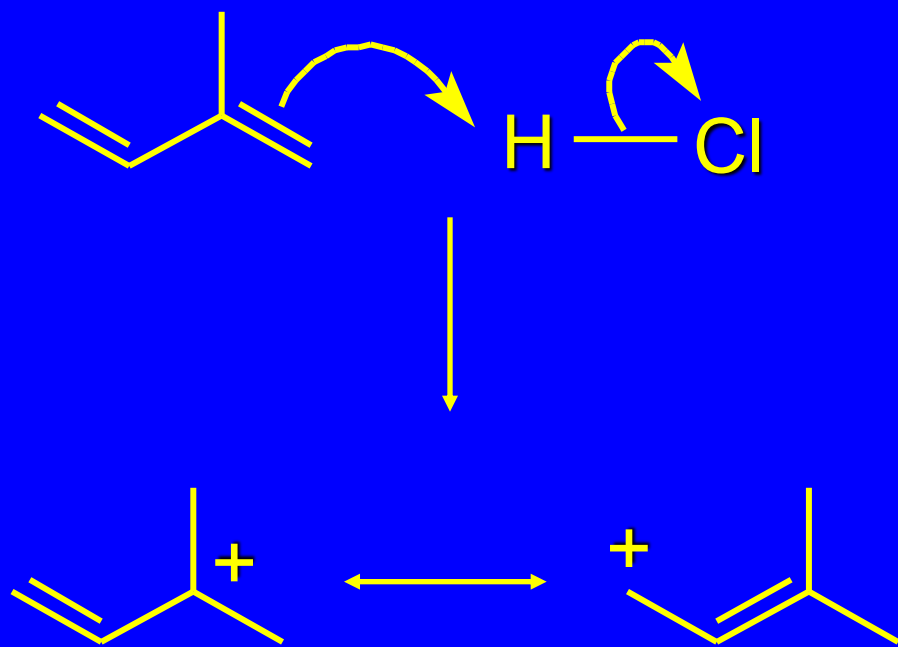
Kinetically controlled product corresponds to attack by chloride ion at carbon that has the greatest share of positive charge in the carbocation

Think mechanistically

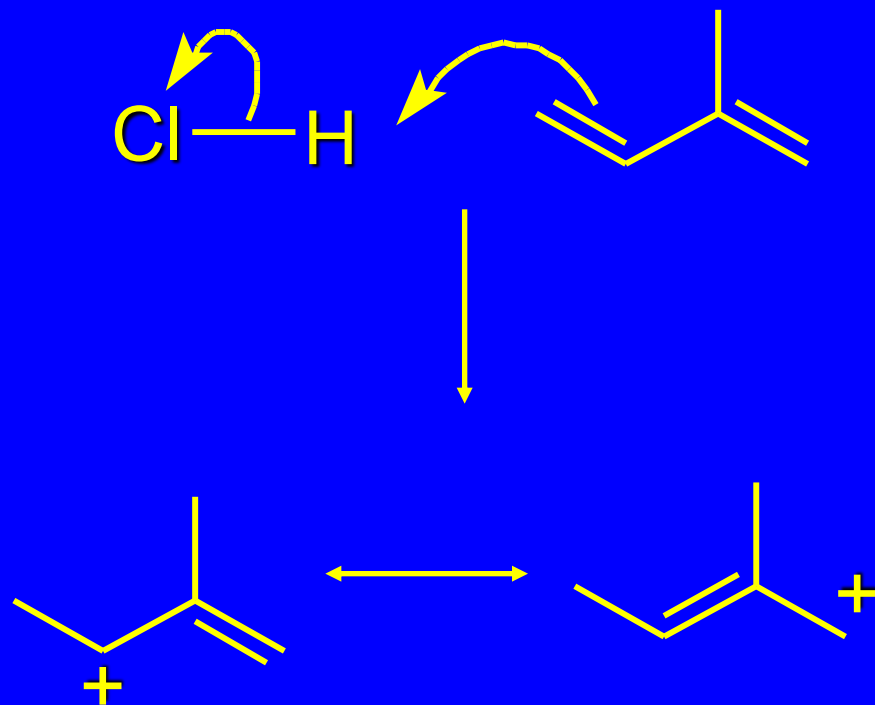


one resonance form is  
tertiary carbocation;  
other is primary

Think mechanistically

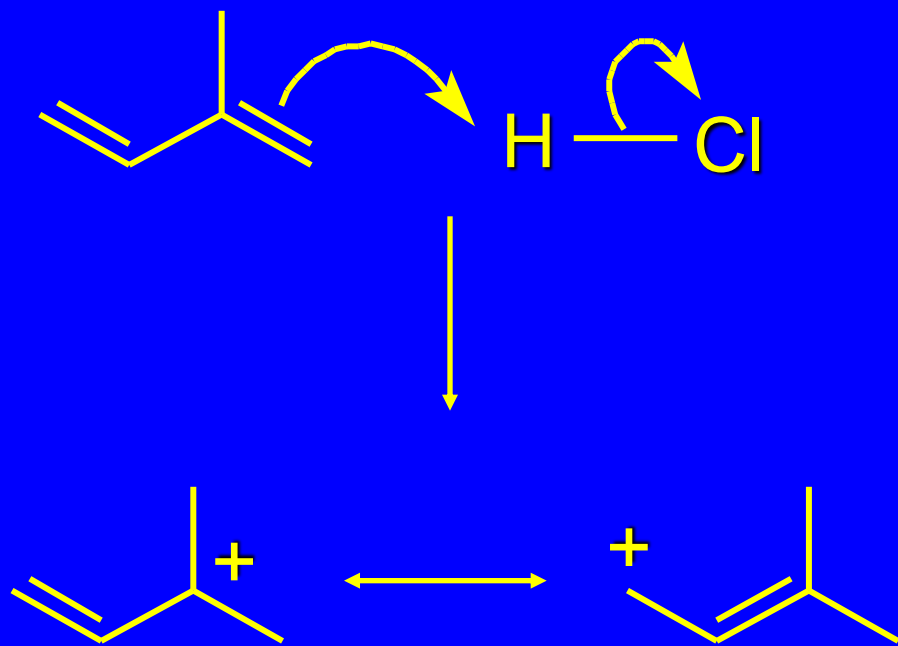


one resonance form is  
tertiary carbocation;  
other is primary



one resonance form is  
secondary carbocation;  
other is primary

Think mechanistically

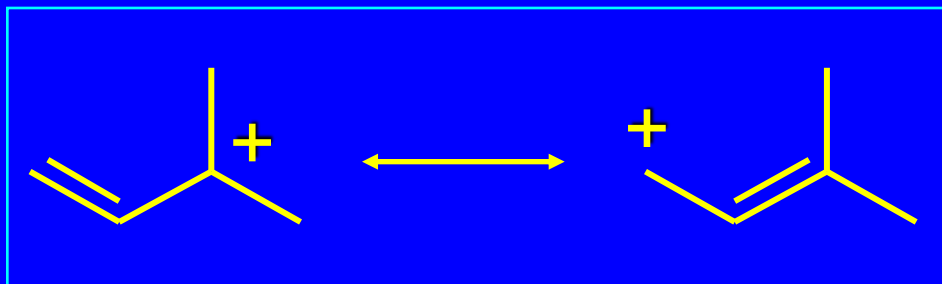
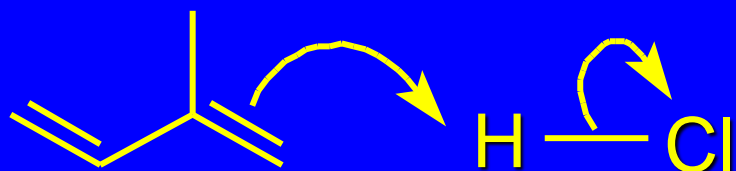


one resonance form is  
tertiary carbocation;  
other is primary

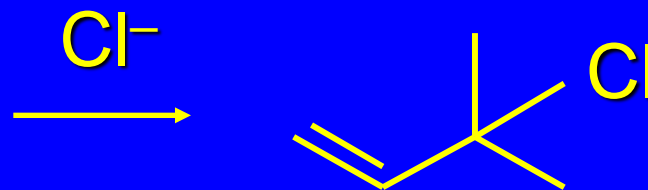
More stable carbocation

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

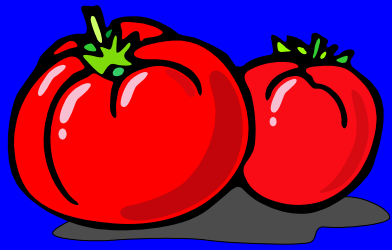
Think mechanistically



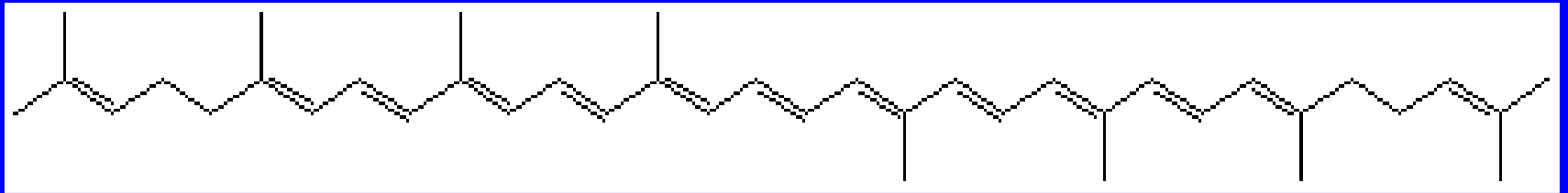
one resonance form is  
tertiary carbocation;  
other is primary



major  
product

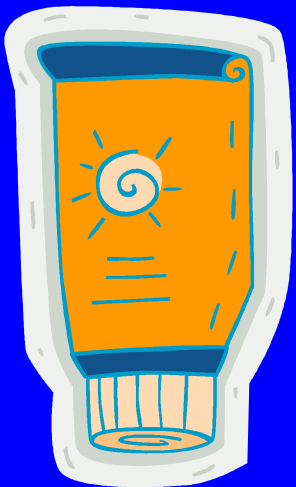


# Tomates

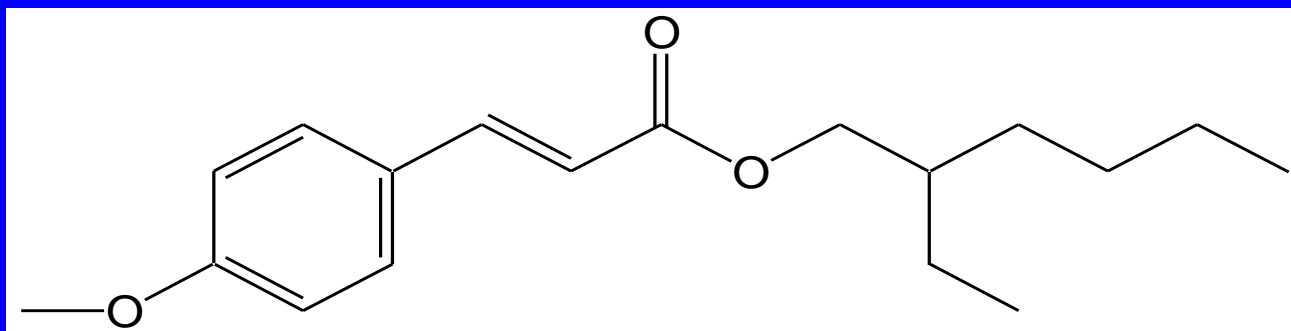


## Licopeno

- 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