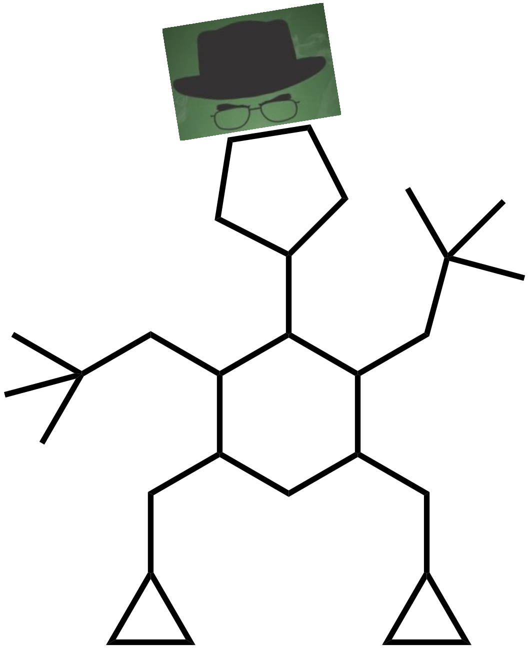
QFL0341 - Estrutura e Propriedades de Compostos Orgânicos - Noturno (agosto/09/2019)

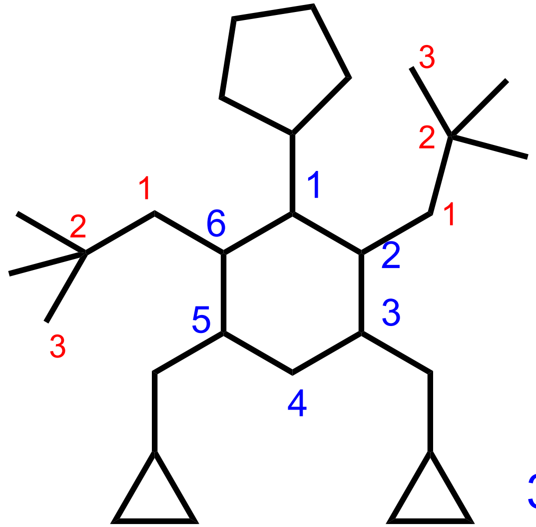
Ligações químicas e grupos funcionais.

Nomenclatura e representação de moléculas orgânicas.

Hidrocarbonetos (alcanos, alcenos e alcinos)

Say my name now!!!





Bis-2,6-(2,2-dimetil)propil-

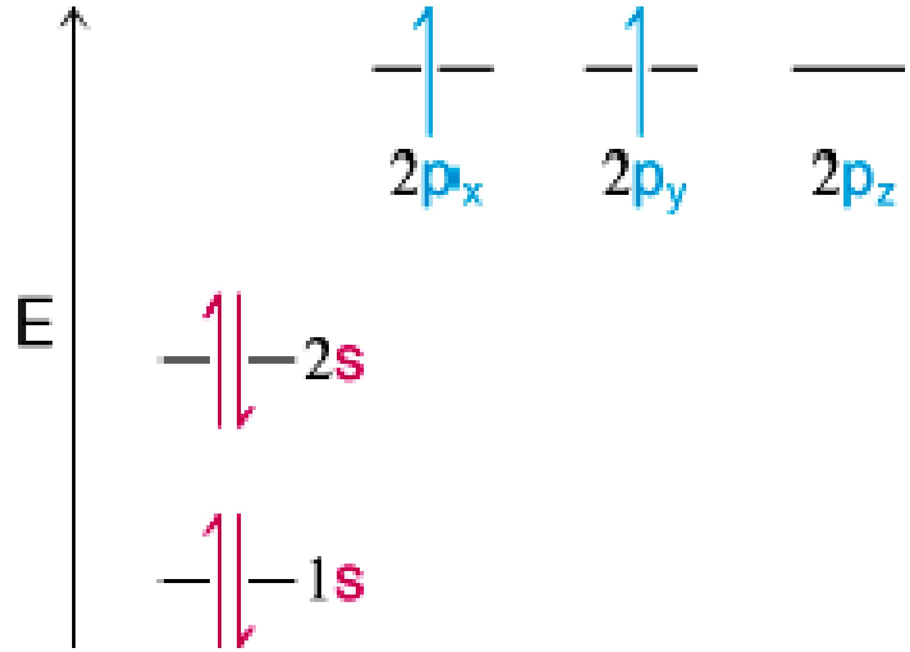
3,5-ciclopropilmetil-

1-**c**iclopentil-bis-2,6-(2,2-di**m**etil)propil-3,5-**ciclop**ropil**m**etil-ciclohexano

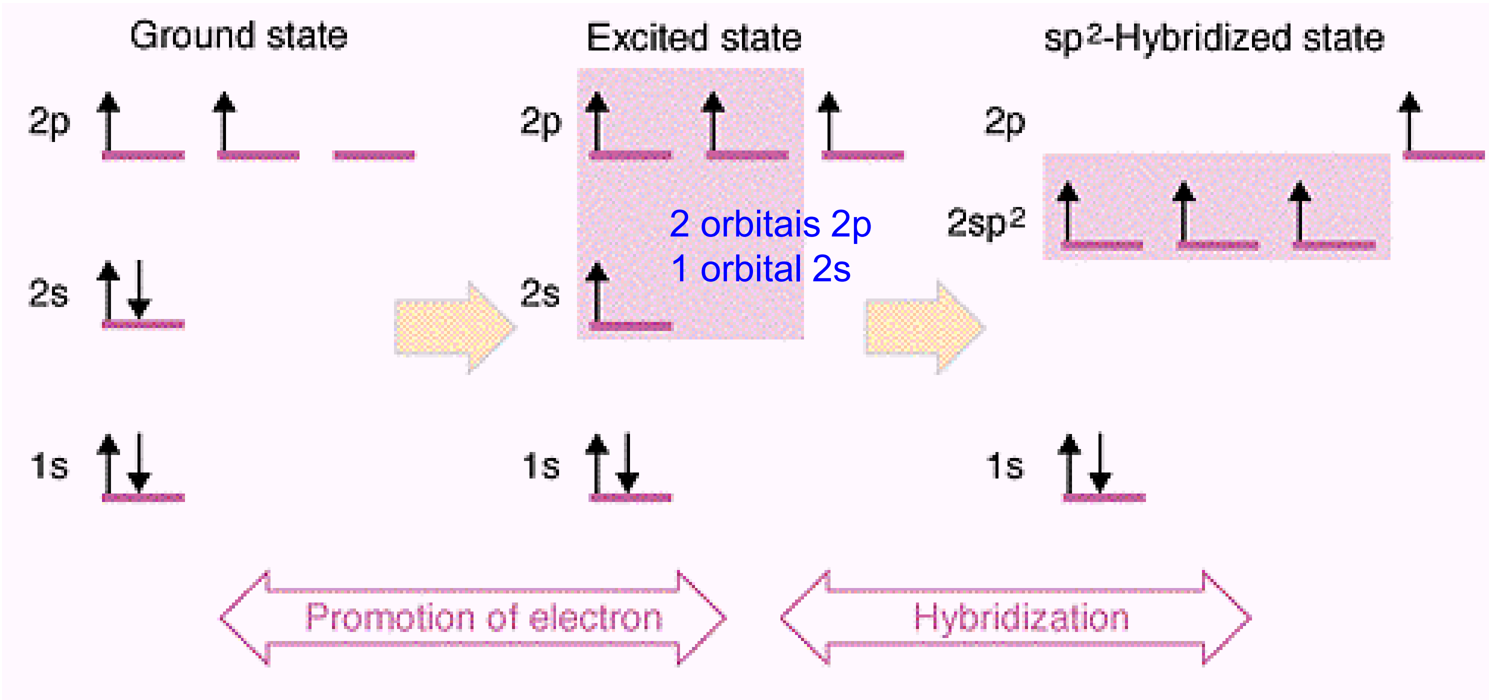
Alcenos e alcinos

Átomo de carbono no estado fundamental:

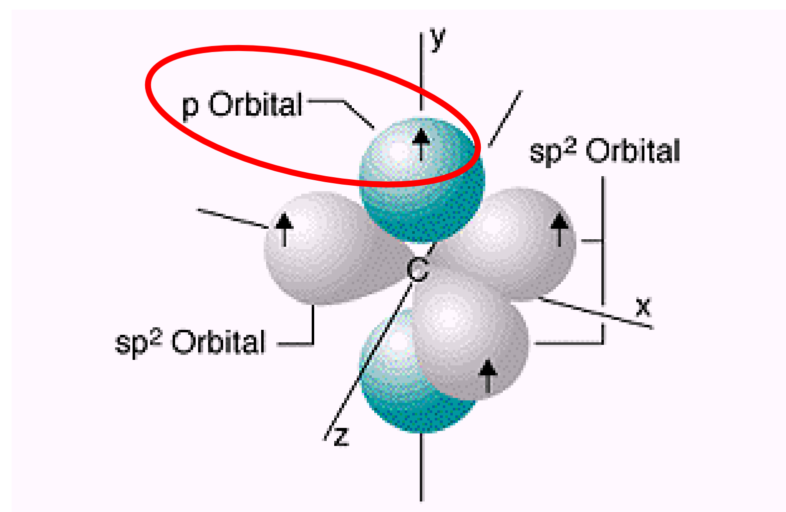
(número atômico=6): $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$



Obtaining sp2-hybridized carbon atoms

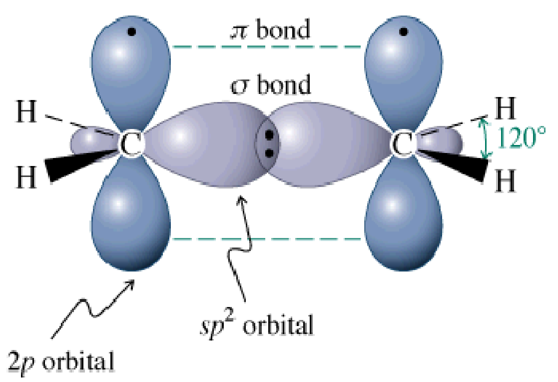


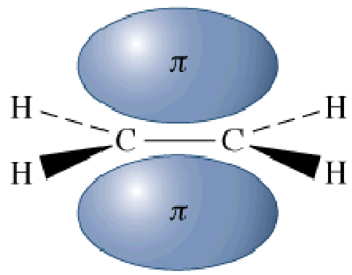
1 ligação
π
3 ligações
σ

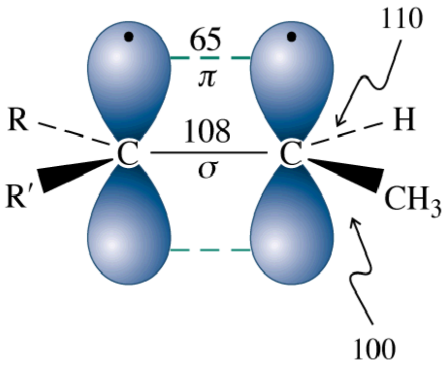


Etileno

Orbitais híbridos sp² são usados na formação de ligações duplas

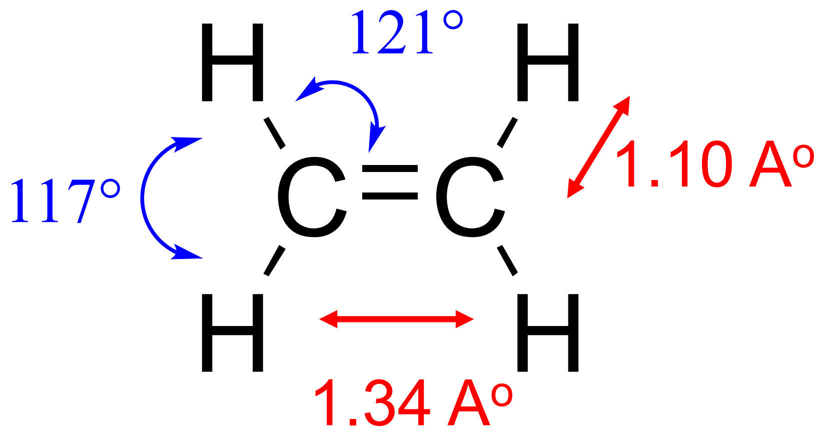


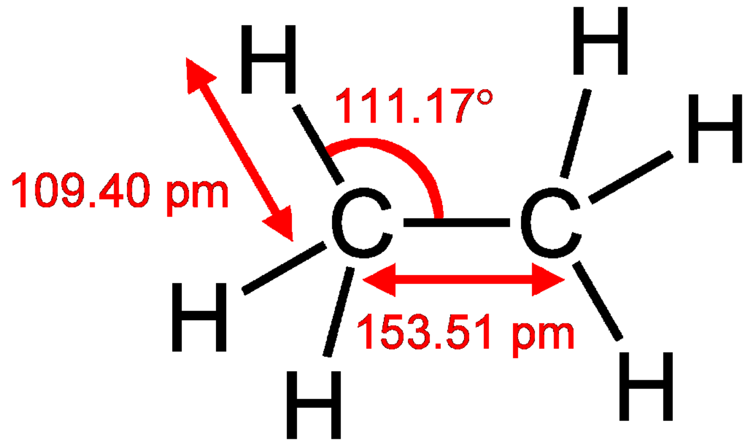




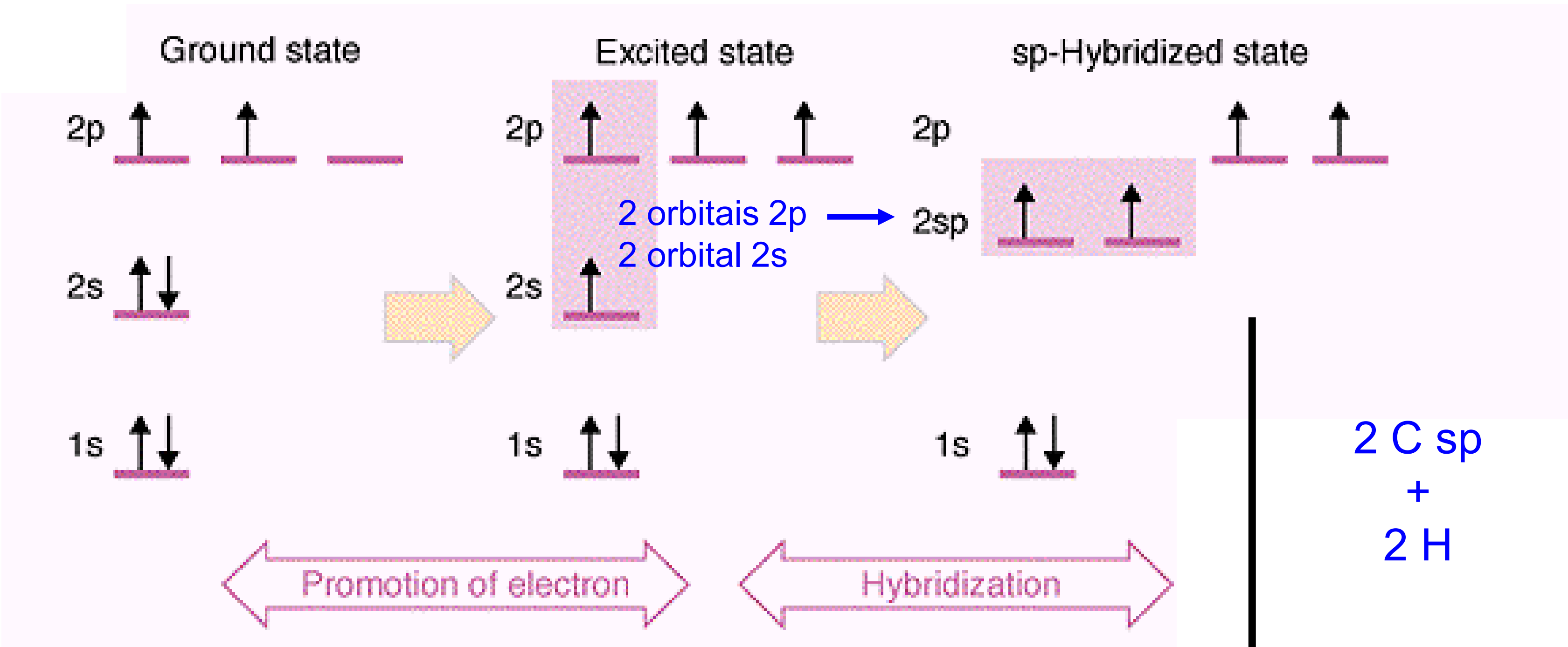
Energy in kcal/mol
(σ+π=total of 173)

Structure and Bonding in ethylene x ethane

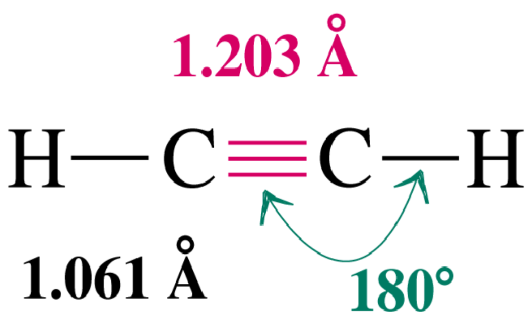


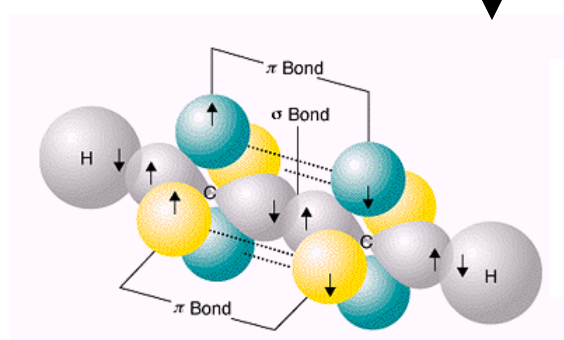


Obtaining **sp**-hybridized carbon atoms



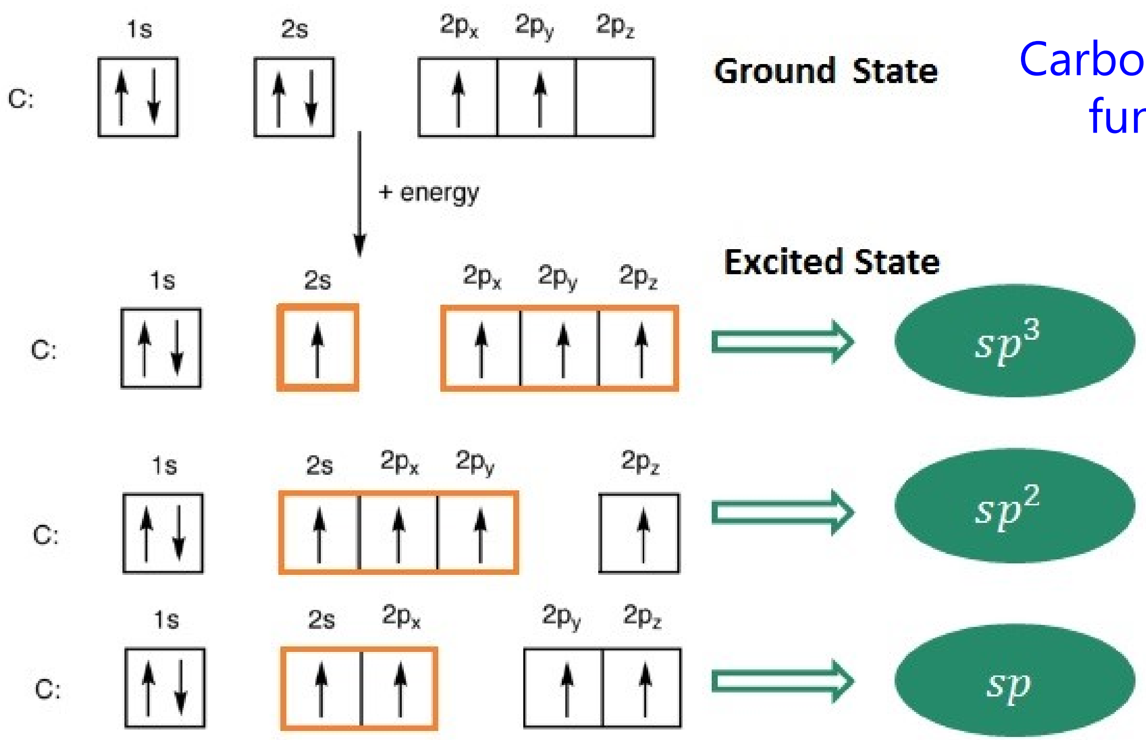
2 C sp
+
2 H





Tripla ligação é linear

Summary of the hybridized orbitals



Carbono no estado fundamental

Carbonos hibridizados

Table 1.7 Comparison of the Bond Angles and the Lengths and Strengths of the Carbon–Carbon and Carbon–Hydrogen Bonds in Ethane, Ethene, and Ethyne

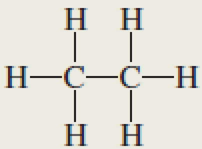
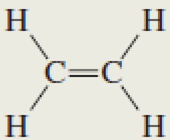
Molecule	Hybridization of carbon	Bond angles	Length of C—C bond (Å)	Strength of C—C bond (kcal/mol)	Strength of C—C bond (kJ/mol)	Length of C—H bond (Å)	Strength of C—H bond (kcal/mol)	Strength of C—H bond (kJ/mol)
 ethane	sp^3	109.5°	1.54	90	377	1.10	101	423
 ethene	sp^2	120°	1.33	174	720	1.08	111	466
H—C≡C—H ethyne	sp	180°	1.20	231	967	1.06	131	548

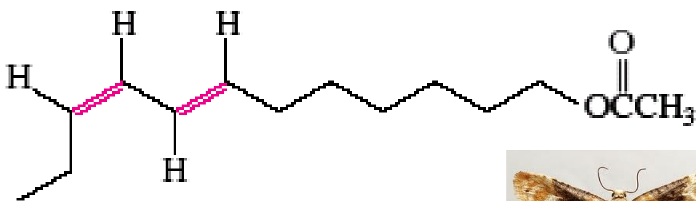
Table 8.2 Dependence of the Length of a Carbon–Carbon Single Bond on the Hybridization of the Orbitals Used in Its Formation

Compound	**Hybridization**	**Bond length (Å)**
H_3C-CH_3	*sp*^{3}–*sp*^{3}	1.54
$H_3C-CH=CH_2$	*sp*^{3}–*sp*^{2}	1.50
$H_2C=CH-CH=CH_2$	*sp*^{2}–*sp*^{2}	1.47
$H_3C-C\equiv CH$	*sp*^{3}–*sp*	1.46
$H_2C=CH-C\equiv CH$	*sp*^{2}–*sp*	1.43
$HC\equiv C-C\equiv CH$	*sp*–*sp*	1.37

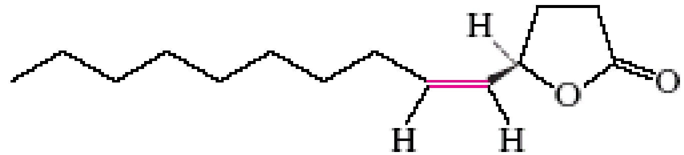
Alkenes in Nature: Insect Pheromones

Pheromones are chemical substances used for communication within a living species. Pheromones are used for sex, trail, alarm, and defense signaling, to name a few uses.

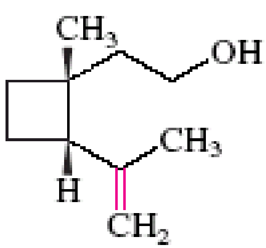
Insect Pheromones



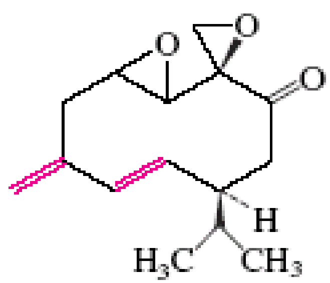
European vine moth



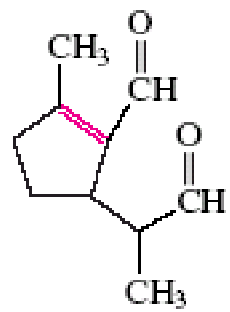
Japanese beetle



Male boll weevil



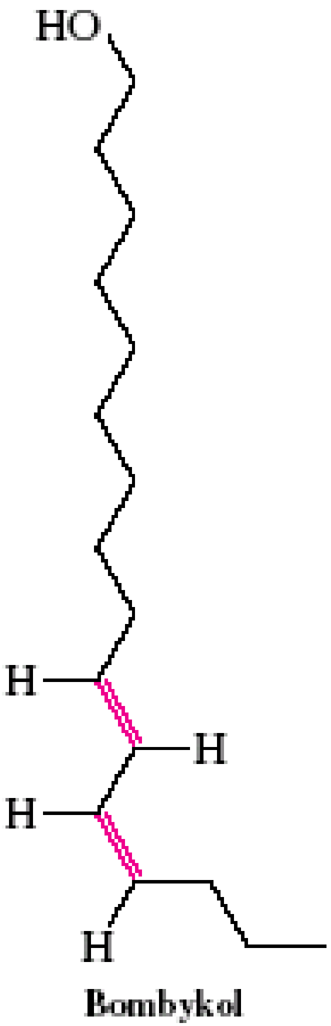
American cockroach



Defense pheromone of larvae of chrysomelid beetle

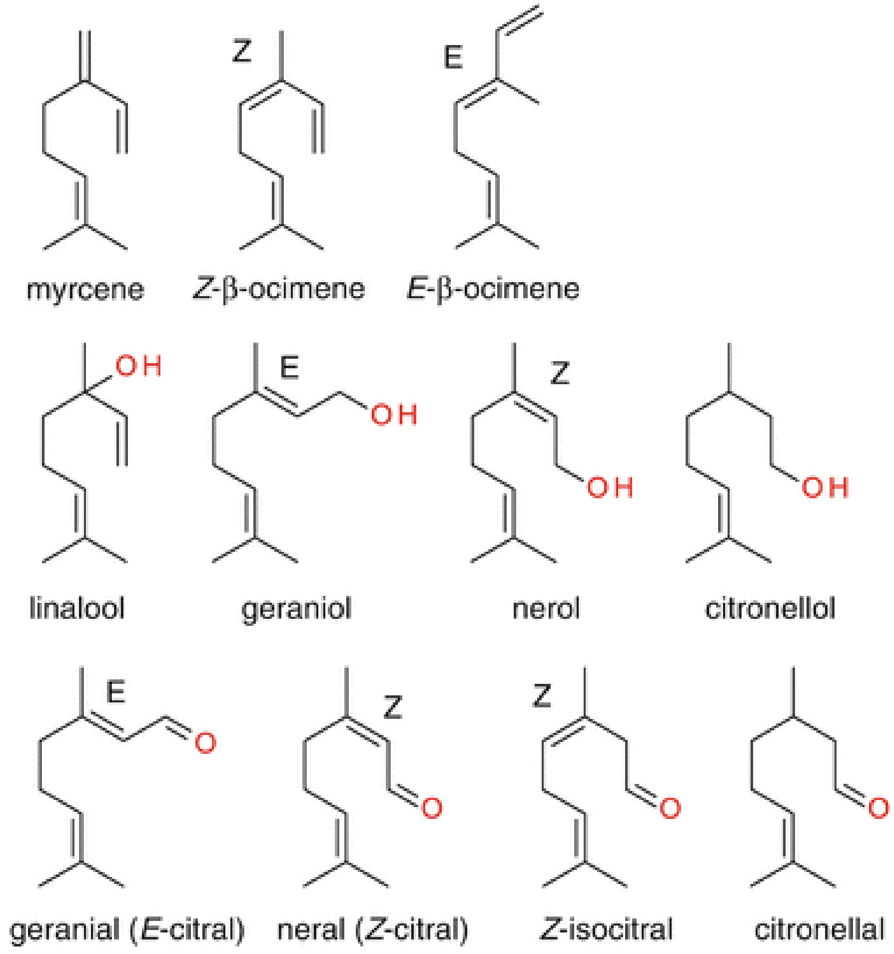
The sex attractant for the male silkworm moth is 10-*trans*-12-*cis*-hexadecadien-1-ol (bombykol)

The natural pheromone (10-*trans*-12-*cis* isomer) is 10 billion times more active in eliciting a response than is the 10-*cis*-12-*trans* isomer, and 10 trillion times more active than the *trans, trans* isomer.



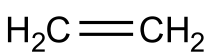
10-*trans*-12-*cis* isomer

Alkenes in essential oils (monoterpenes)



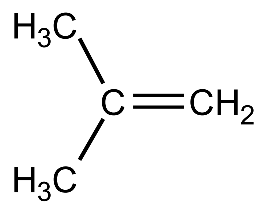
Nomes Comuns

- Apesar da precisão e da aceitação universal da nomenclatura IUPAC, alguns alcenos, particularmente os de baixa massa molecular, são conhecidos quase que exclusivamente por seus nomes comuns

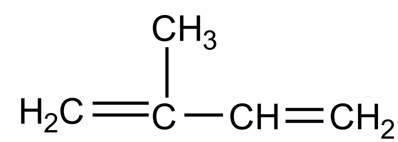


ethylene
(ethene)

propylene
(propene)

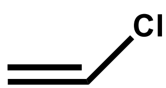


isobutylene
(2-methylpropene)

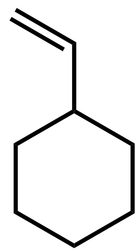


isoprene
(2-methyl-1,3-butadiene)

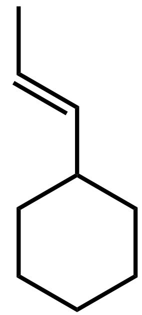
Alcenos como grupos substituíntes:



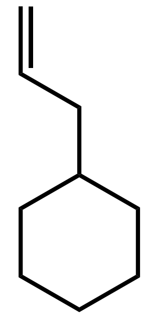
cloreto de vinila



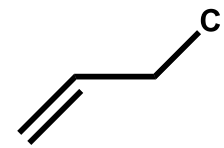
etenila ou vinila
(etenilcicloexano ou
vinilcicloexano)



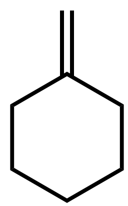
propenila
(propenilcicloexano)



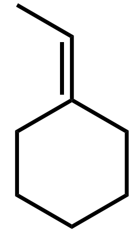
alila
(alilcicloexano)



cloreto de alila

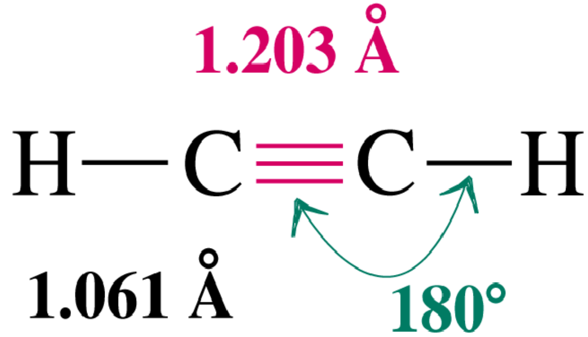


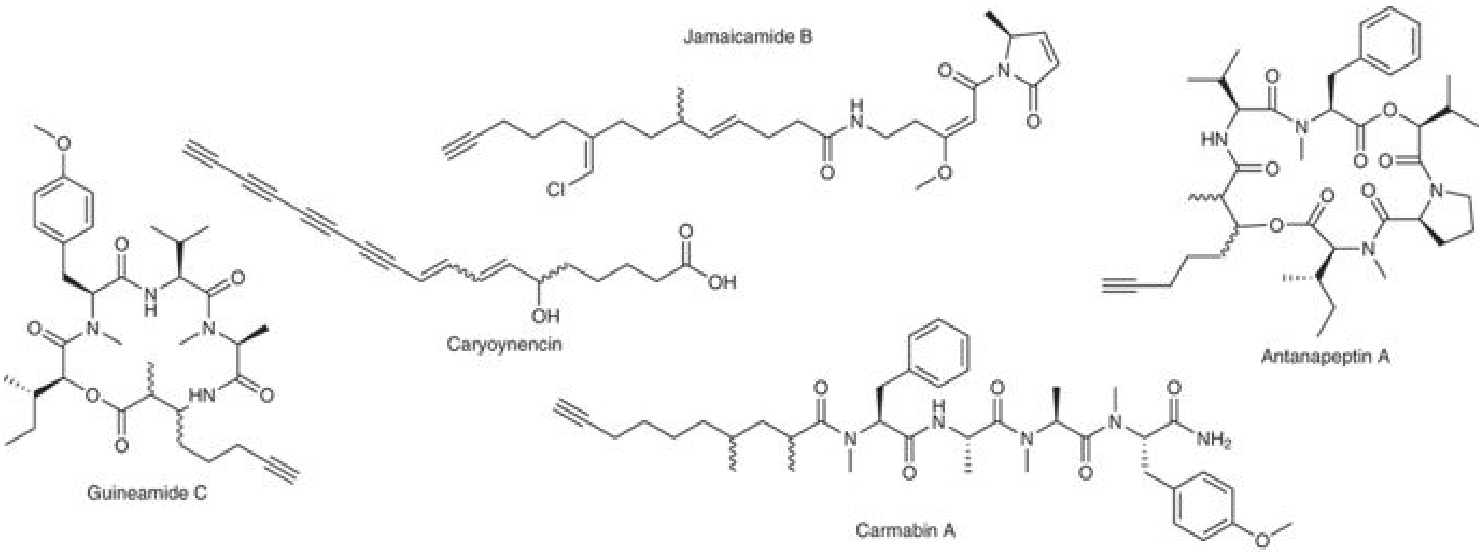
metileno
(metilenocicloexano)



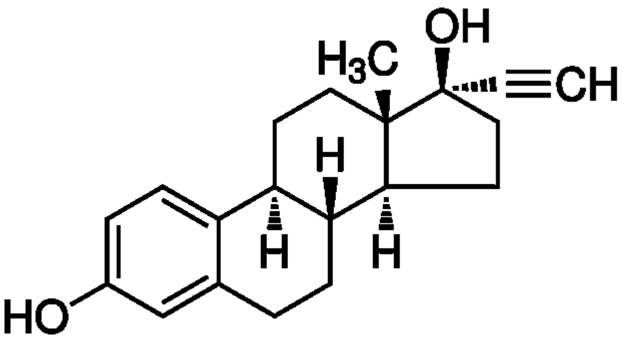
etilideno
(etilidenocicloexano)

ALCINOS


1.203 Å
H—C≡C—H
1.061 Å
180°


Jamaicamide B
Caryoynencin
Antanapeptin A
Guineamide C
Carmabin A

Alcinos



Etinil-estradiol (contraceptivos orais)

Nome IUPAC

(9S,13S,14S,17S)-13-methyl-17-(prop-1-yn-1-yl)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3,17-diol

Nomes comerciais

Nordette®, Microvlar®

Mercilon®, Femina®

Microdiol®

Naming Alkenes and Alkynes (similar to alkanes)

When the carbon chain has 4 or more C atoms, number the chain to give the lowest number to the double or triple bond.

1 2 3 4 $CH_2{=}CHCH_2CH_3$	**1-butene**	**but-1-ene**
$CH_3CH{=}CHCH_3$	**2-butene**	**but-2-ene**
$CH_3C{\equiv}CCH_3$	**2-butyne**	**but-2-yne**

Nomenclatura de alcenos e alcinos

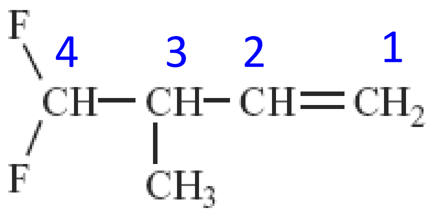
(parte alquílica é semelhante a de hidrocarbonetos saturados)

1) Alcenos e alcinos possuem a mesma prioridade, mas devem ter a menor numeração possível;

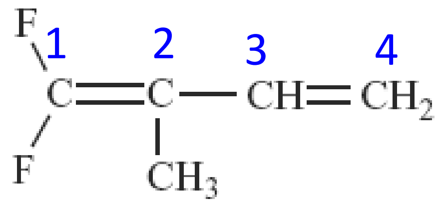
2) Em uma molécula contendo uma dupla e uma tripla ligação, aquela que estiver mais próxima do início da cadeia determina a direção da numeração;

3) Se a dupla ou tripla estivem em posições com a numeração análoga, a dupla ligação possui prioridade (por causa da ordem alfabética)

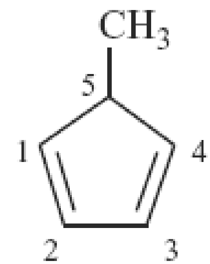
Naming alkenes and alkynes



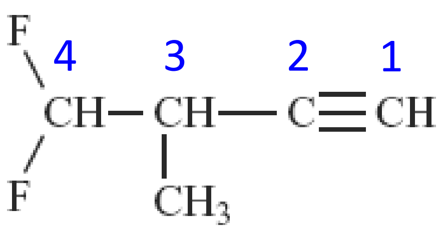
4,4-difluoro-3-methylbut-1-ene



1,1-difluoro-2-methyl-buta-1,3-diene

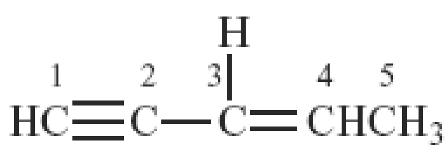


5-methylcyclopenta-1,3-diene



4,4-difluoro-3-methylbut-1-yne

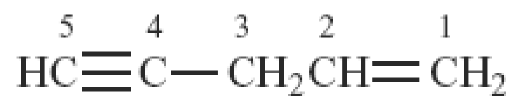
Regra 1
(o que estiver
Mais próximo do inicio)



pent-3-en-1-yne

("yne" closer to end of chain)

Regra 2
(o que estiver
Mais próximo do inicio)



pent-1-en-4-yne

("ene" and "yne" have equal priority unless they have the same position number, when "ene" takes the lower number)

Regra 3 (ordem alfabética)

Isomerism in Alkenes

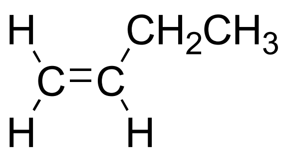
Isomers are different compounds that have the same molecular formula.

Constitutional (structural) : different connectivity

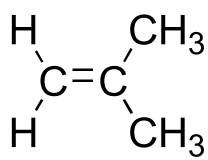
Stereoisomers: same connectivity, but different spatial arrangement of atoms or groups.

C_4H_8: IDH? ($CnH_2n + 2$)
How many isomers?

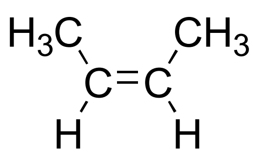
IDH= nC+1 – nH(X)/2 + nN/2
C_4H_8 (5-4= **1** IDH)



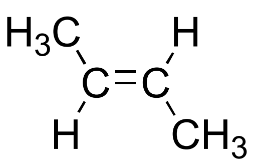
1-butene



2-methylpropene



cis-2-butene



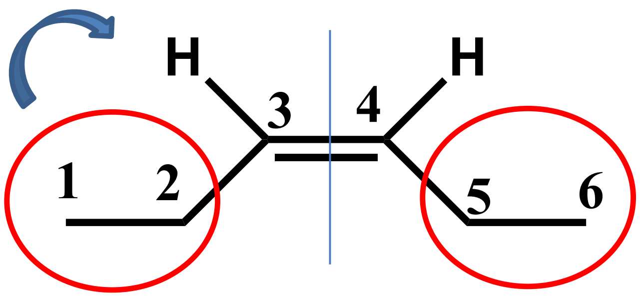
trans-2-butene

Could also include cyclobutane and methylcyclopropane (CnH2n + 2)
IDH= 1 (double bond or ring)

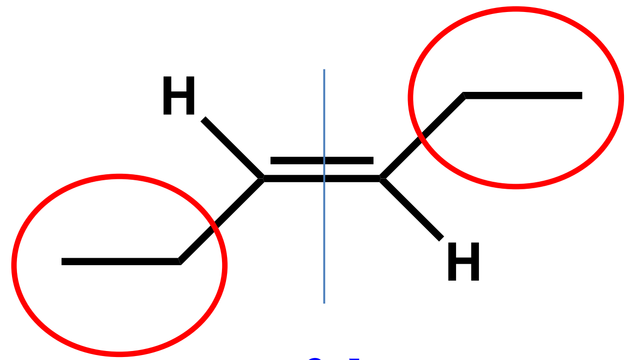
Configuração *cis-trans*

- A configuração é determinada pela orientação dos átomos da cadeia principal em torno da ligação dupla.

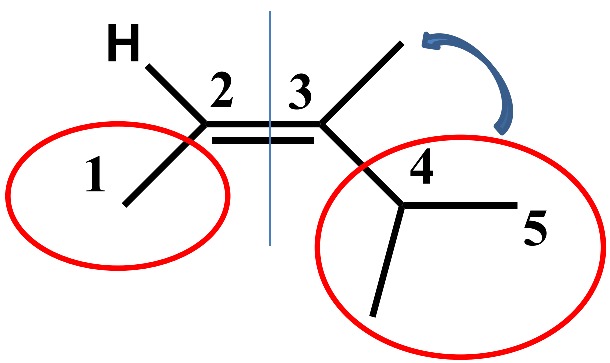
Tem preferência sobre o H



***cis*-3-hexeno**



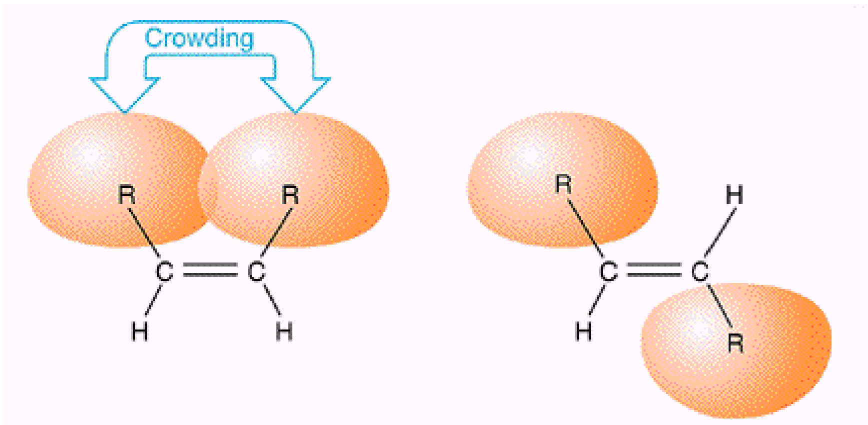
***trans*-3-hexeno**



Tem preferência sobre o CH_3

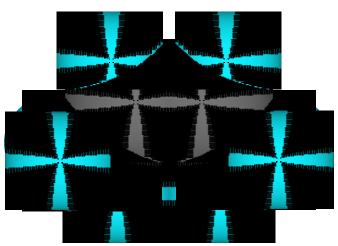
***cis*-3,4-dimetil-2-penteno**

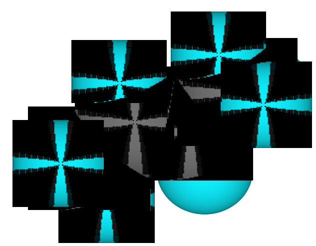
Estabilidade dos Alcenos

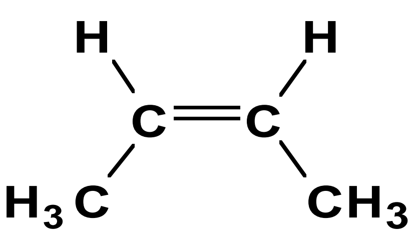


alceno *cis* (*Z*)

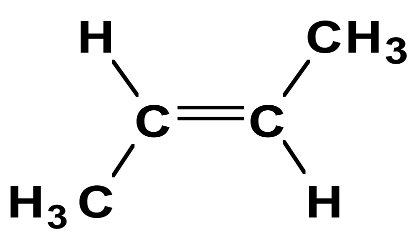
alceno *trans* (*E*)







cis-2-Butene
mp -139°C, bp 4°C

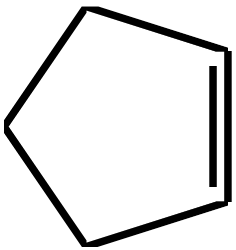


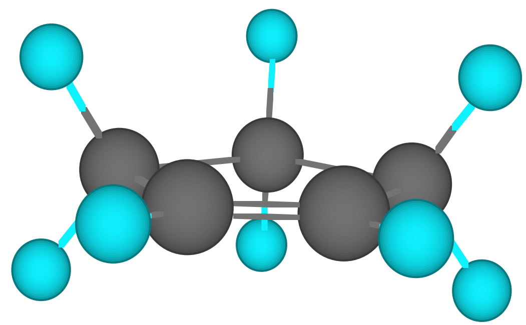
trans-2-Butene
mp -106°C, bp 1°C

- Os alcenos *trans* são mais estáveis que os *cis* devido a interações estéricas.

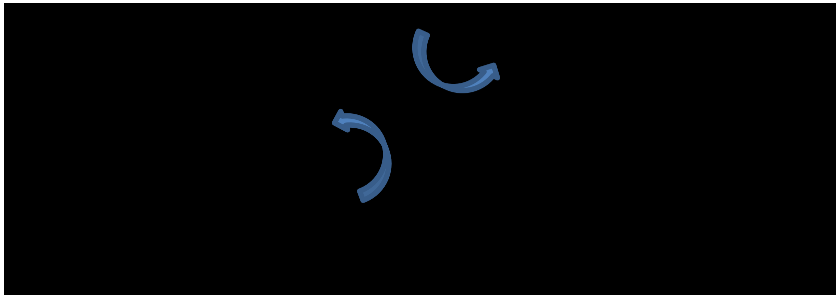
Isomeria *Cis-Trans* em cicloalcenos

- Do ciclopropeno ao ciclohepteno a configuração da dupla ligação é sempre *cis (não há como torna-las trans)*
- O ciclopenteno é planar





No caso do cicloocteno cis, os ângulos internos ficam muito maiores do que 109º
Então torna-se possível ter o trans-cicloocteno que leva a um alívio das tensões.



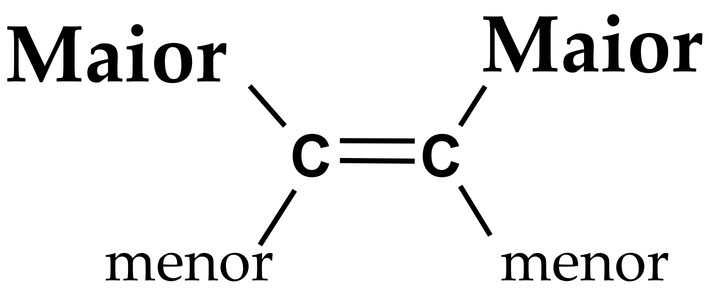
Configuração - E,Z

- O sistema *E,Z* usa as regras de prioridade (ordem do número atômico)

- Se os grupos de maior prioridade estão do mesmo lado, a configuração é ***Z*** (em alemão, *zusammen*)

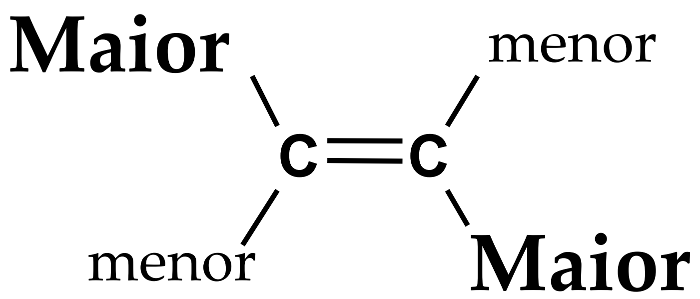
- Se os grupos de maior prioridade estão de lados opostos, a configuração é *E* (em alemão, *entgegen*)

Configuração - *E,Z*



***Z* (zusammen)**

(junto)



***E* (entgegen)**

(oposto)

Configuração - E,Z

Nomeie cada alceno e especifique sua configuração pelo sistema *E,Z*

[redacted]

(*Z*)-3-metil-2-penteno

(*E*)-2-cloro-2-penteno

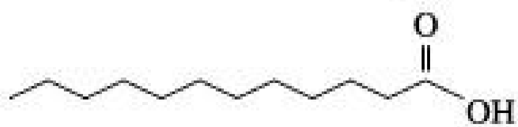
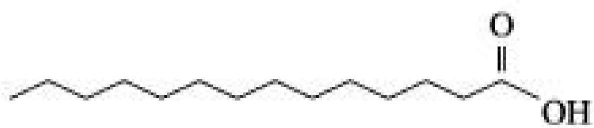
[redacted]

(*E*)-1-cloro-2,3-dimetil-2-penteno

(*Z*)-1-bromo-1-cloro-1-propeno

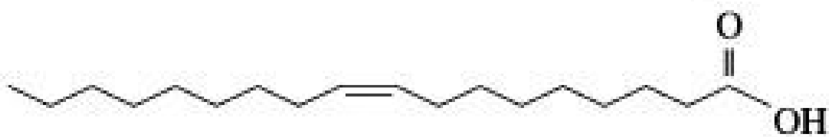
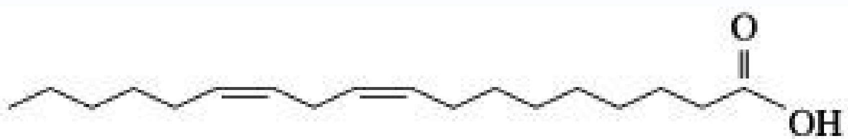
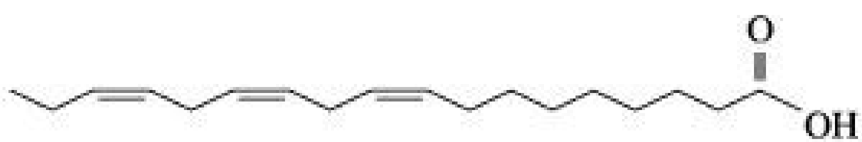
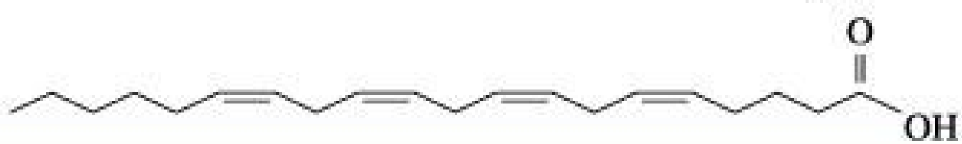
Structures and Melting Points of Saturated Fatty Acids
(effect of introduction of *cis* double bond in saturated compounds)

Table 18.1 Structures and Melting Points of Common Fatty Acids

Name	Carbon Atoms	Structure	Melting Point (°C)	Source
Saturated Fatty Acids				
Capric acid	10		32	Saw palmetto
Lauric acid	12		43	Coconut
Myristic acid	14		54	Nutmeg
Palmitic acid	16		62	Palm
Stearic acid	18		69	Animal fat
Arachidic acid	20		76	Peanut oil, vegetable and fish oils

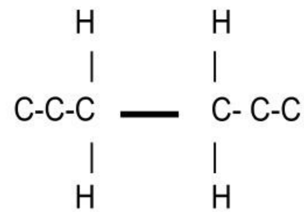
Structures and Melting Points of Unsaturated Fatty Acids

Table 18.1 Structures and Melting Points of Common Fatty Acids *(Continued)*

Name	Carbon Atoms	Structure	Melting Point (°C)	Source
Monounsaturated Fatty Acids				
Palmitoleic acid	16		0	Butter
Oleic acid	18		13	Olives, corn
Polyunsaturated Fatty Acids				
Linoleic acid	18		−9	Soybean, safflower, sunflower
Linolenic acid	18		−17	Corn
Arachidonic acid	20		−50	Prostaglandins

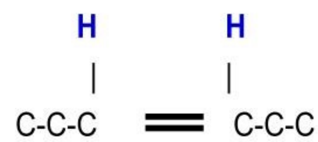
Saturated Fatty Acid

Stearic acid 18:0
melting point 70 °C



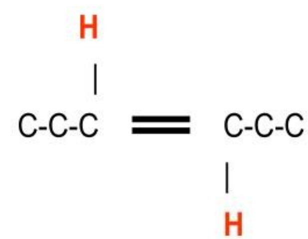
Unsaturated Fatty Acid

(cis) **Oleic acid c 18:1 n-9**
melting point 16 °C



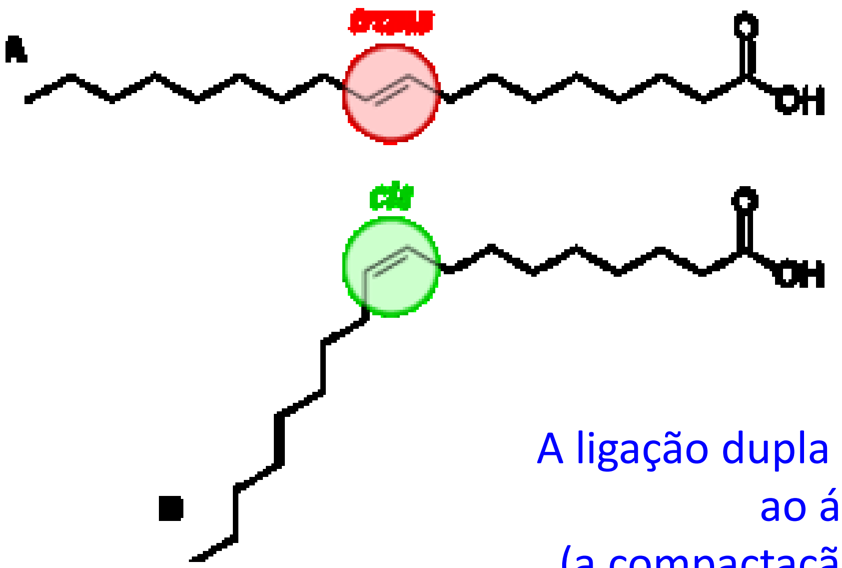
Unsaturated Fatty Acid

(trans) **Elaidic acid t 18:1 n-9**
melting point 43 °C




Gordura Trans

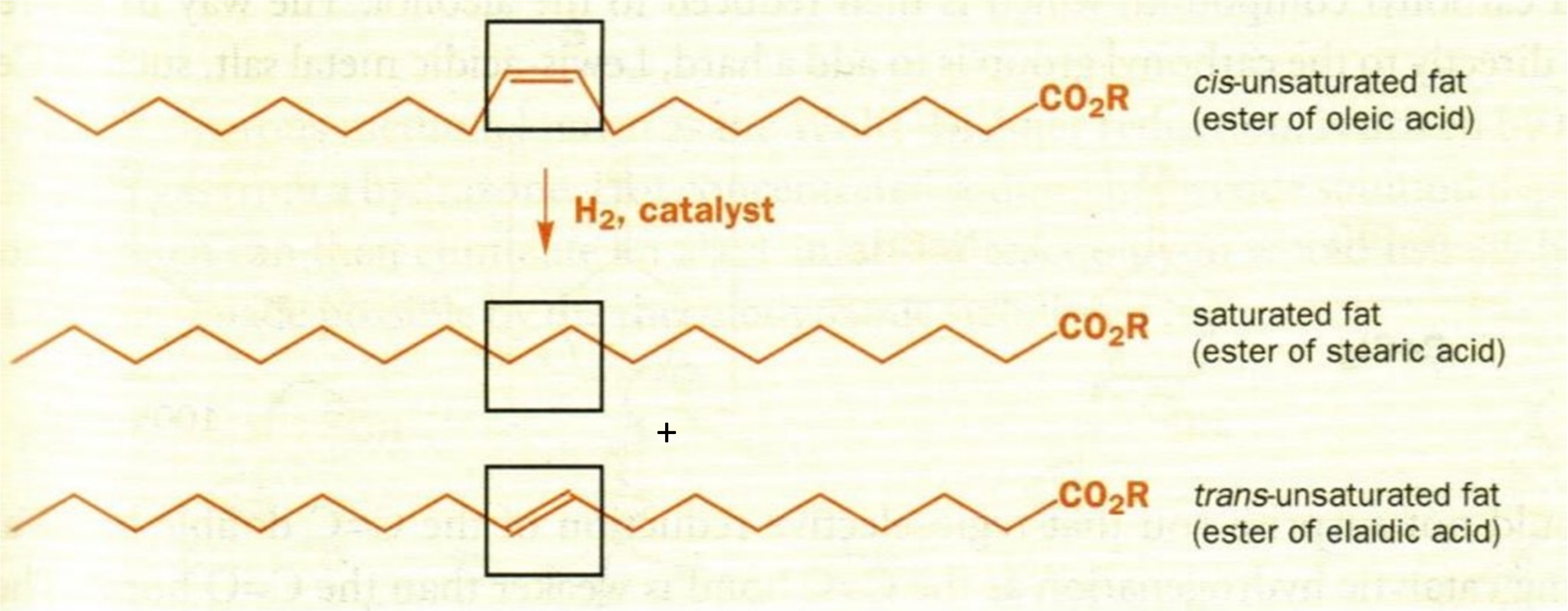
A gordura *trans* age como a gordura saturada ao elevar o nível da lipoproteína (concentração endoplasmática) de baixa densidade no sangue (LDL ou "colesterol ruim”).



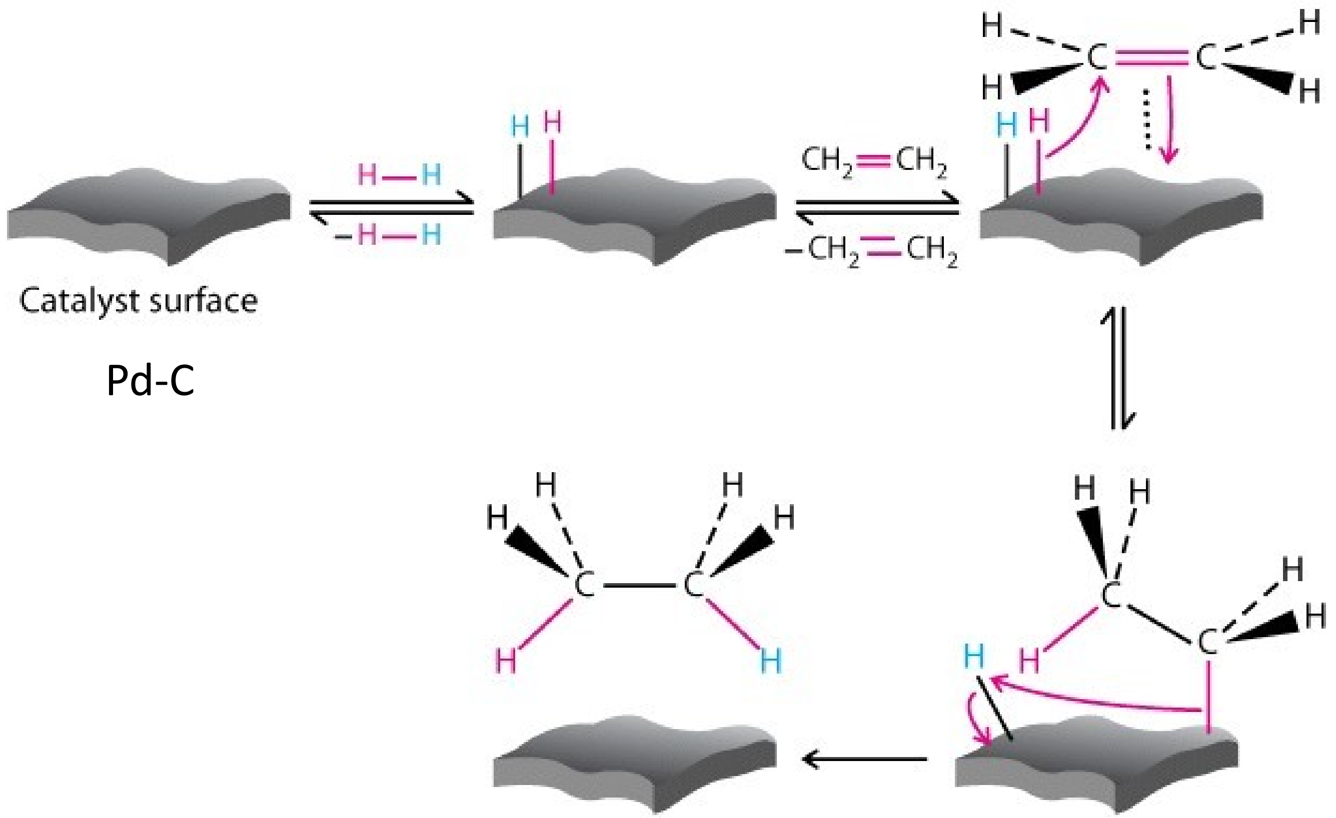
A ligação dupla cis abaixa o ponto de fusão com relação ao ácido graxo saturado ou trans (a compactação entre as cadeias torna-se dificultada)

A hidrogenação catalítica de óleos vegetais (líquidos a temperature ambiente devido a grande quantidade de ácidos graxos cis) é realizada industrialmente objetivando torná-los sólidos (como margarinas ou gordura vegetal hidrogenada).

No entanto, no processo de hidrogeração catalítica, parte das duplas ligações cis são convertidas em duplas ligações trans.



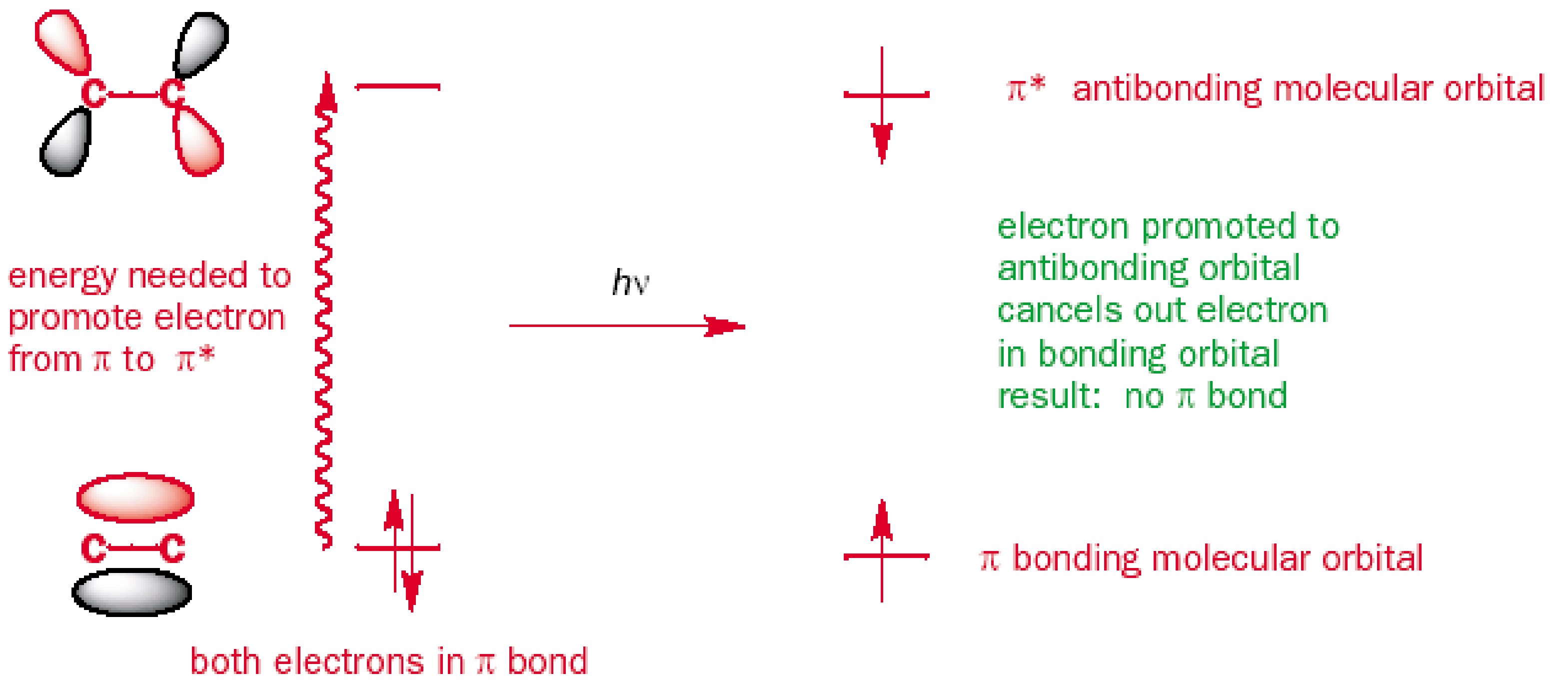
The primary function of a catalyst in hydrogenation reactions is to provide metal-bound hydrogen atoms on the catalyst surface.

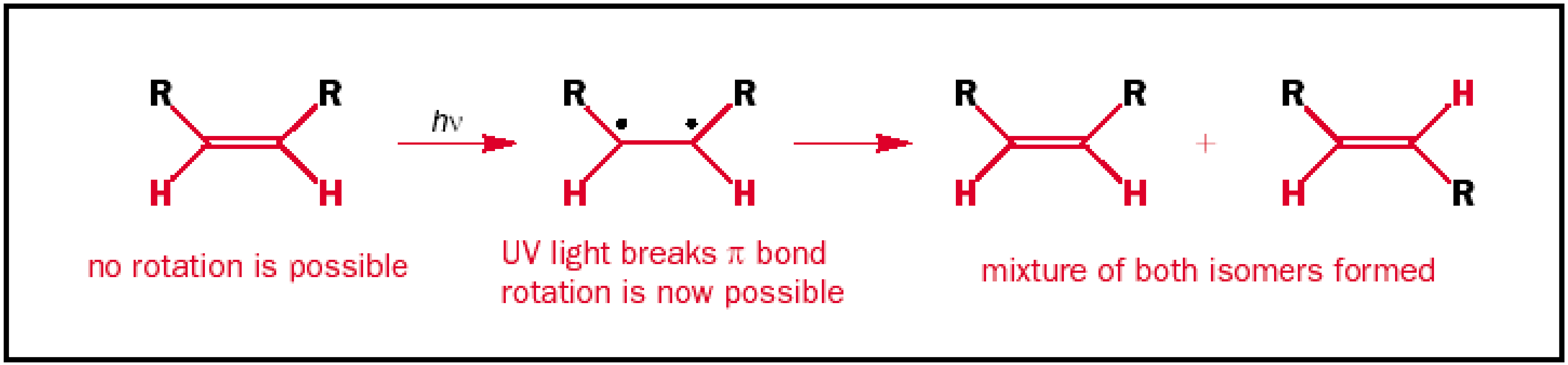


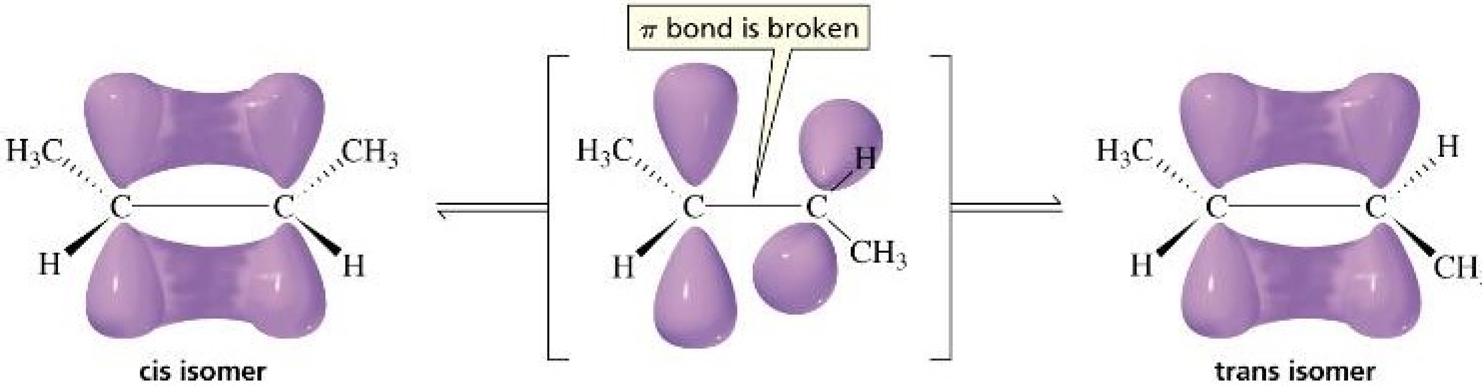
Pd-C

Common solvents used for hydrogenations include methanol, ethanol, acetic acid, and ethyl acetate.

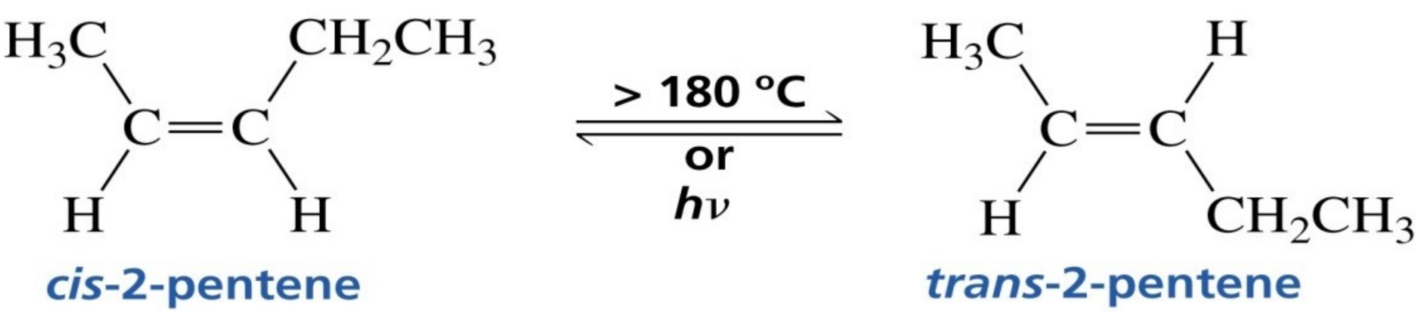
Reversibilidade da Ruptura de uma Ligação Dupla de Alcenos





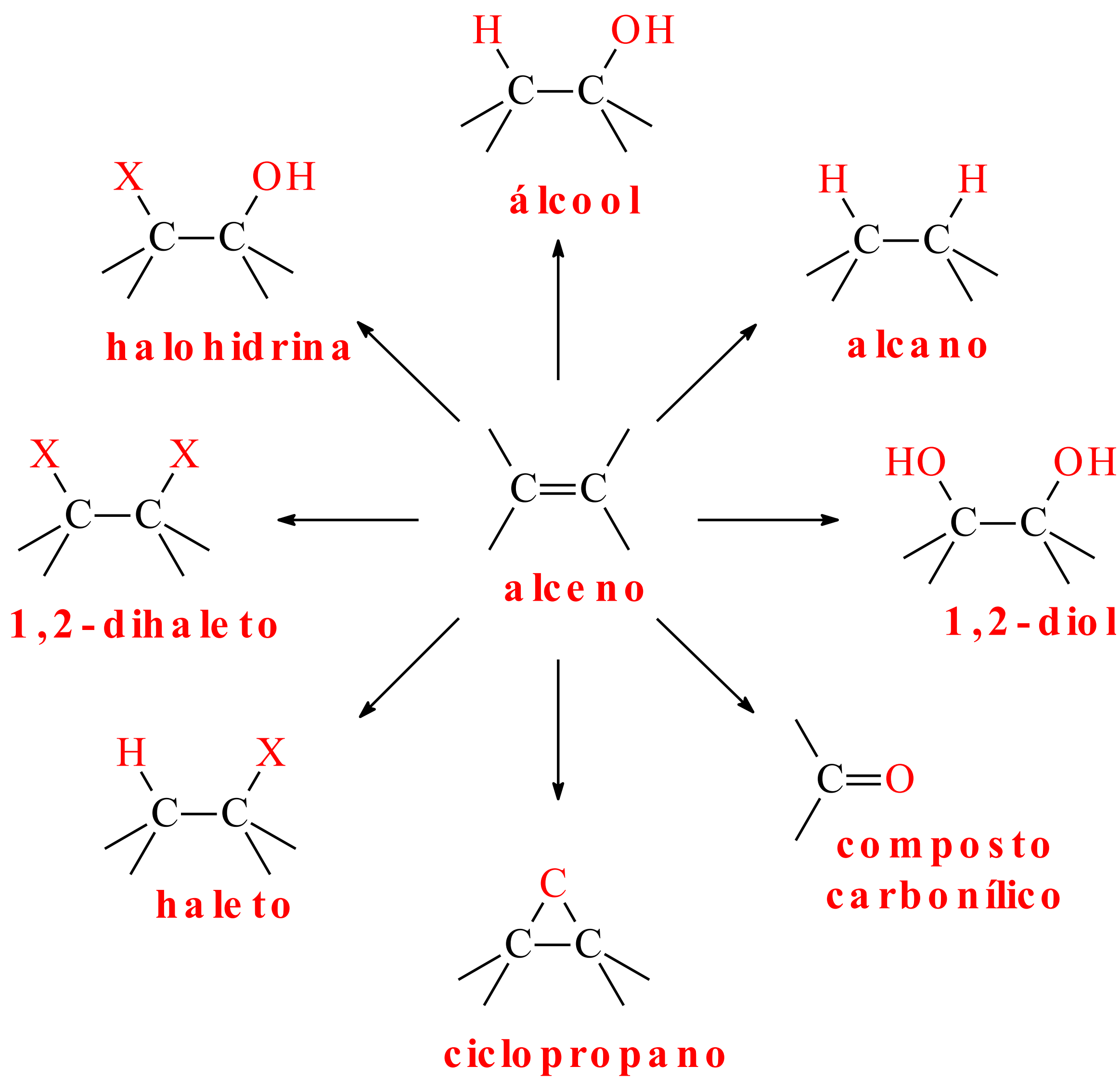


Ocorre rotação da ligação



As isomerizações podem ocorrer sob temperaturas Elevadas ou também através de reação fotoquímica

Reações de Adição Eletrofílica
(QFL0342 Estrutura e Reatividade de Compostos Orgânicos)



Reactions of alkanes

alkane + H_2SO_4 → no reaction (NR)

alkane + NaOH → NR

alkane + Na → NR

alkane + $KMnO_4$ → NR

alkane + H_2,Ni → NR

alkane + Br_2 → NR

alkane + H_2O → NR

Alkanes are typically non-reactive. They don’t react with acids, bases, active metals, oxidizing agents, reducing agents, halogens, etc.)

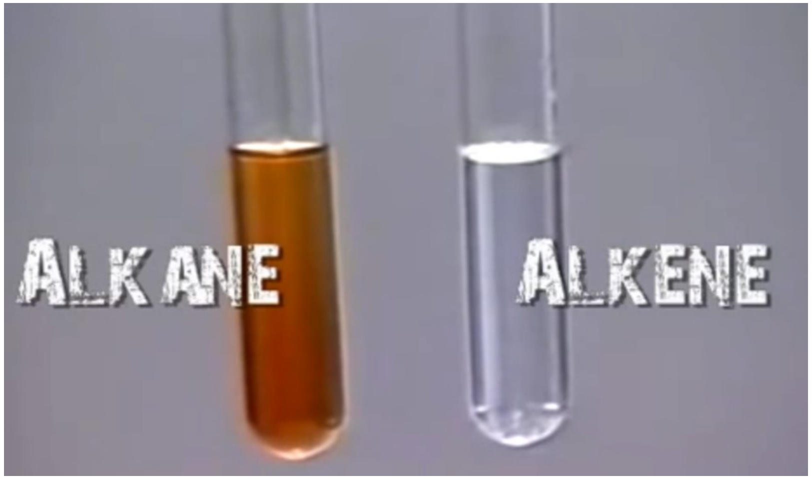
Alkane, reactions:

1. Combustion (oxidation)

2. Pyrolysis (cracking)

3. **Halogenation (depending on conditions)**

Teste para insaturações: como diferenciar alcanos de alcenos (ou alcinos)



video   cicloexano vs. cicloexeno

A reação de bromo com sistemas saturados é um processo radicalar mais lento e requer a iniciação por calor ou luz.

$$\underset{\textbf{Alcano (incolor)}}{R{-}H} + \underset{\textbf{Bromo (marrom-avermelhado)}}{Br_2} \xrightarrow[\text{no escuro, } CCl_4]{\text{temperatura ambiente,}} \text{não ocorre reação apreciável}$$

Reações de adição de halogênios

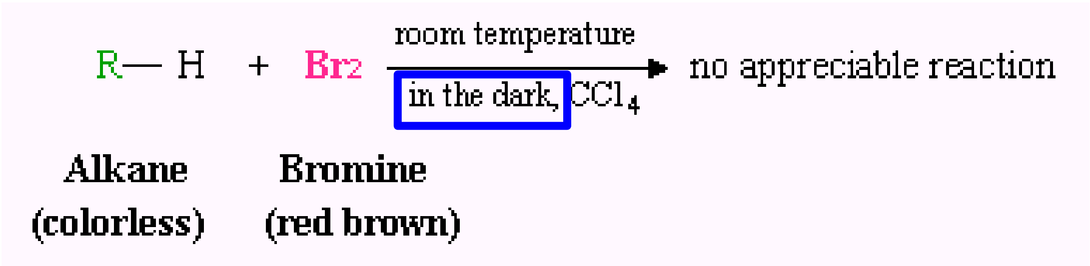
Em alcanos: adições radicalares !!

$$R\text{—}H + Br_2 \xrightarrow[\text{in the dark, } CCl_4]{\text{room temperature}} \text{no appreciable reaction}$$

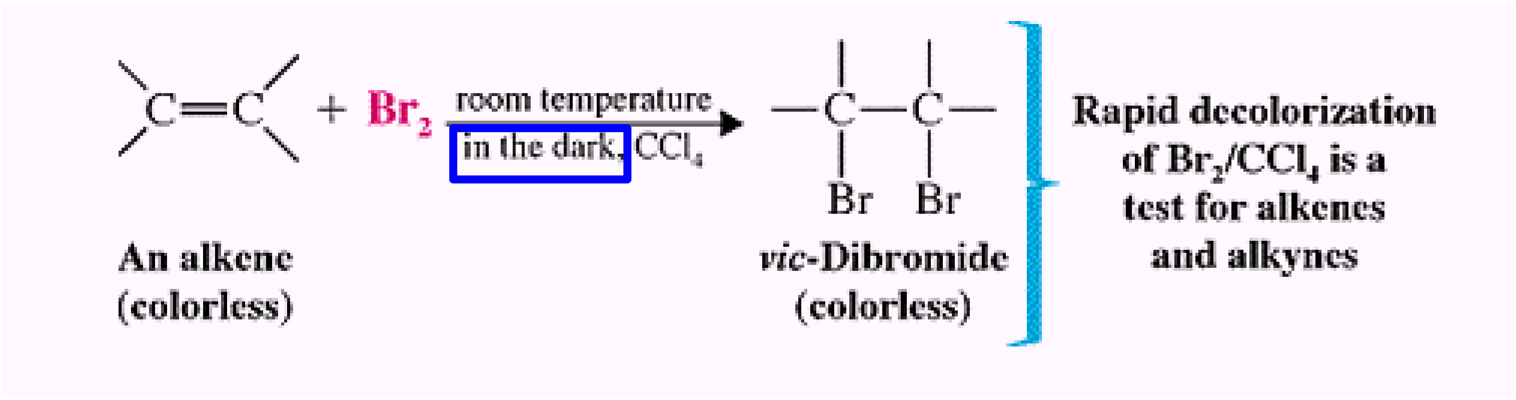
Alkane (colorless) | **Bromine (red brown)**

$$R\text{—}H + Br_2 \xrightarrow[\text{sunlight, } CCl_4]{\text{room temperature}} R\text{—}Br + HBr$$

Alkane (colorless) | **Bromine (red brown)** | **Alkyl halide (colorless)** | **Hydrogen bromide (detected by moist blue litmus)**

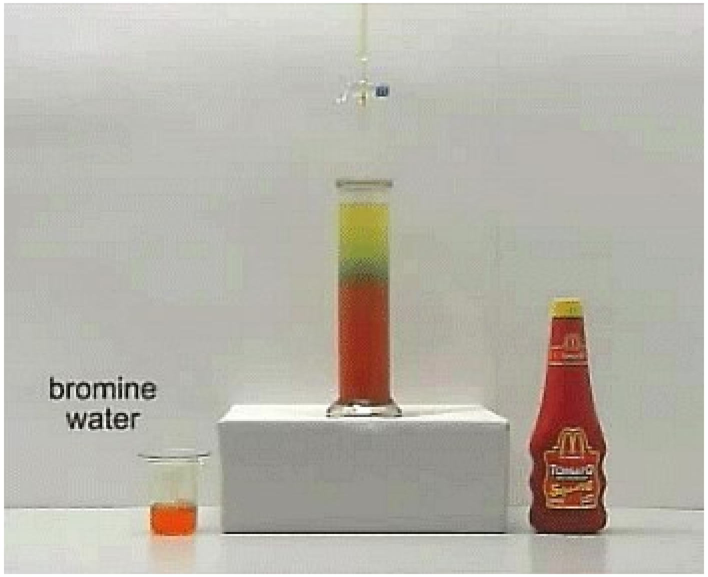


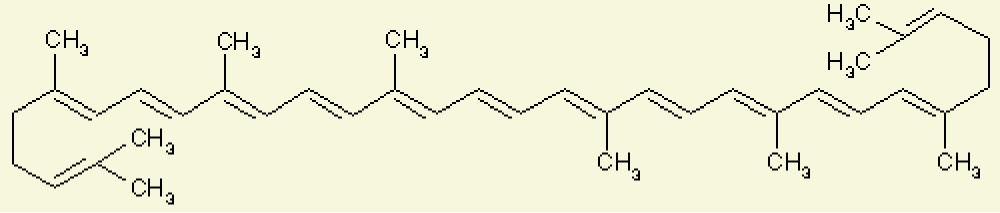
Em alcenos: adições eletrofilicas !!



Fading of Ketchup using Bromine

Electrophilic Addition to the C=C Double Bond



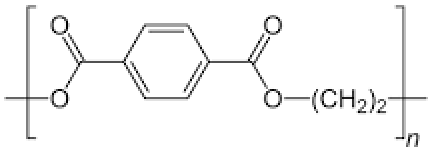


Ethylene

- In terms of quantity produced, ethylene is the most important organic chemical
- Ranked # 4 among all chemicals after
  - 1. Sulfuric acid
  - 2. Nitrogen
  - 3. Oxygen
  - 4. Ethylene

Ethylene Uses

- Polyethylene 55% (2017, over 100 million tonnes of polyethylene resins are produced annually, accounting for 34% of the total plastics market)
- Ethylene dichloride, 16%
- ~20 million tons of 1,2-dichloroethane are produced in the USA, Western Europe, and Japan.
- Ethylene glycol, 13% (PET)

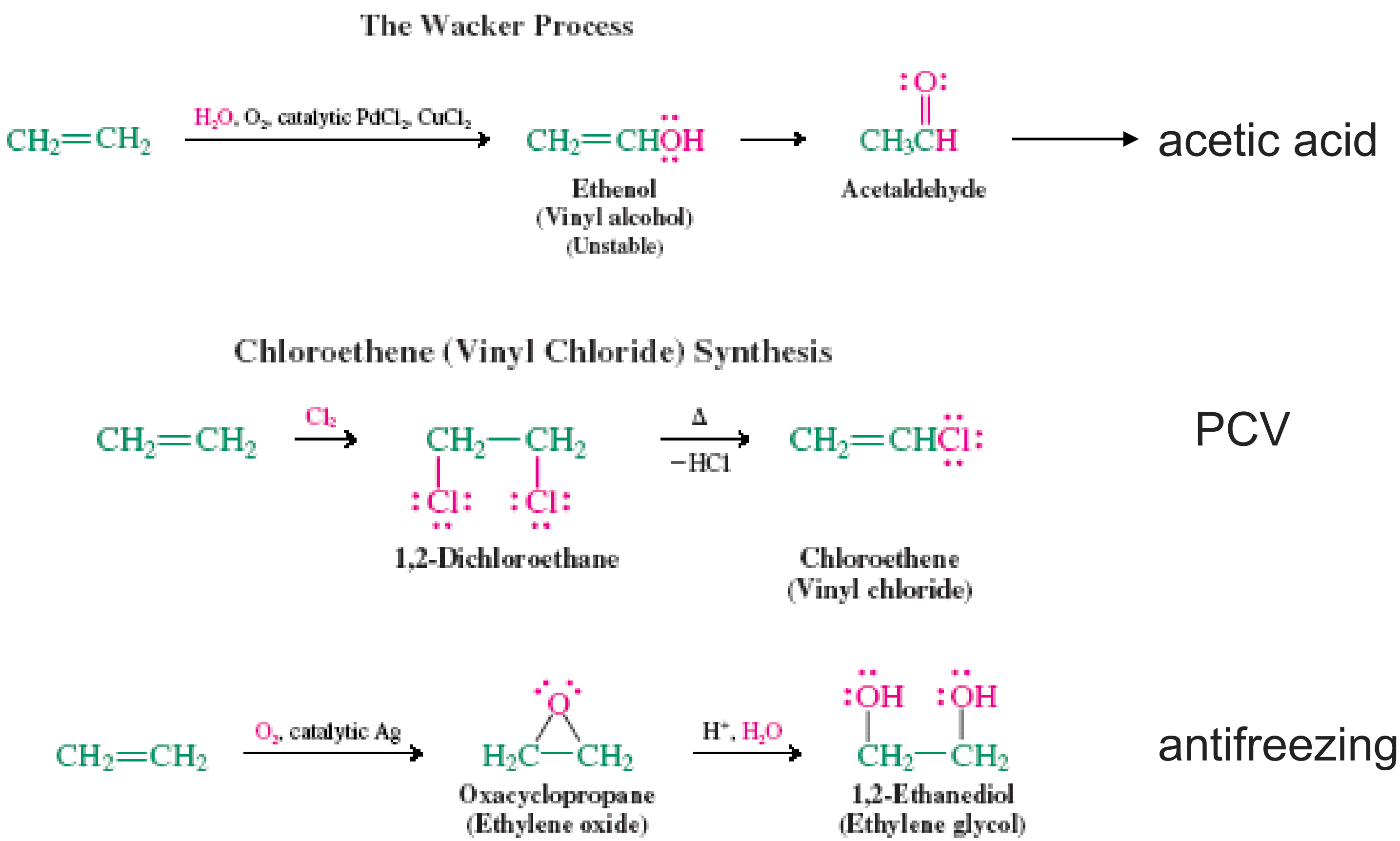


- Ethylbenzene, 6 % (styrene synthesis -> polystyrene)
- Linear alcohols, 4%
- Vinyl acetate, 2%
- Miscellaneous, 4%

The major source of ethene is the pyrolysis of petroleum, or hydrocarbons derived from natural gas.

Ethene is the basis for the production of polyethene (polyethylene).

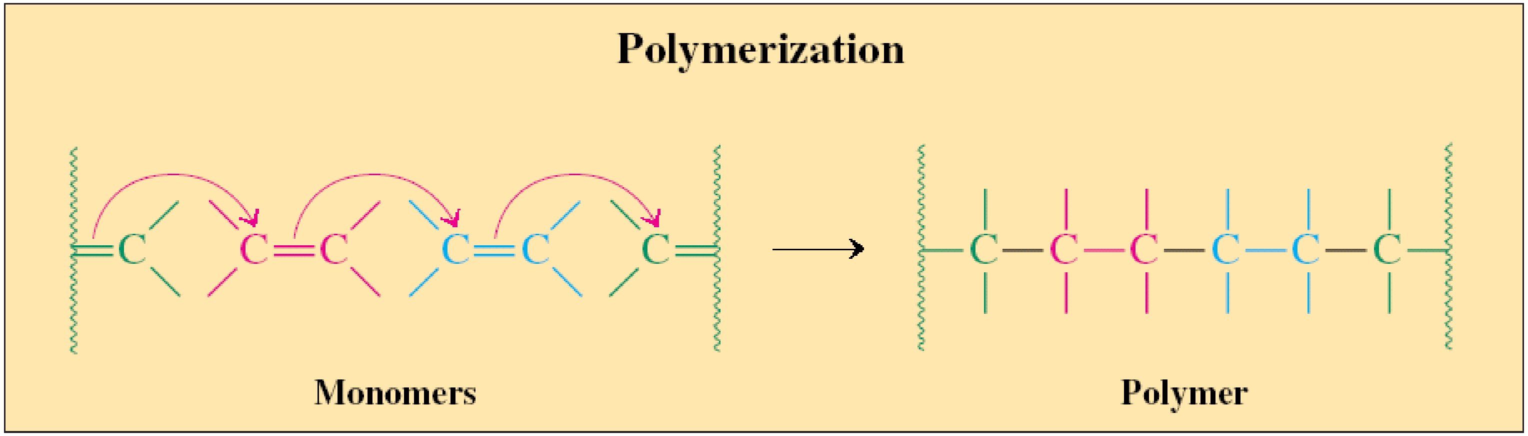
Ethene is the starting material for the production of many other industrial chemicals:



Dimerization, Oligomerization, and Polymerization of Alkenes

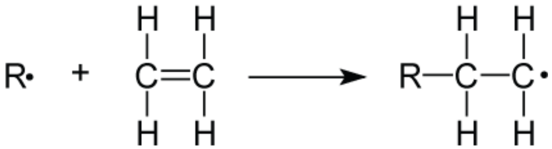
Alkenes can react with one another in the presence of an appropriate catalyst: an acid, a radical, a base, or a transition metal.

Polymer synthesis is of great industrial importance:

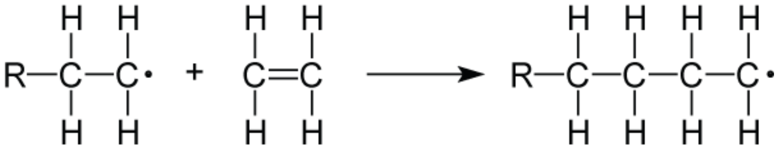


Addition (Chain) Polymerization

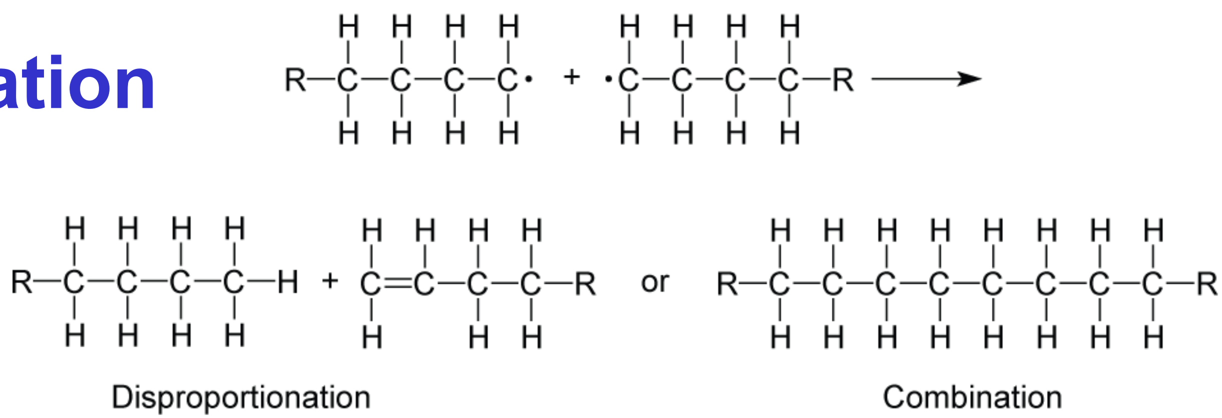
– **Initiation**



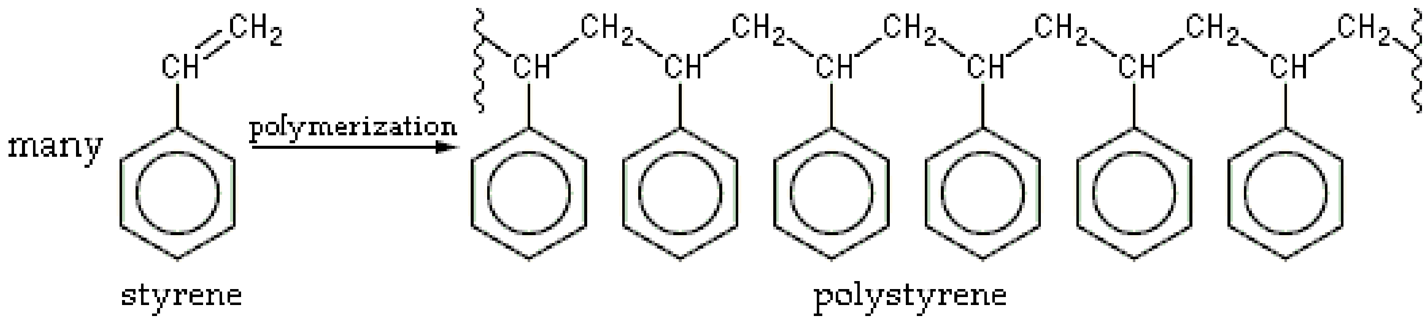
– **Propagation**



– **Termination**



A adição cabeça-cauda de um etileno substituído resulta em um polímero no qual todos os outros carbonos têm um substituinte.



Synthesis of Acetylene

- Heat coke with lime in an electric furnace to form calcium carbide.
- Then drip water on the calcium carbide:

$$\underset{\textit{coke}}{3\ C} + \underset{\textit{lime}}{CaO} \longrightarrow CaC_2 + CO$$

$$CaC_2 + 2\ H_2O \longrightarrow H-C\equiv C-H + Ca(OH)_2$$

This reaction was used to produce light for miners' lamps and for the stage.

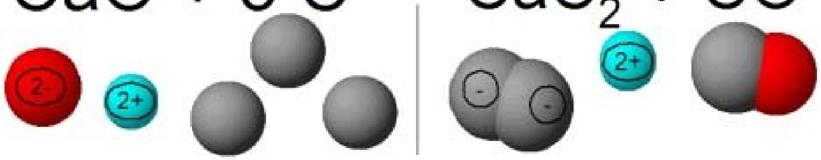
Videos sobre a combustão do acetileno

https://www.youtube.com/watch?v=YQ_l2RpSgMs

https://www.youtube.com/watch?v=i-shpoG6jeM

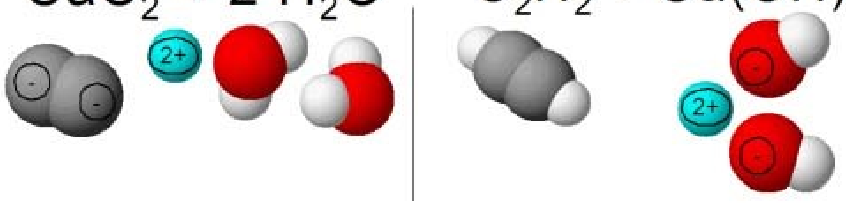
Calcium carbide is manufactured by the reaction of charcoal (carbon) and calcium oxide, at 2000°C, to produce calcium carbide and carbon monoxide:

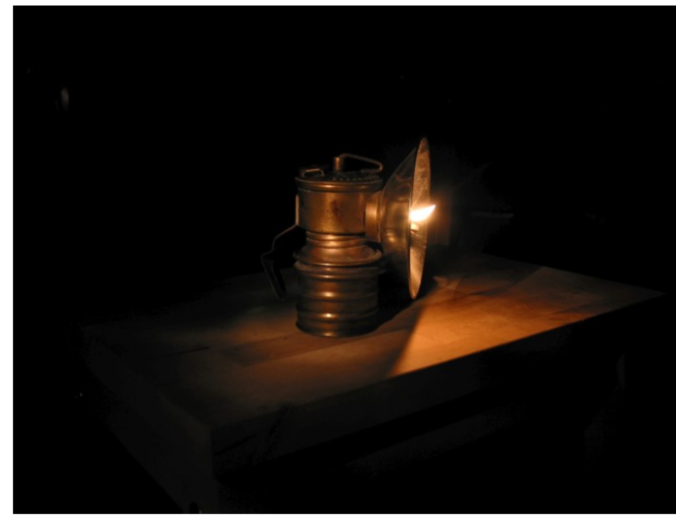
$$CaO + 3\,C \xrightarrow{2000^{\circ}C} CaC_2 + CO$$



Inside the lamp, calcium carbide (7) reacts with water, giving acetylene gas, which flows up to the burner (4), and calcium hydroxide waste:

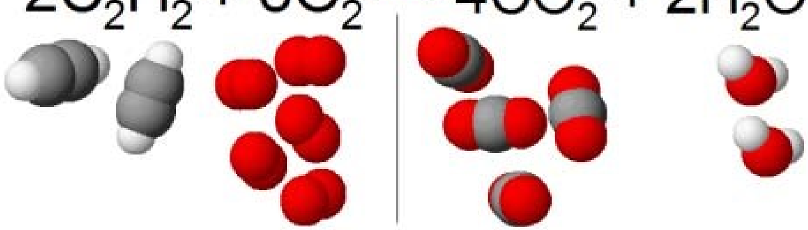
$$CaC_2 + 2\,H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$





The acetylene gas is mixed with air at the burner (4) and combusts, producing a bright white flame (8). The products of the reaction are carbon dioxide and water vapor:

$$2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O$$



(+) denotes a cation (ion) with a positive charge.
(-) denotes an anion with negative charge.
Atoms that are touching are bonded to each other.