HIDROCARBUROS ALIFATICOS

- ALCANOS, ALQUENOS Y ALQUINOS -

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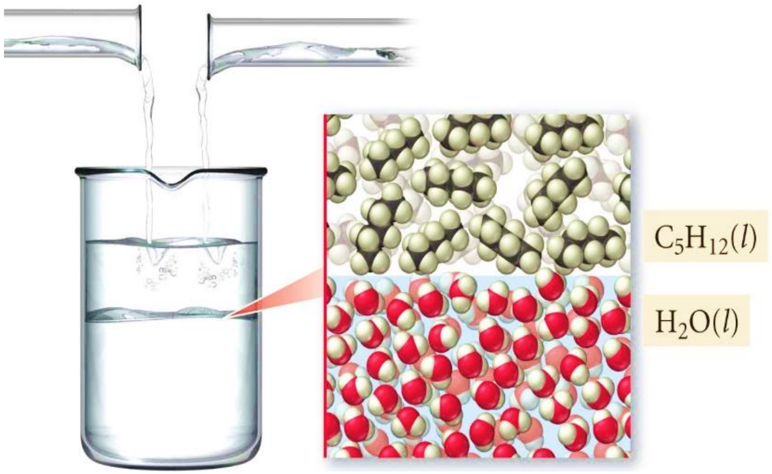
Hidrocarburos alifáticos

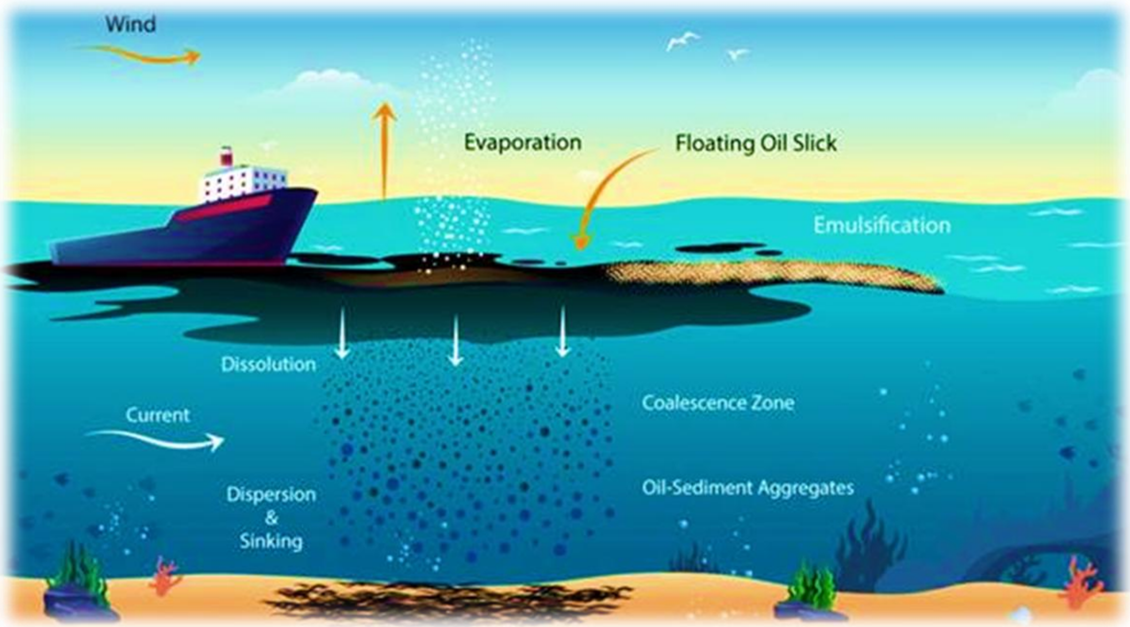
- Alifáticos
  - Cadena abierta
    - Saturados: alcanos
    - Insaturados: alquenos y alquinos
  - Cíclicos
    - Saturados: cicloalcanos
    - Insaturados: cicloalquenos

- Aromáticos
  - Monocíclicos
  - Diciclicos
  - Tricíclicos

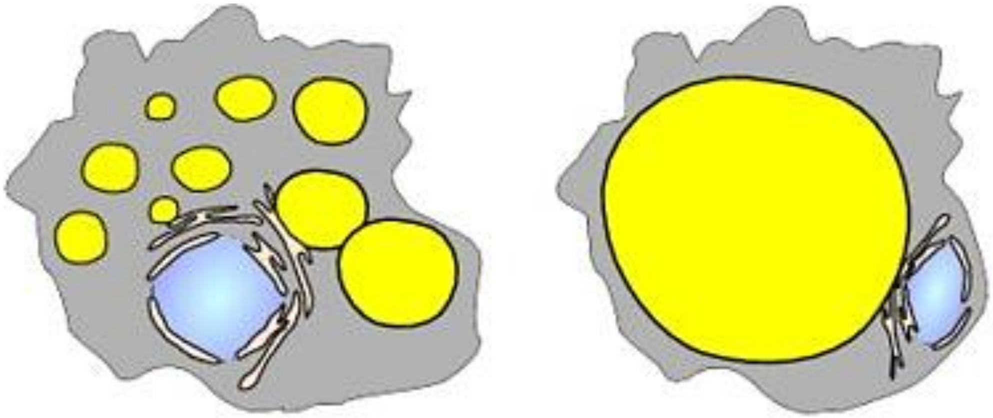
- Son apolares
- Son insolubles en agua
- Son solubles en solventes orgánicos apolares o de baja polaridad (ej benceno, CCl_4, Cloroformo, otros)



- Tienen una menor densidad que el agua (0,6-0,8 g/mL)

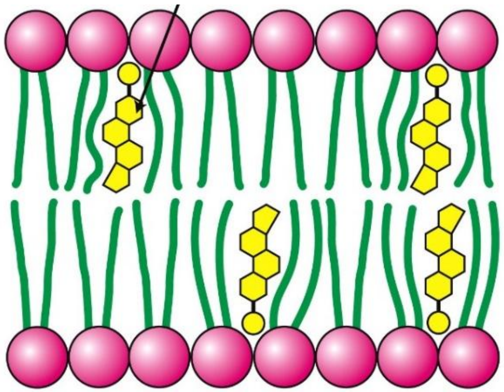


• Los lípidos celulares contienen estructuras hidrocarbonadas (alcanos, cicloalcanos, alquenos).



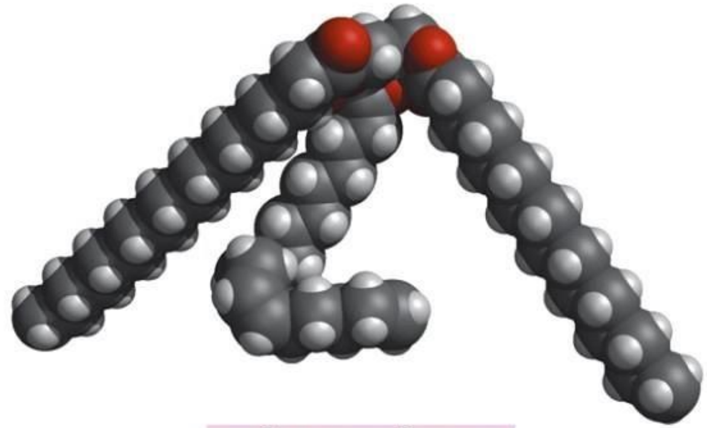
Thiam AR, Beller M. J Cell Sci. 2017 Jan 15;130(2):315-324.

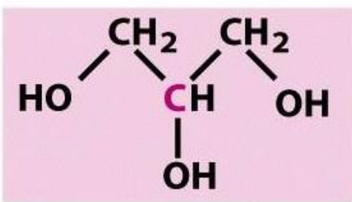
• Constituyen reserva energética y membranas celulares.



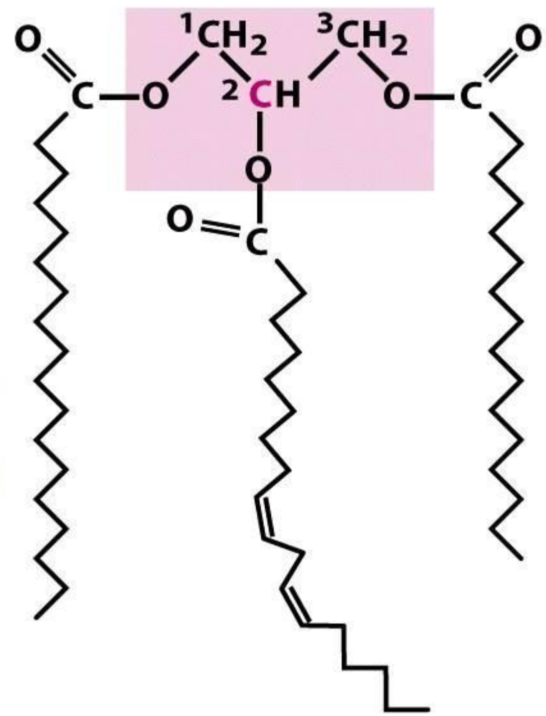
Lípidos - TAG

Triacilgliceroles



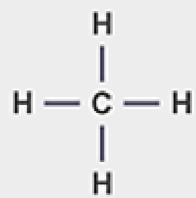
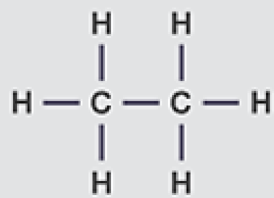
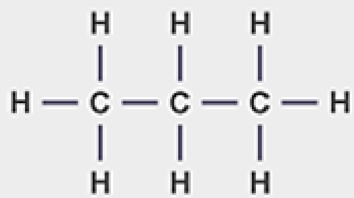
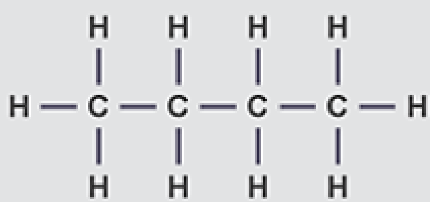
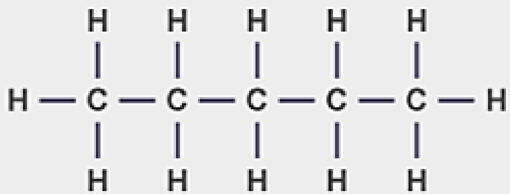
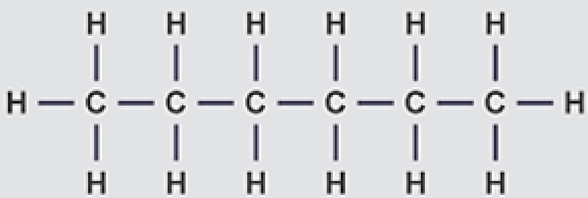
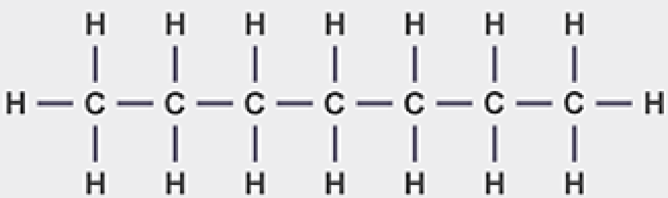
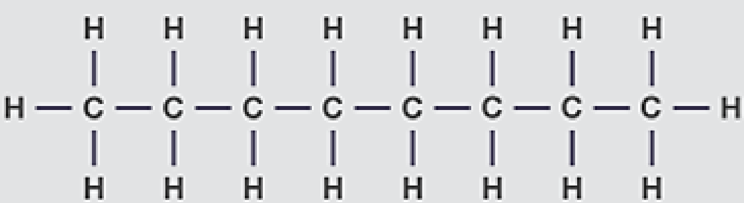


Glicerol

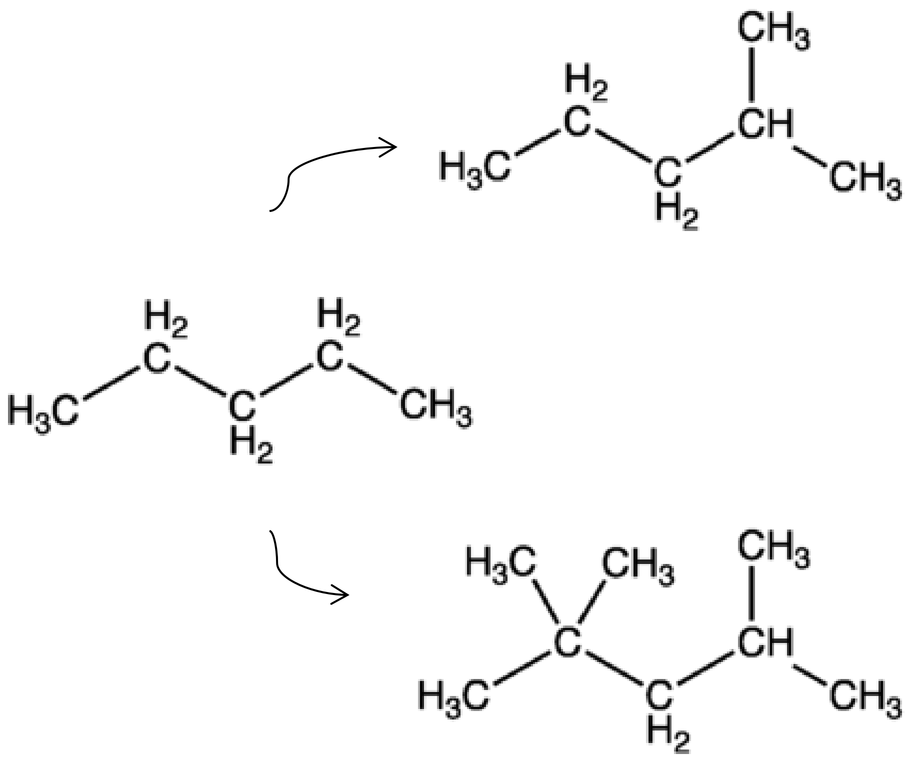


1-estearoil
2-linoleoil
3-palmitoil
glicerol

A. Alcanos de cadena contínua ($C_n H_{2n+2}$)

Molecular formula	Full structural formula
CH_4 Metano	
C_2H_6 Etano	
C_3H_8 Propano	
C_4H_{10} Butano	
C_5H_{12} Pentano	
C_6H_{14} Hexano	
C_7H_{16} Heptano	
C_8H_{18} Octano	

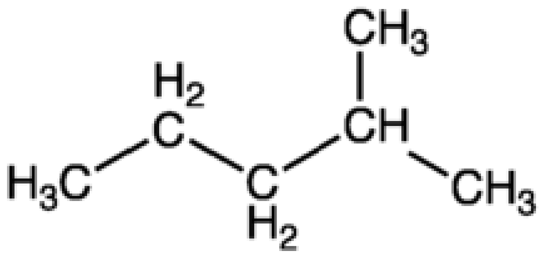
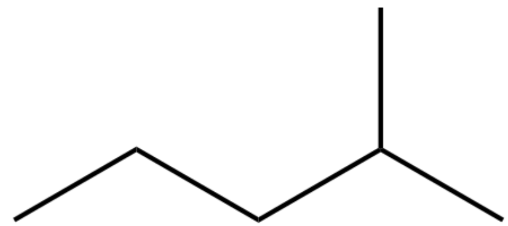
B. Alcanos de cadena ramificada:
Un hidrógeno unido a un carbono “interno” de la cadena, es reemplazado por un carbono o una cadena corta de carbonos

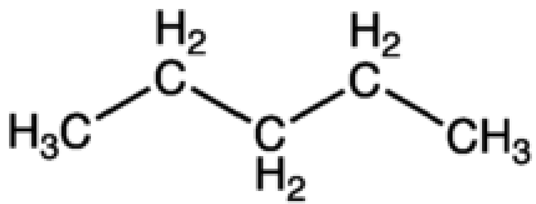
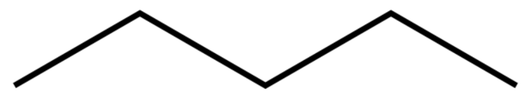


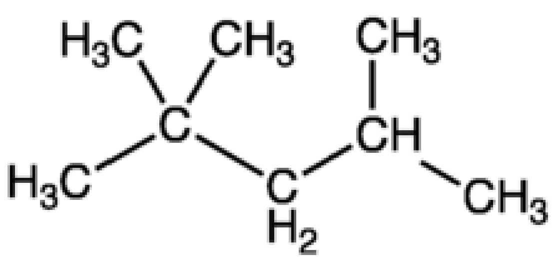
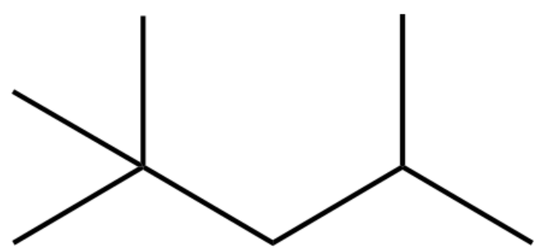
# C	formula	nombre
1	$-CH_3$	metil
2	$-CH_2CH_3$	etil
3	$-CH_2CH_2CH_3$	propil
4	$-CH_2(CH_2)_2CH_3$	butil
5	$-CH_2(CH_2)_3CH_3$	pentil

Alcanos

C. Alcanos lineales y ramificados: formula estructural condensada

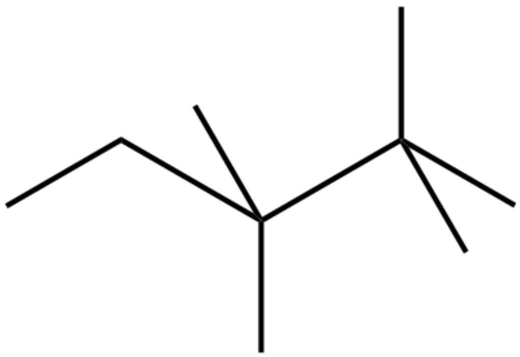



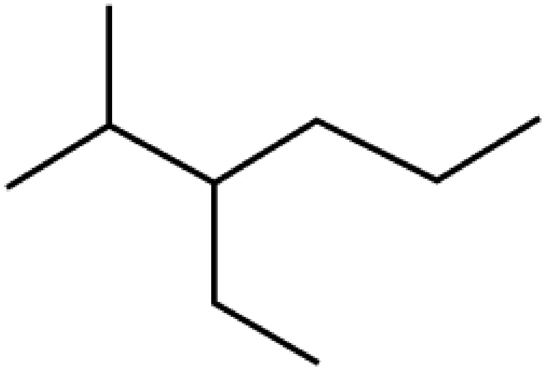



C. Alcanos ramificados: nociones de nomenclatura

a) Identificar cadena hidrocarbonada de mayor longitud
b) Identificar grupos alquilo sustituyentes
c) Asignar posiciones de grupos alquilo de tal forma que <u>*la suma de ellas sea la menor posible*</u> – considerar prioridad alfabética



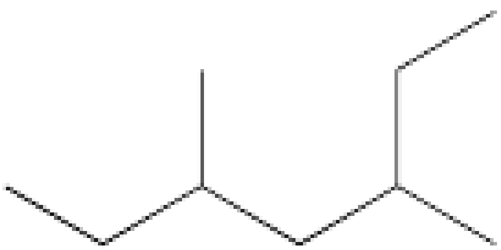
2,2,3,3-tetrametilpentano
no 3,3,4,4-tetrametil



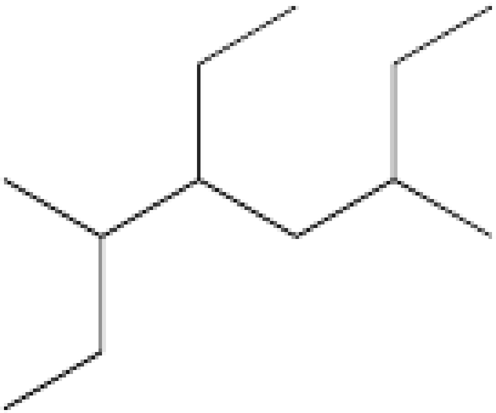
3-etil-2-metilhexano
no 4-etil-5-metil

C. Alcanos ramificados: nociones de nomenclatura (cont)

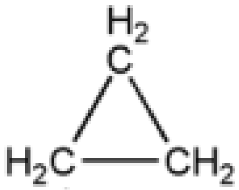
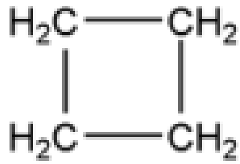
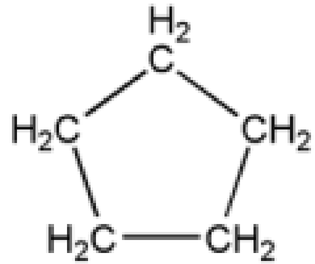
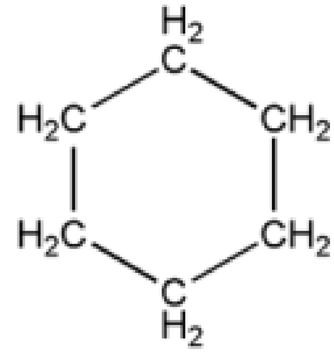
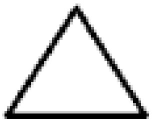
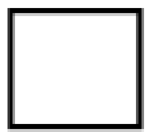
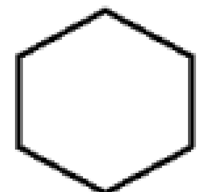
a) Identificar cadena hidrocarbonada de mayor longitud
b) Identificar grupos alquilo sustituyentes
c) Asignar posiciones de grupos alquilo de tal forma que *la suma de ellas sea la menor posible* – considerar prioridad alfabética

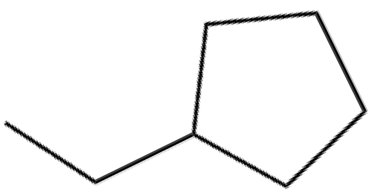


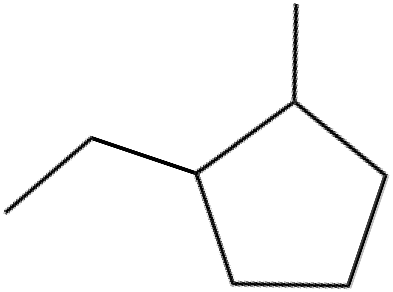
3,5-dimetilheptano

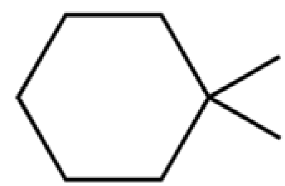


4-etil-3,6-dimetiloctano
no 5-etil-3,6-dimetil

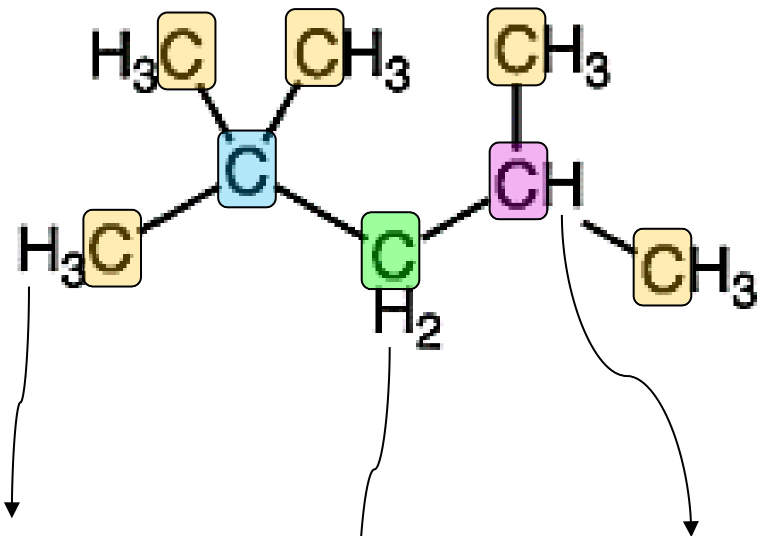
ciclopropano	ciclobutano	ciclopentano	ciclohexano
			
			
C_3H_6	C_4H_8	C_5H_{10}	C_6H_{12}







Tipos de carbonos e hidrógenos



15 H primarios

2 H secundarios

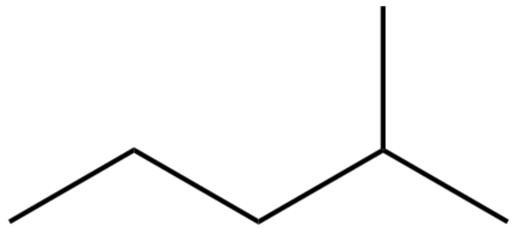
1 H terciario

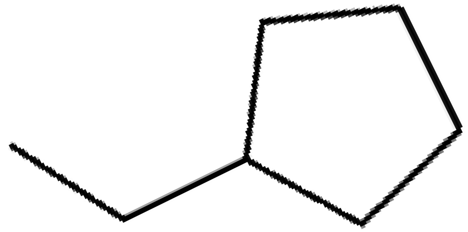
Hidrógenos

Carbonos

- primario
- cuaternario
- secundario
- terciario

Ejercicio 1: Identifique los tipos y numero de carbonos e hidrógenos en las siguientes moléculas.





B.1 Alcanos de cadena contínua – T° fusión y ebullición

Compuesto	*# C*	*Formula*	*T fusión (°C)*	*T ebullición (°C)*
Metano	1	CH_4	-182.5	-161.5
Etano	2	C_2H_6	-183.2	-88.6
Propano	3	C_3H_8	-187.7	-42.1
Butano	4	C_4H_{10}	-138.3	-0.5
Pentano	5	C_5H_{12}	-129.7	36.1
Hexano	6	C_6H_{14}	-95.3	68.7
Heptano	7	C_7H_{16}	-90.6	98.4
Octano	8	C_8H_{18}	-56.8	125.7
Nonano	9	C_9H_{20}	-53.6	150.8
Decano	10	$C_{10}H_{22}$	-29.7	174.0

T° amb

Gas

Líquido

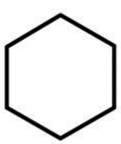
Ejercicio 2: Grafique PM versus T fusión y versus T ebullición

Combustión de hidrocarburos

$$2\ C_nH_{2n+2} + (3n+1)\ O_2 \rightarrow 2n\ CO_2 + (2n+2)\ H_2O + \text{calor}$$

$$C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O + \text{calor}$$

ENTALPIAS DE COMBUSTION [kcal(kJ)/mol], 25°C

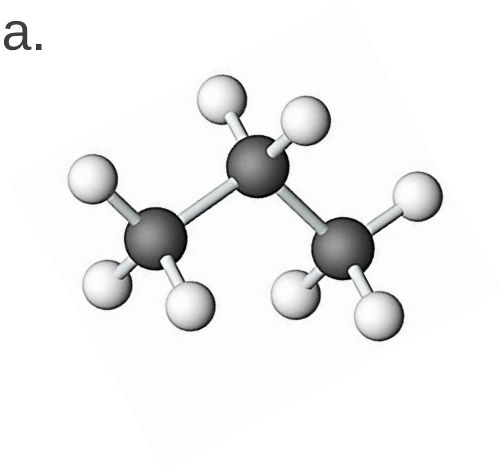
Compound (state)	Name	ΔH°_{comb}
CH_4 (gas)	Methane	−212.8 (−890.4)
C_2H_6 (gas)	Ethane	−372.8 (−1559.8)
$CH_3CH_2CH_3$ (gas)	Propane	−530.6 (−2220.0)
$CH_3(CH_2)_2CH_3$ (gas)	Butane	−687.4 (−2876.1)
$(CH_3)_3CH$ (gas)	2-Methylpropane	−685.4 (−2867.7)
$CH_3(CH_2)_3CH_3$ (gas)	Pentane	−845.2 (−3536.3)
$CH_3(CH_2)_3CH_3$ (liquid)	Pentane	−838.8 (−3509.5)
$CH_3(CH_2)_4CH_3$ (liquid)	Hexane	−995.0 (−4163.1)
 (liquid)	Cyclohexane	−936.9 (−3920.0)
CH_3CH_2OH (gas)	Ethanol	−336.4 (−1407.5)
CH_3CH_2OH (liquid)	Ethanol	−326.7 (−1366.9)
$C_{12}H_{22}O_{11}$ (solid)	Cane sugar (sucrose)	−1348.2 (−5640.9)

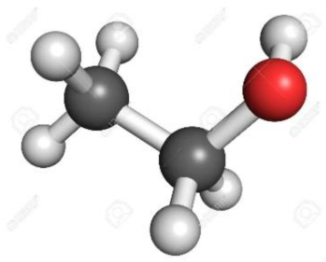
Ejercicio 3: Considere la reacción de combustión del propano:

$$\mathbf{C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O} + \textit{calor}$$

Determine los ***estados de oxidación*** de los C del propano y del C del CO_2

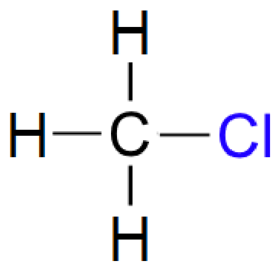
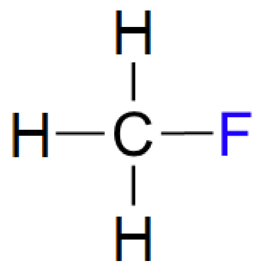
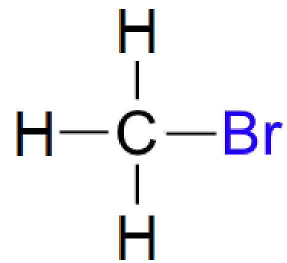
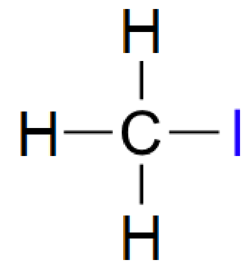
Ejercicio 4: De la tabla anterior, observamos que los ΔH_{COMB} del propano (PM=44) y del etanol (PM=46) son **-530,6** y **-336,4** kcal/mol, respectivamente. Proponga una explicación para esta diferencia.

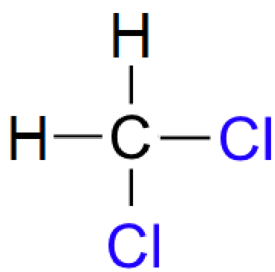
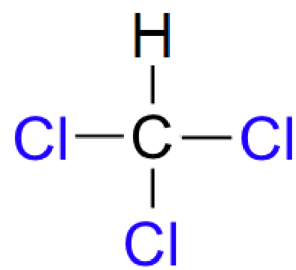
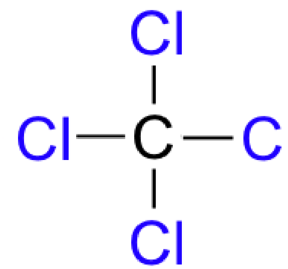


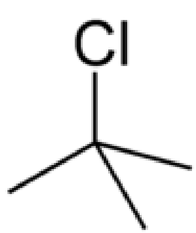
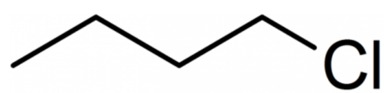
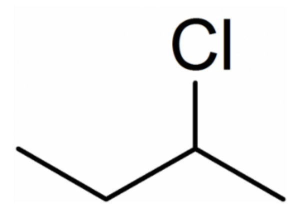
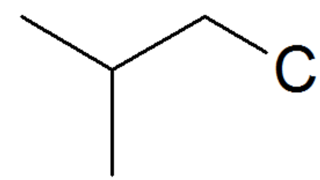


Haloalcanos

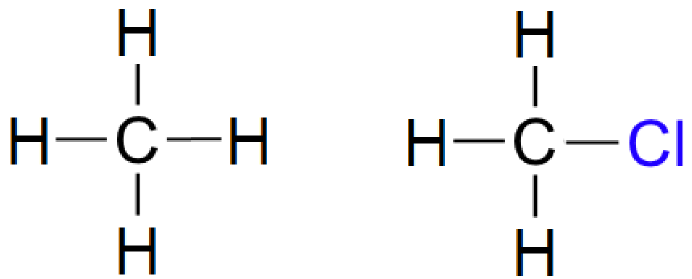
clorometano fluorometano bromometano iodometano

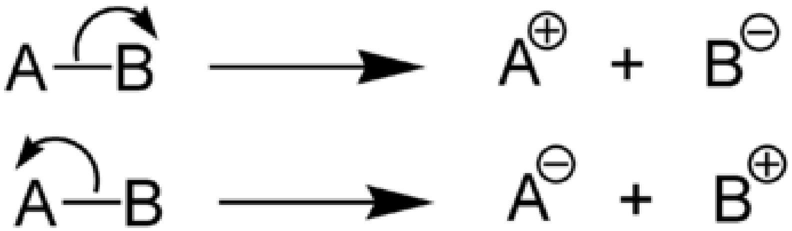




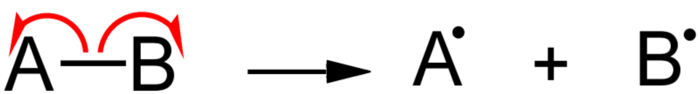
Alcanos - Halogenación



Sustitución por radicales libres



heterólisis



homólisis

Alcanos - Halogenación

$$\underset{\text{Alcano}}{RCH_3} + \underset{\text{Halogeno}}{X_2} \longrightarrow \underset{\text{Haloalcano}}{RCH_2X} + \underset{\text{Haluro de hidrogeno}}{HX}$$

		$\underline{\Delta H°\ (kcal/mol)}$
Iniciación	$\underset{\text{Halógeno}}{X_2} \xrightarrow{h\nu} \underset{\text{Radicales haluro}}{2\,X\cdot}$	+58
Propagación	$\underset{\text{Radical haluro}}{X\cdot} + \underset{\text{Alcano}}{RCH_3} \longrightarrow \underset{\text{Radical alquilo}}{RCH_2\cdot} + HX$	+2
	$X_2 + RCH_2\cdot \longrightarrow RCH_2X + X\cdot$	-27
Terminación	$X\cdot + RCH_2\cdot \longrightarrow RCH_2X$	
	$X\cdot + X\cdot \longrightarrow X_2$	
	$RCH_2\cdot + RCH_2\cdot \longrightarrow RCH_2CH_2R$	

Halogenación – más de un producto

	43%	57%	

$$Cl_2 + CH_3CH_2CH_3 \xrightarrow{h\nu} CH_3CH_2CH_2Cl + CH_3CH(Cl)CH_3 + HCl$$

1-cloropropano

2-cloropropano

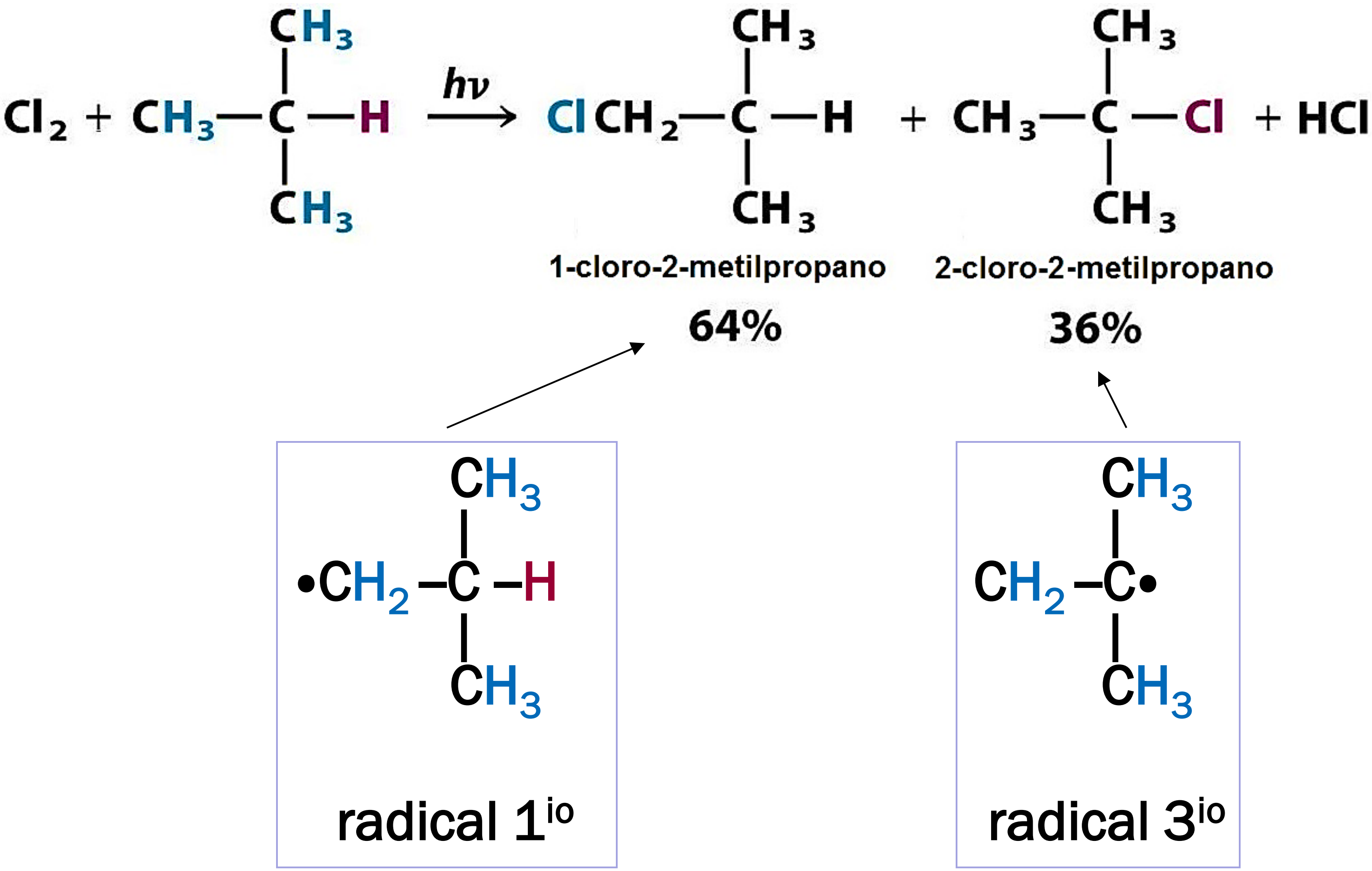
CH_3-CH_2-$CH_2\bullet$

radical 1io

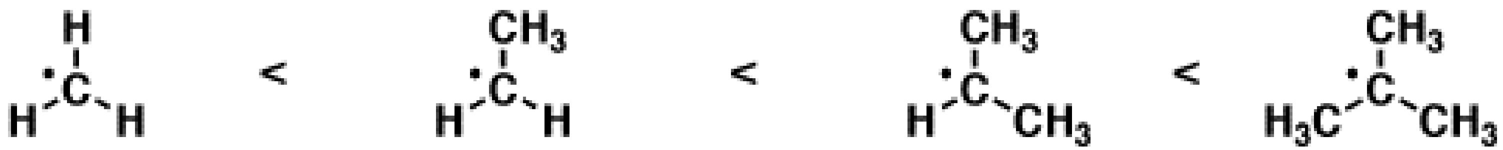
CH_3-$\dot{C}H$-CH_3

radical 2io

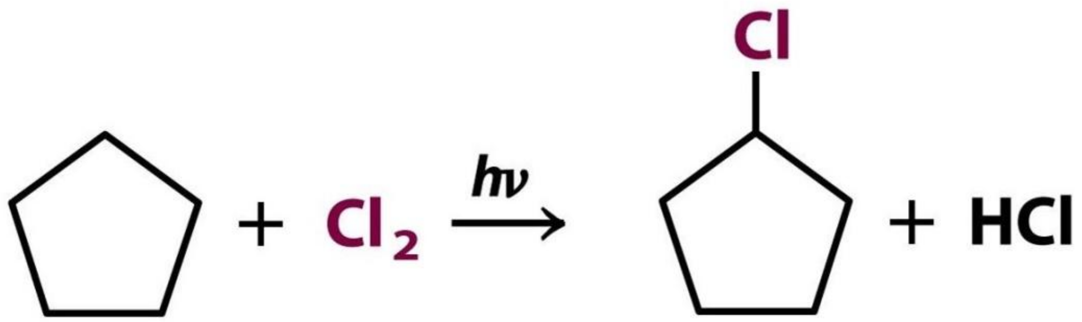
Halogenación – más de un producto



Metilo | Primario | Secundario | Terciario



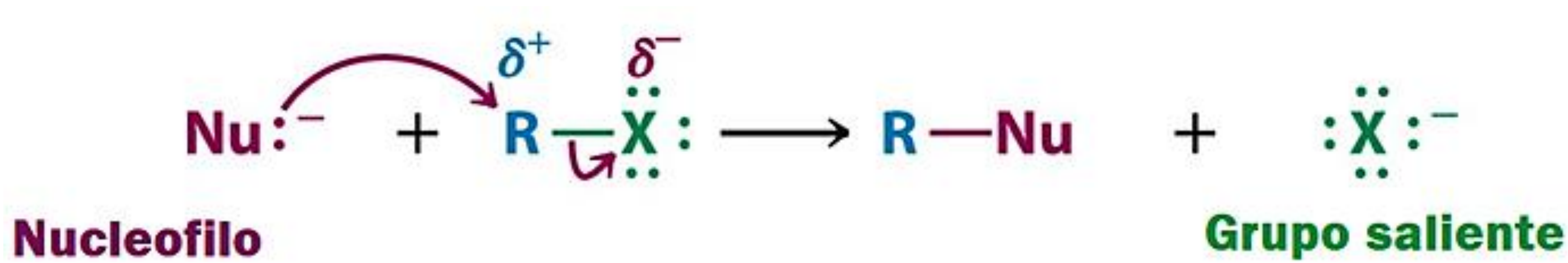
– estable | + estable



Ciclopentano | Clorociclopentano 92.7%

Sustitución nucleofílica (SN)

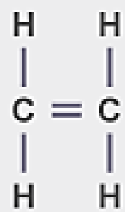
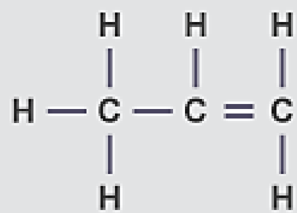
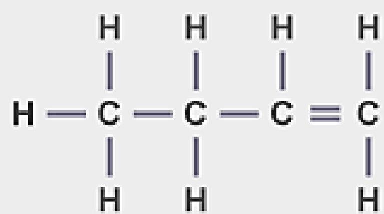
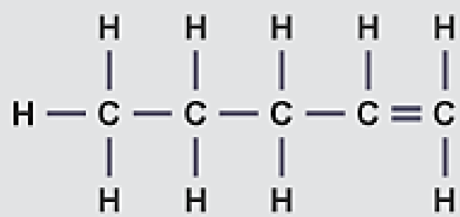
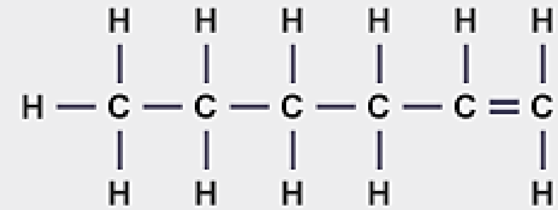
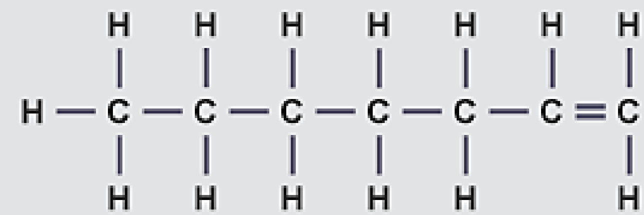
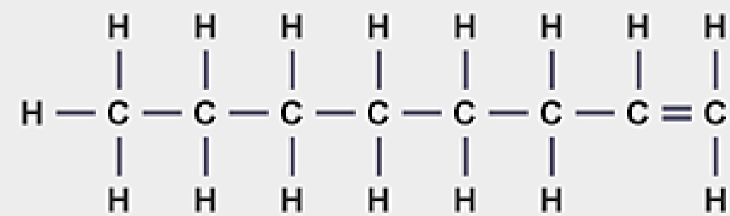
- Reacción en la que un nucleófilo reemplaza a un “grupo saliente” (X), por ej. en un haloalcano.
- Cuando X sale, se “lleva” ambos electrones del enlace R–X.
- Ej: es posible la síntesis de un alcohol a partir de un haloalcano.



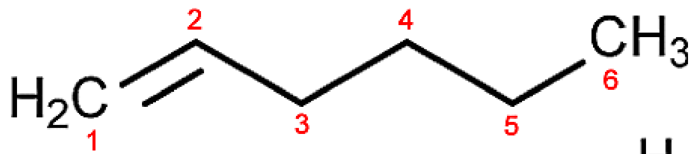
$$OH^{-} + CH_3\text{–}Cl \rightarrow CH_3OH + Cl^{-}$$

$$NH_3 + CH_3\text{–}Cl \rightarrow CH_3NH_2 + HCl$$

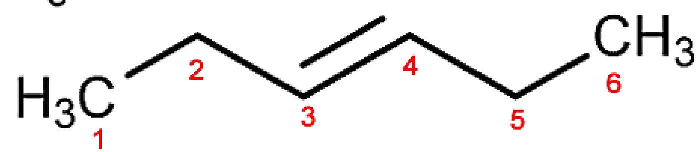
Alquenos

Molecular formula	Full structural formula
C_2H_4 Eteno	
C_3H_6 Propeno	
C_4H_8 1-buteno	
C_5H_{10} 1-penteno	
C_6H_{12} 1-hexeno	
C_7H_{14} 1-hepteno	
C_8H_{16} 1-octeno	

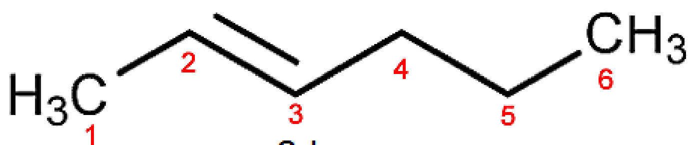
Alquenos – isómeros de posición y geométricos



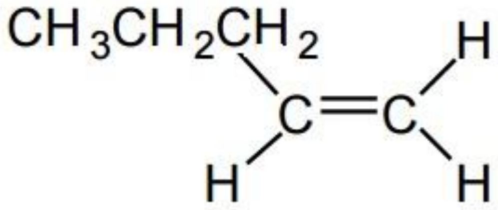
1-hexeno



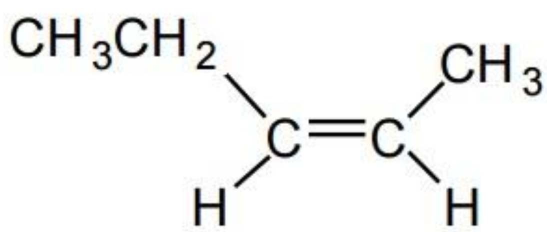
3-hexeno



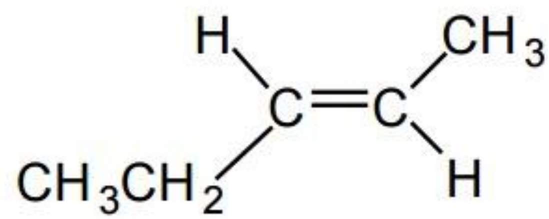
2-hexeno



1-penteno

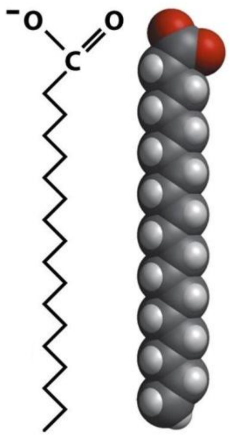


cis-2-penteno

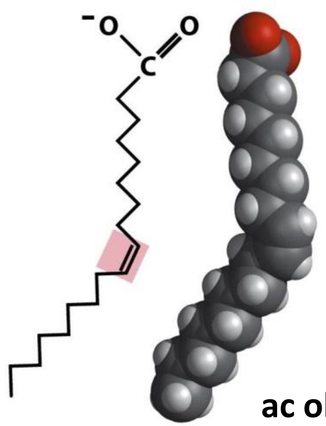


trans-2-penteno

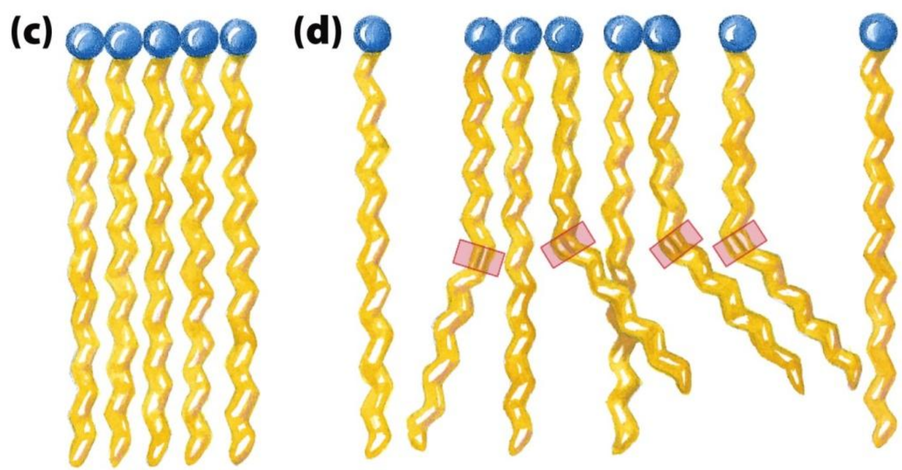
Ácidos grasos – propiedades físicas



ac esteárico
18:0

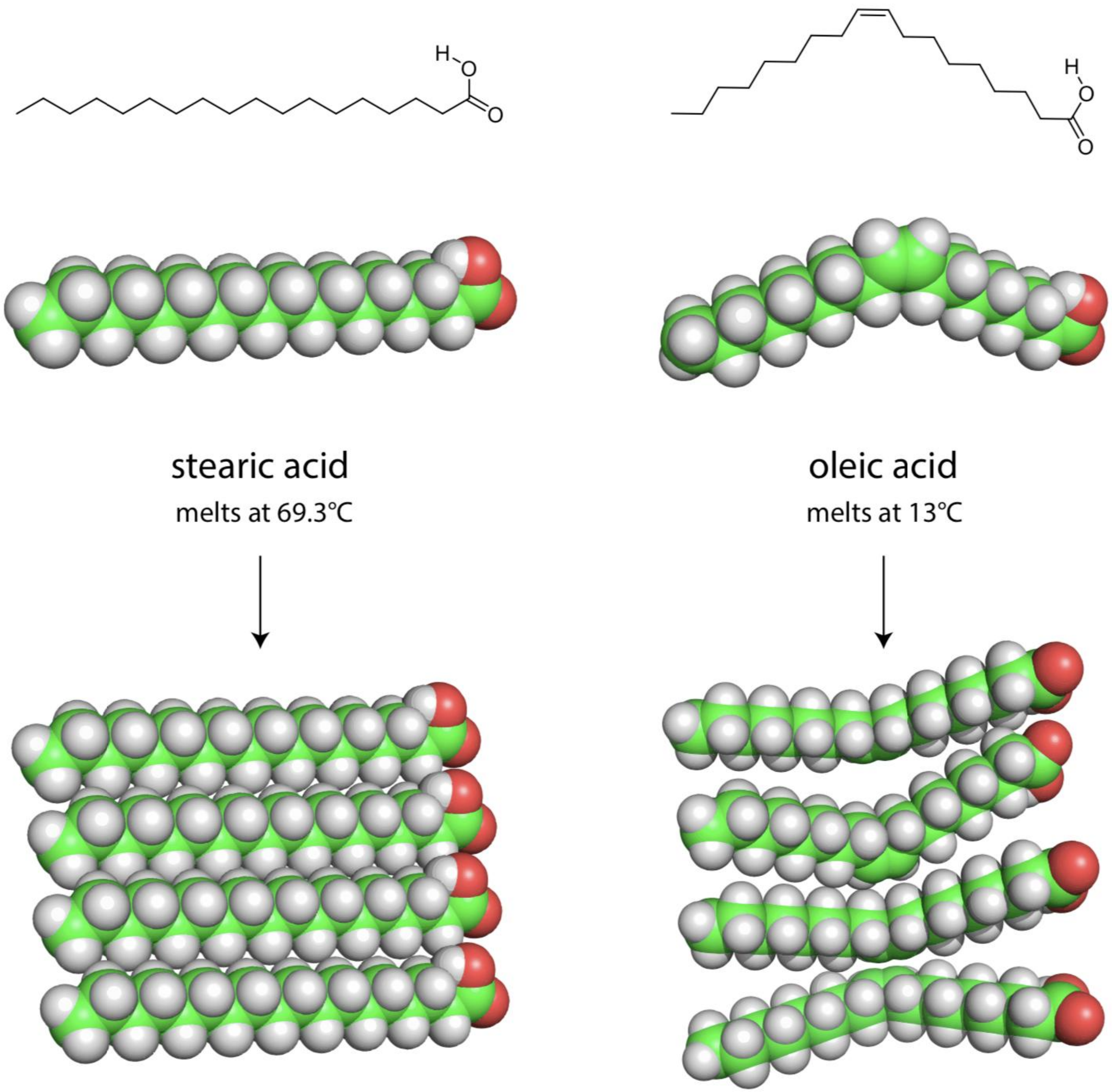


ac oleico
18:1(Δ^9)

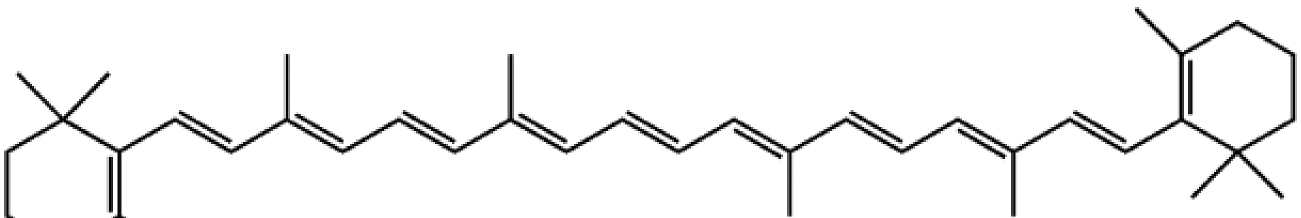


C: (=)	Formula	Nombres		T fusion (°C)
18:0	$CH_3(CH_2)_{16}COOH$	*n*-Octadecanoic acid	Stearic acid	69.6
18:1(Δ^9)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	*cis*-9-Octadecenoic acid	Oleic acid	13.4
18:2($\Delta^{9,12}$)	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	*cis*-,*cis*-9,12-Octadecadienoic acid	Linoleic acid	1–5
18:3($\Delta^{9,12,15}$)	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	*cis*-,*cis*-,*cis*-9,12,15-Octadecatrienoic acid	α-Linolenic acid	−11

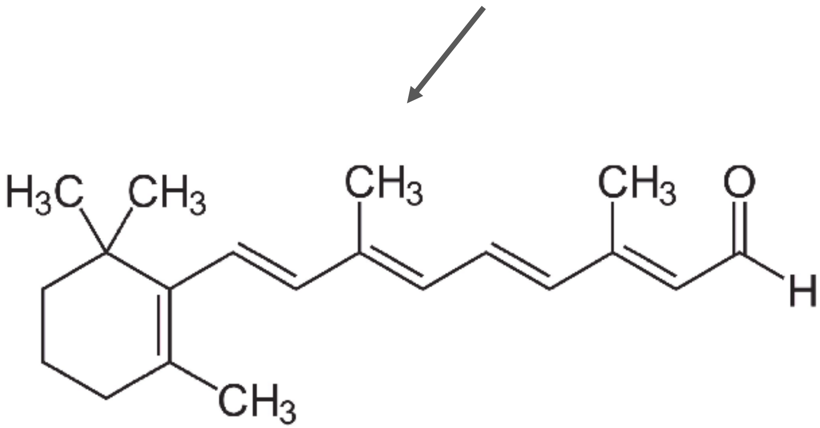
Ácidos grasos – propiedades físicas



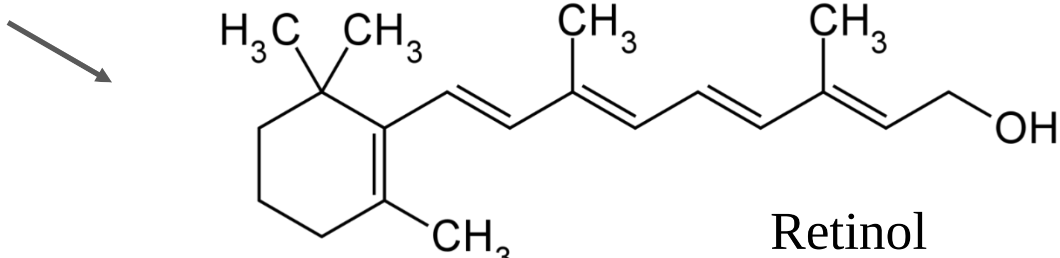
Carotenos – Vitamina A



β-Carotene

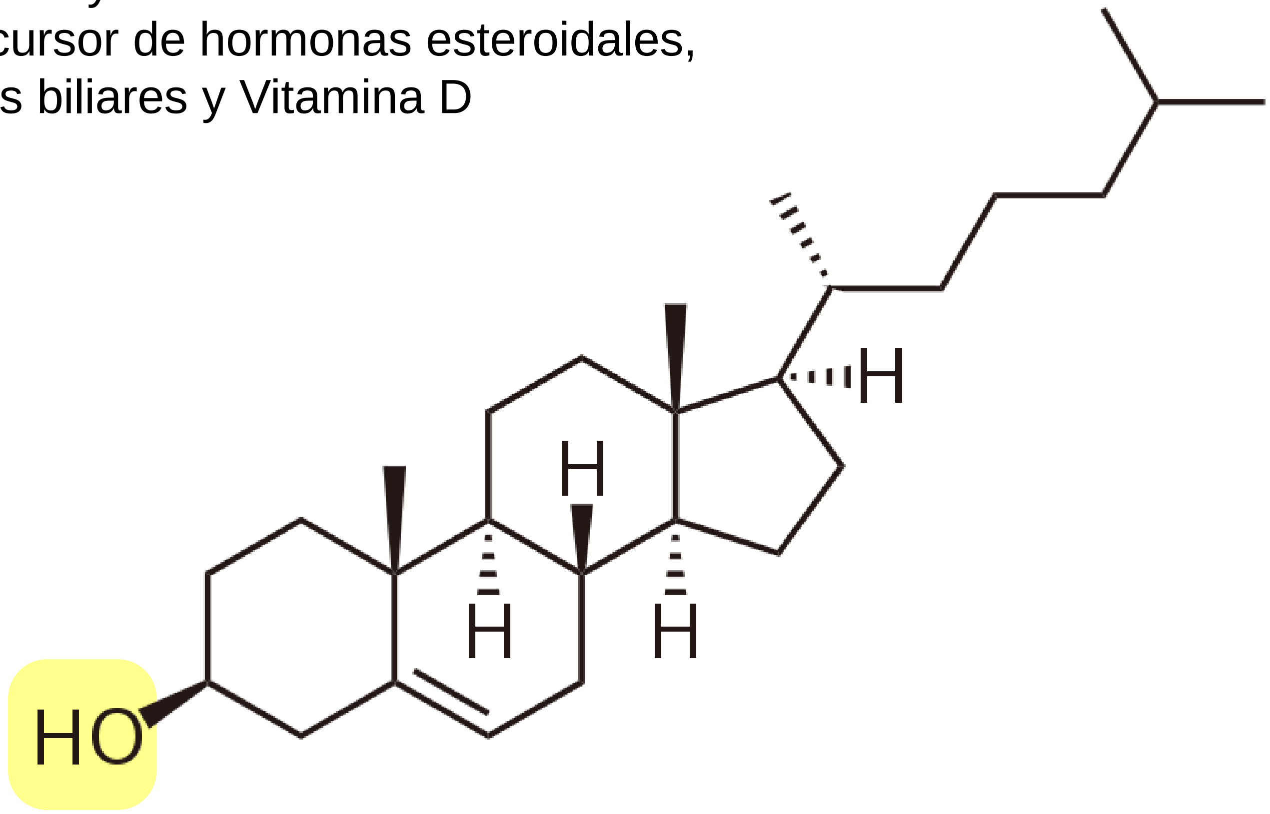


Retinal

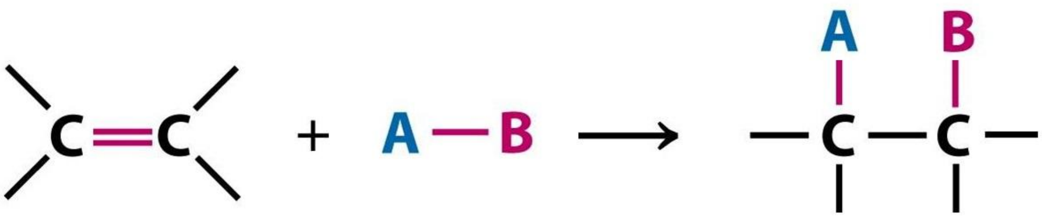


Retinol

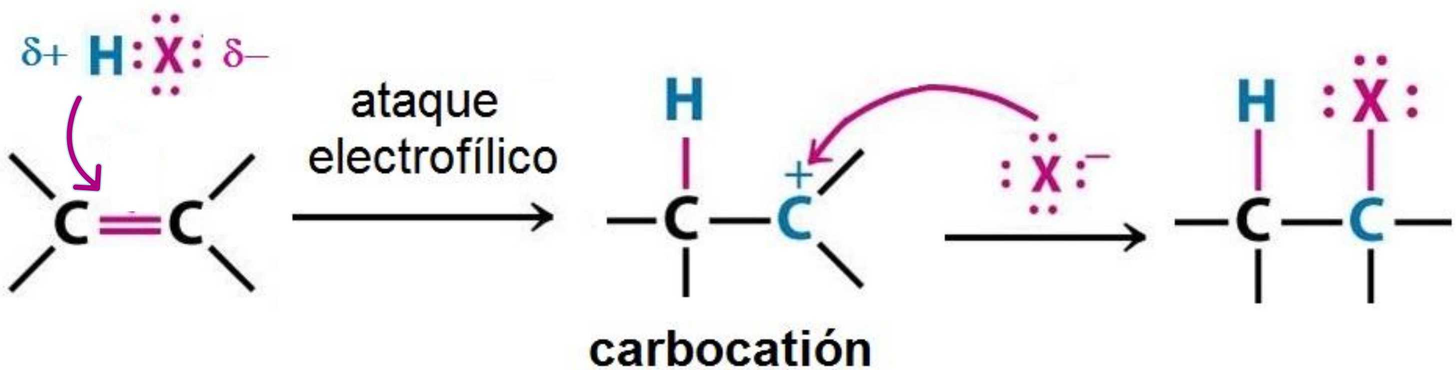
- ✓ Molécula anfipática
- ✓ Constituyente de membranas celulares
- ✓ Precursor de hormonas esteroidales, sales biliares y Vitamina D



Adición electrofílica al doble enlace



A – B
H_2
HX
X_2
H_2O



ΔH°

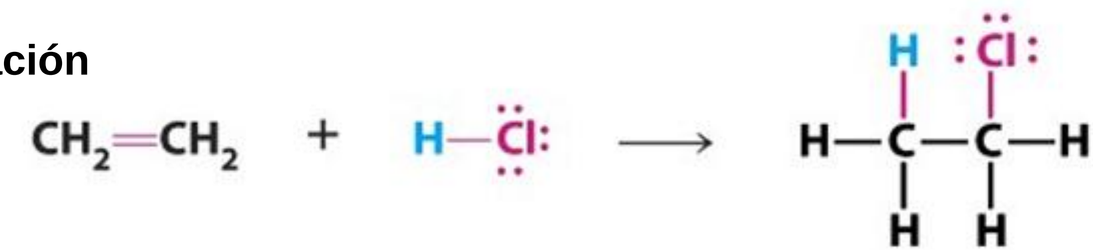
- **Hidrogenación**

−33

- **Halogenación**

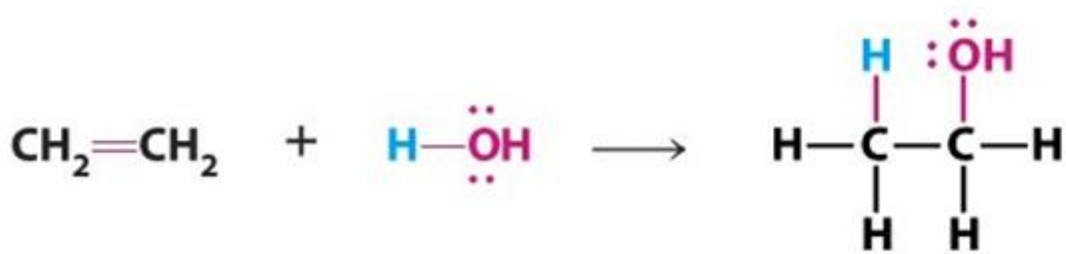
−29

- **Hidrohalogenación**

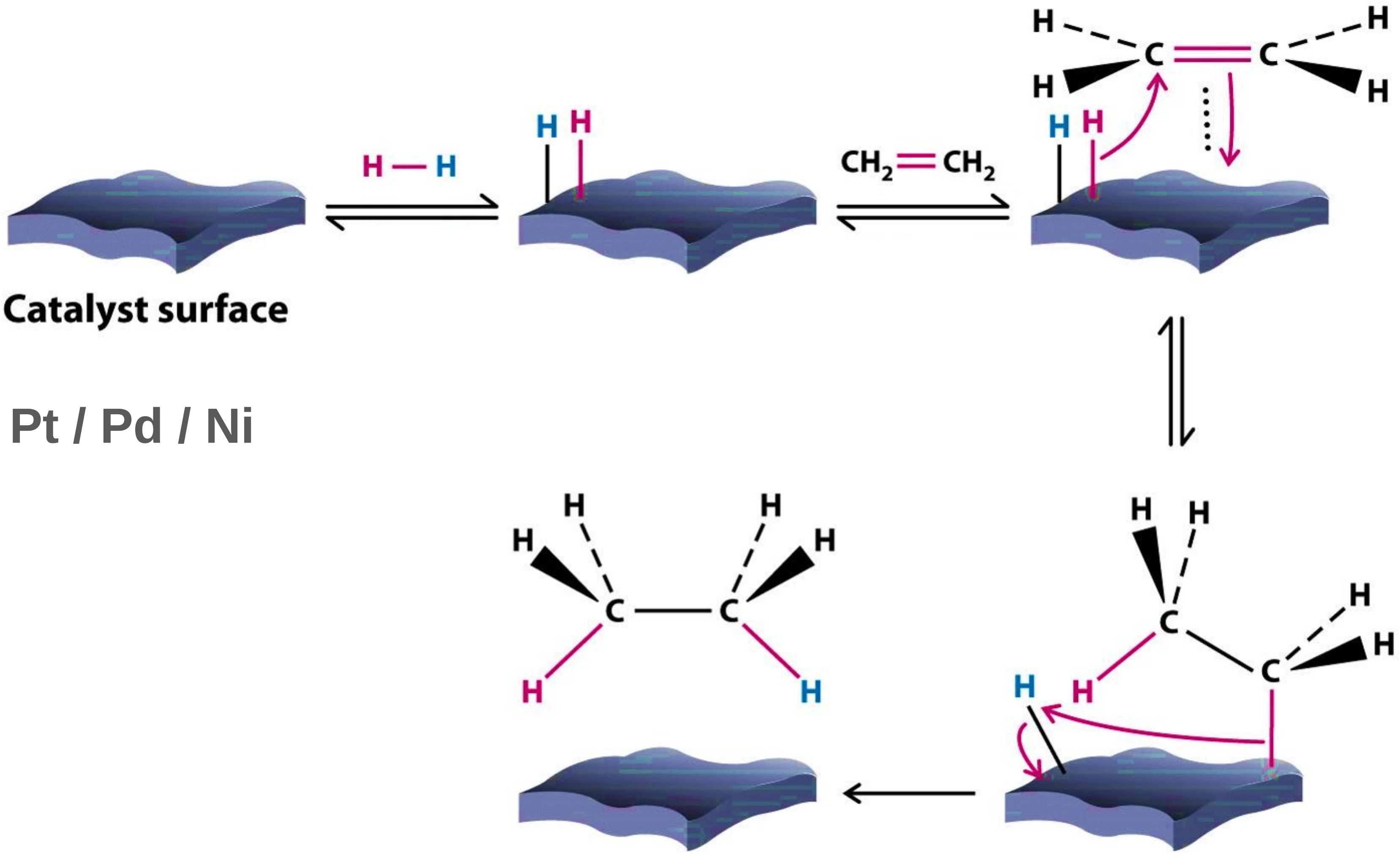


−17

- **Hidratación**



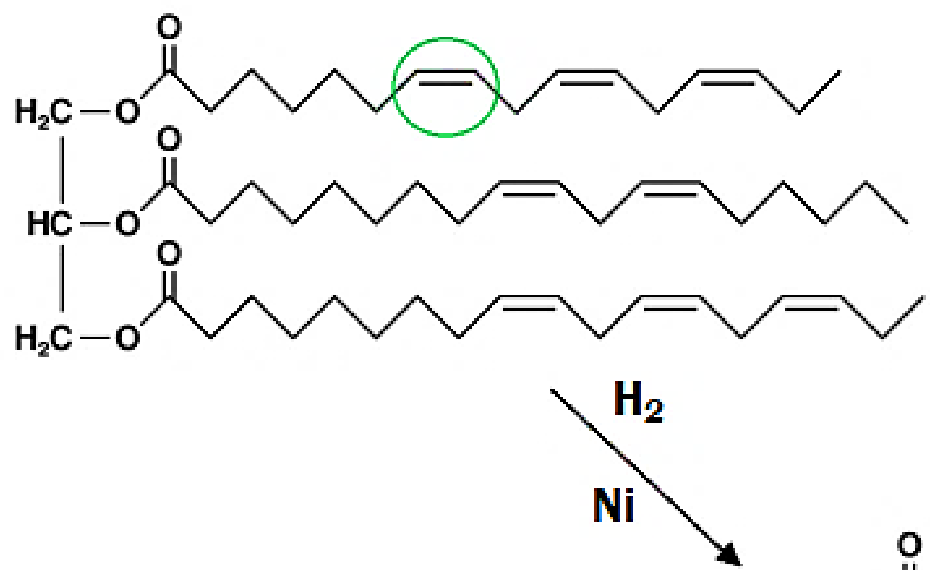
−11

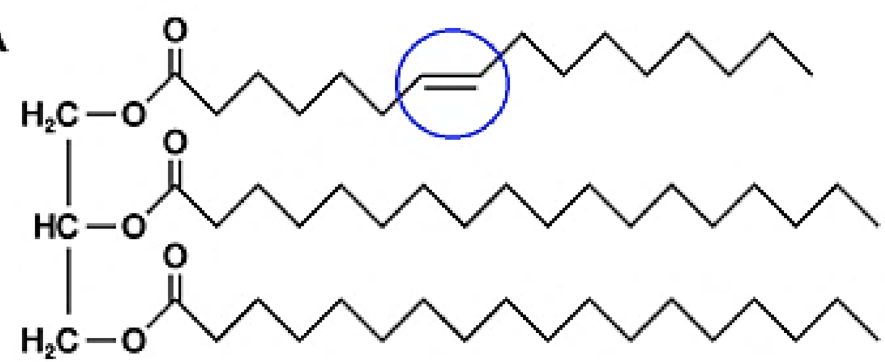


Pt / Pd / Ni

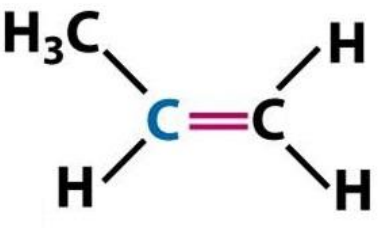
Figure 12-1
Organic Chemistry, Fifth Edition

Hidrogenación – Acs grasos insaturados

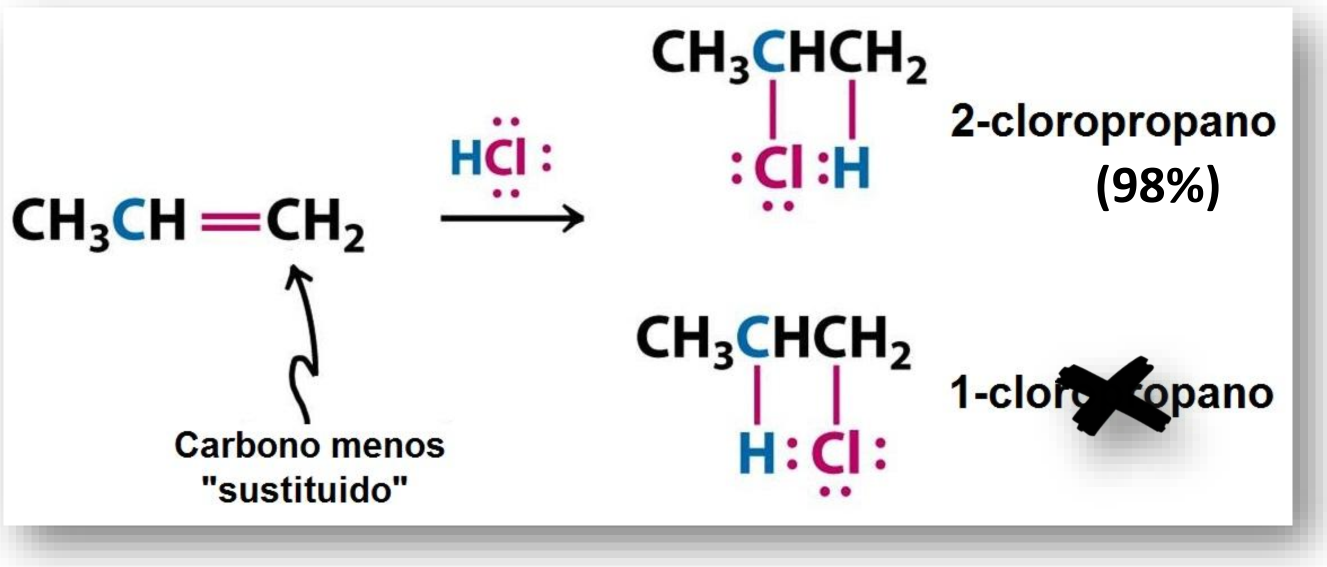




INFORMACIÓN NUTRICIONAL		
Porción: 1/4 Galleton (35 g)		
Porciones por envase: 4		
	100 g	1 porción
Energía (kcal)	570	199
Proteinas (g)	6,4	2,3
Grasa Total (g)	19,1	6,7
Grasa saturada (g)	11,1	3,9
Grasa monoinsaturada (g)	6,0	2,1
Grasa poliinsaturada (g)	1,5	0,5
Grasa trans (g)	1,0	0,4
Colesterol (mg)	38,0	13,3
H.de Carbono Disp. (g)	95,0	33,2
Azucares totales (g)	54,2	18,9
Sodio (mg)	458,2	160,4



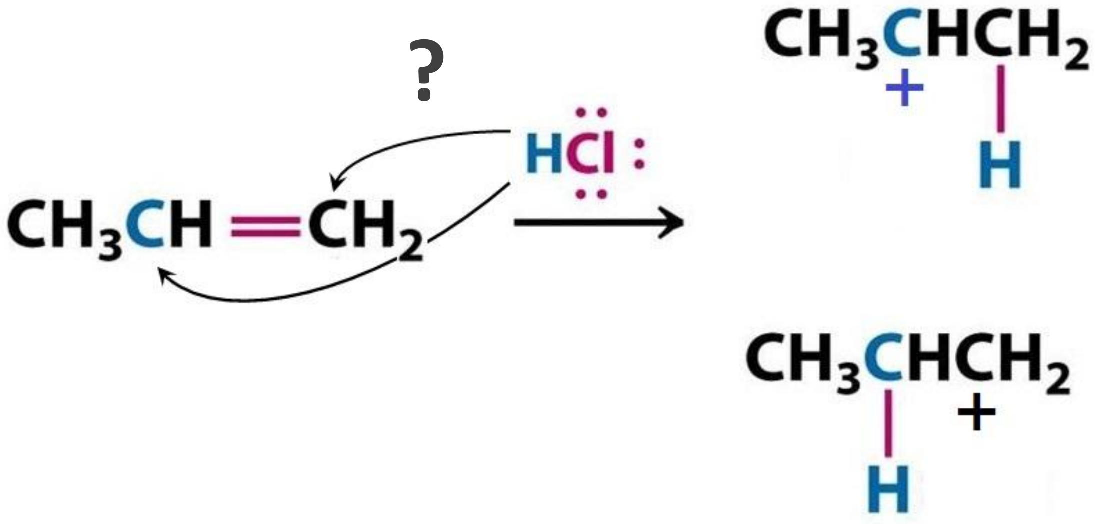
¿Cómo ocurre la adición de un electrófilo asimétrico a un alqueno asimétrico?



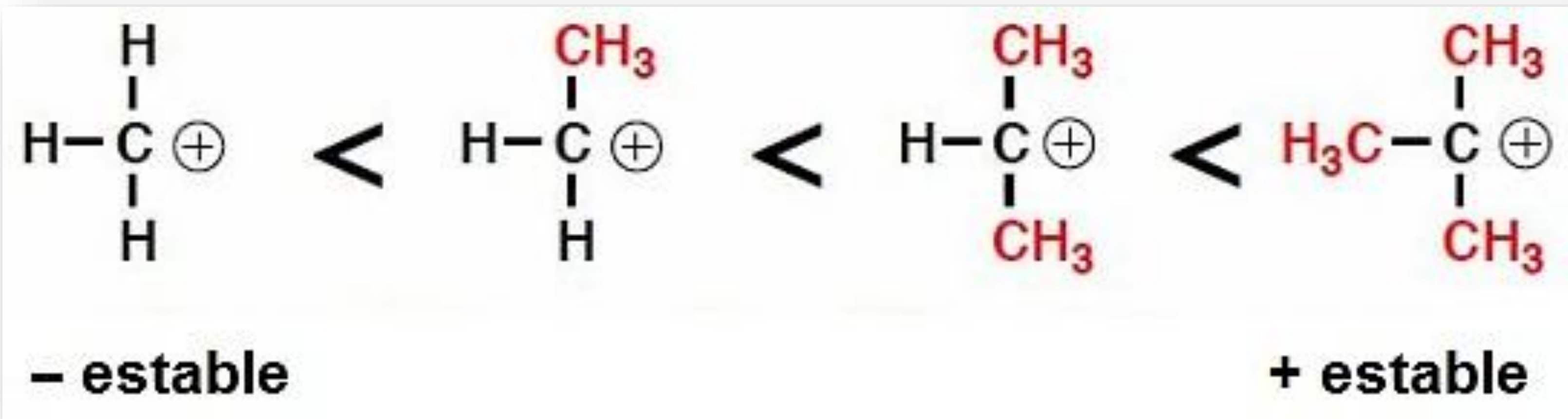
Regla de Markovnikov

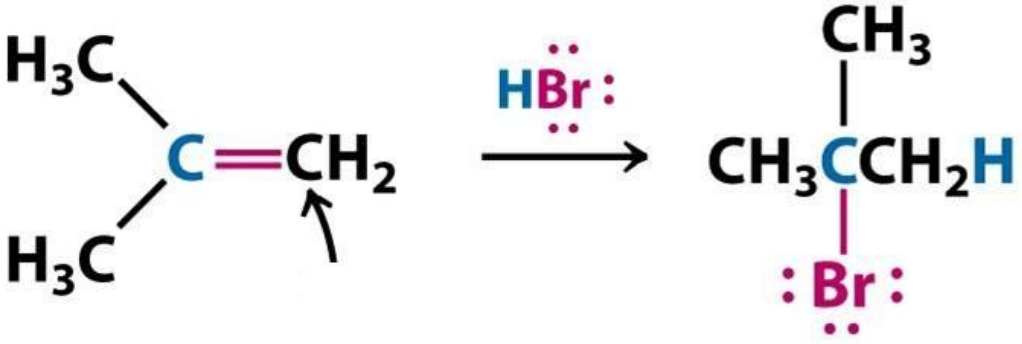
El ataque electrofílico inicial del H^+, ocurre preferentemente sobre **el carbono menos sustituido** (*el que está enlazado a más Hs*).

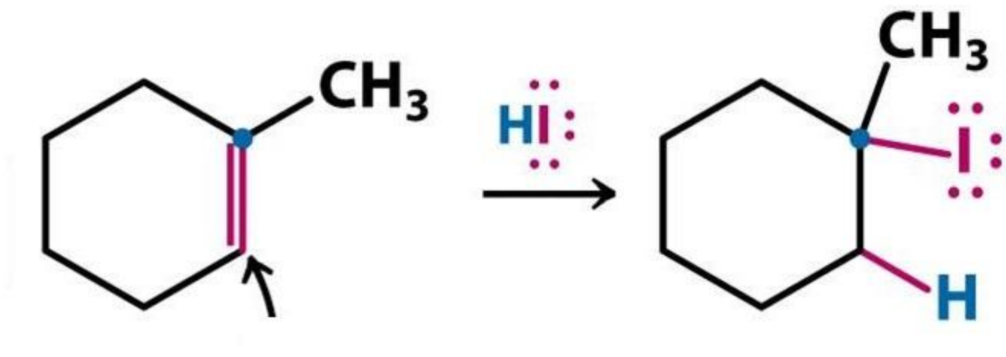
El ataque del H^+ sobre el carbono menos sustituido genera un carbocatión más estable



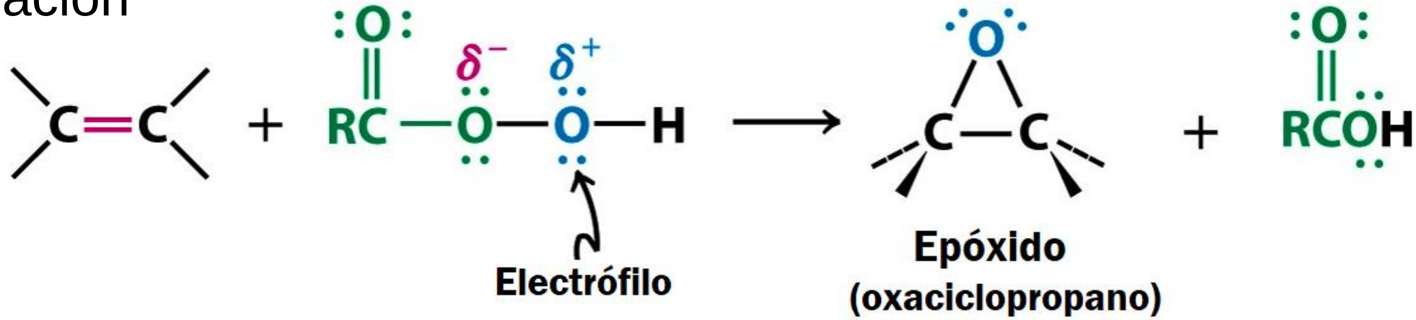
Un carbocatión es más estable cuando tiene más carbonos unidos al carbono (+). Así, se estabiliza mejor la carga positiva


H
H–C⊕
H
<
CH3
H–C⊕
H
<
CH3
H–C⊕
CH3
<
CH3
H3C–C⊕
CH3
– estable
+ estable

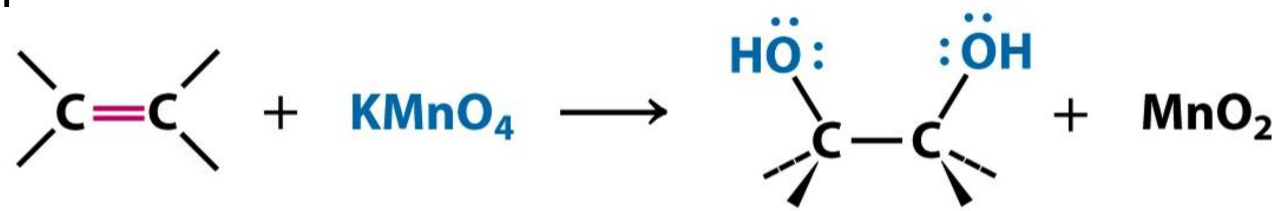

H3C
C
CH2
H3C
HBr
CH3
CH3CCH2H
Br


CH3
HI
CH3
I
H

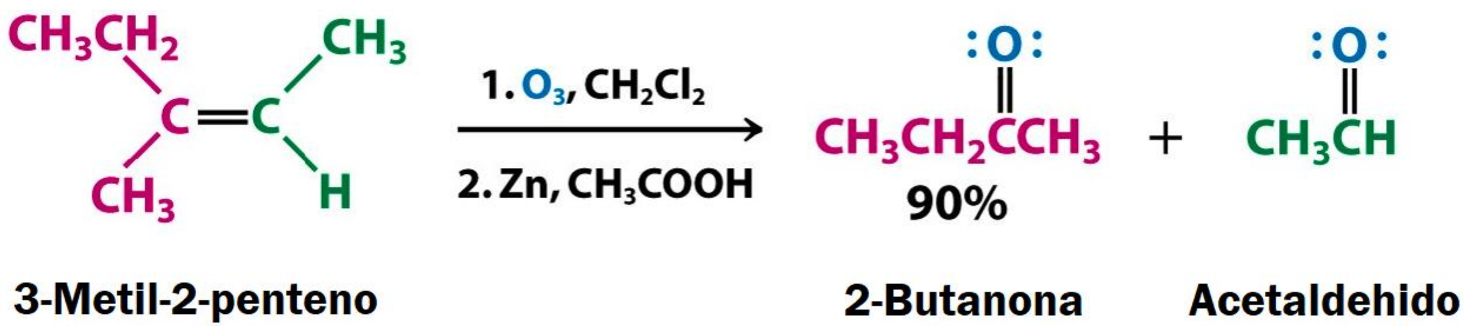
- Epoxidación



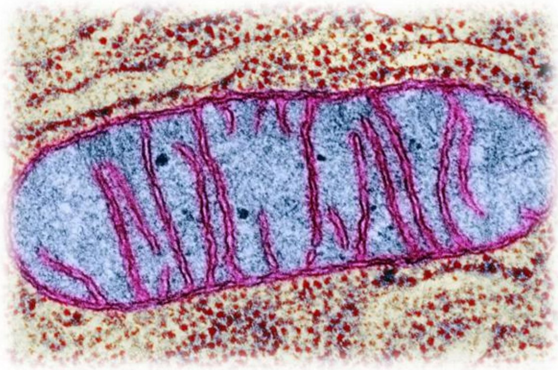
- Oxidación

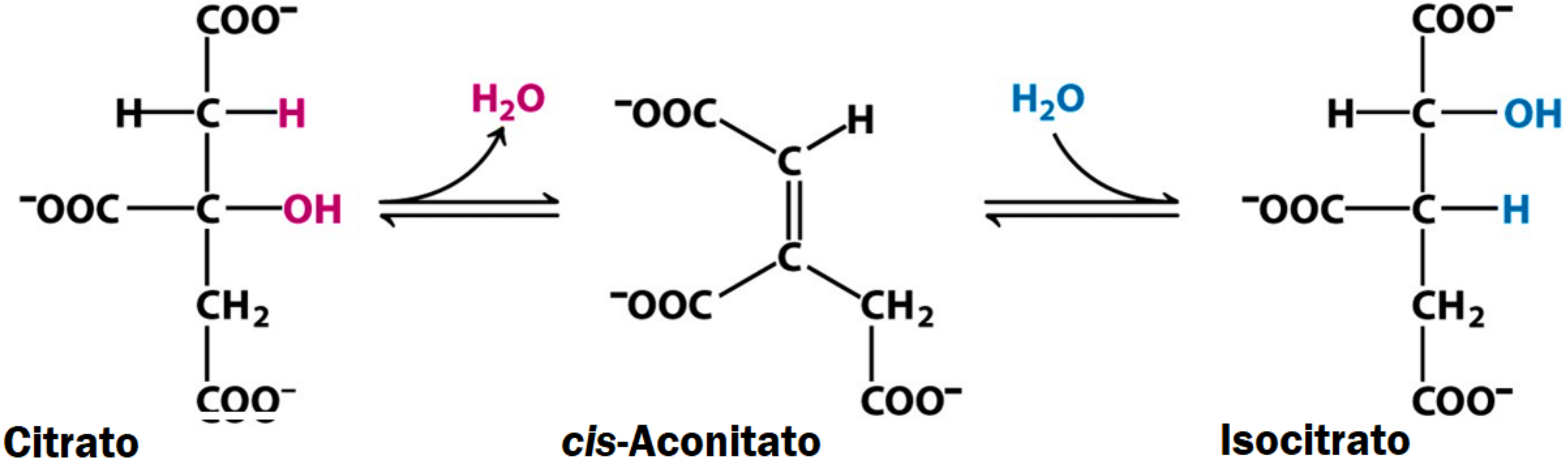


- Ozonolísis

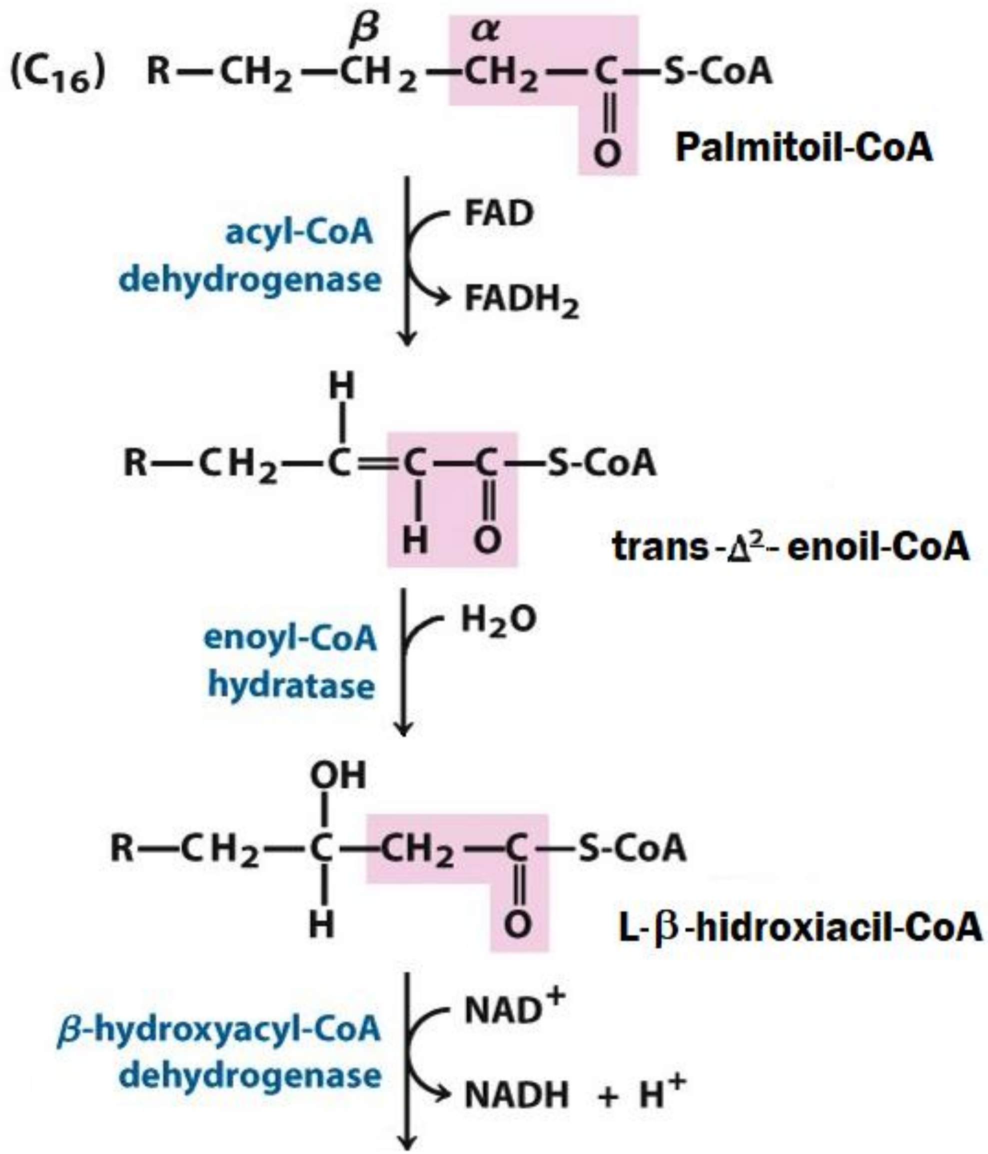


Ciclo de Krebs | Deshidratación-hidratación





β-oxidación ác grasos / Oxidación-hidratación



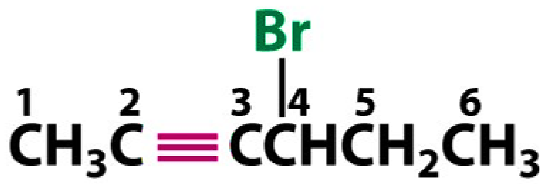
$HC\equiv CH$

Etino

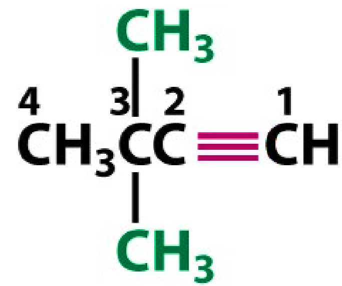
Acetileno

$CH_3C\equiv CCH_3$

2-butino



4-Bromo-2-hexino



3,3-Dimetil-1-butino

$\overset{6}{CH_3}\overset{5}{CH_2}\overset{4}{CH}=\overset{3}{CH}\overset{2}{C}\equiv\overset{1}{CH}$

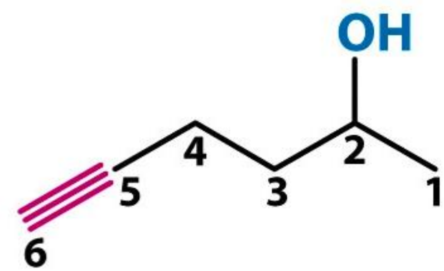
3-Hexen-1-ino

(no 3-hexen-5-ino)

$\overset{1}{CH_2}=\overset{2}{CH}\overset{3}{CH_2}\overset{4}{C}\equiv\overset{5}{CH}$

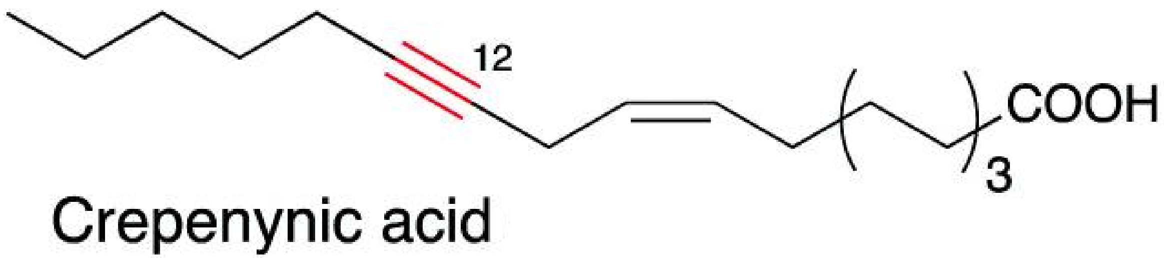
1-Penten-4-ino

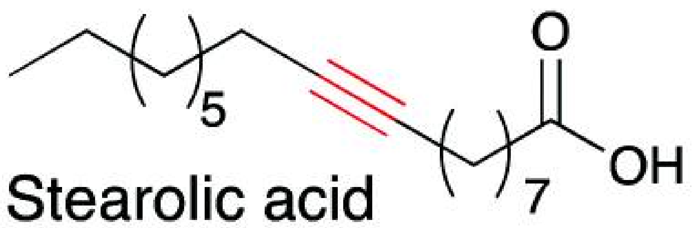
(no 4-penten-1-ino)



5-Hexin-2-ol

(no 1-hexin-5-ol)





Ácidos acetilénicos; se encuentran en algunas plantas, hongos e insectos

Alquinos - reacciones

$$HC{\equiv}CH + 2.5\,O_2 \longrightarrow 2\,CO_2 + H_2O \qquad \Delta H^\circ = -1301\ \mathrm{kJ\,mol^{-1}}$$

$$CH_3CH_2C{\equiv}CH + 2\,H_2 \xrightarrow{\text{Catalyst}} CH_3CH_2CH_2CH_3 \qquad \Delta H^\circ = -292.5\ \mathrm{kJ\,mol^{-1}}$$

$$CH_3C{\equiv}CCH_3 + 2\,H_2 \xrightarrow{\text{Catalyst}} CH_3CH_2CH_2CH_3 \qquad \Delta H^\circ = -272.4\ \mathrm{kJ\,mol^{-1}}$$

	$H_3C{-}CH_3$	<	$H_2C{=}CH_2$	<	$HC{\equiv}CH$
Hibridacion	sp^3		sp^2		sp
pK_a	50		44		25

<u>Bibliografía</u>

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22978-6877

Block E zócalo