

Reattività composti organici

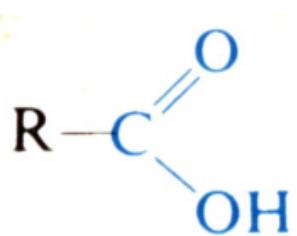
La reattività chimica di composti organici dipende soprattutto da **gruppi funzionali** perché questi hanno **distribuzione di carica disomogenea**. Possono essere più facilmente "attaccati".

Proprietà fisiche dipendono anche da **scheletro idrocarburico, meno reattivo reattivo chimicamente**

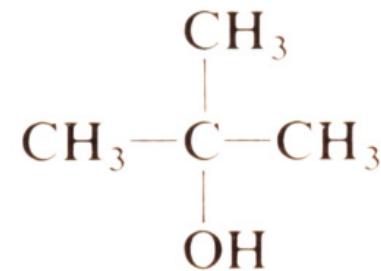
Esempi:



Acido acetico
Acido etanoico



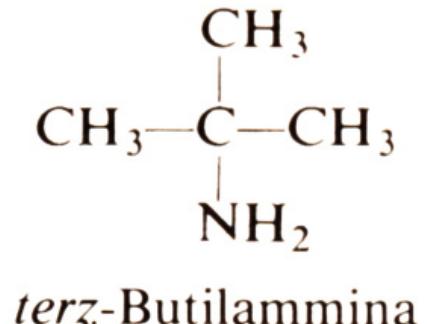
Gruppo funzionale
carbossilico



2-Metil-2-propanolo
Alcool *terz*-butilico

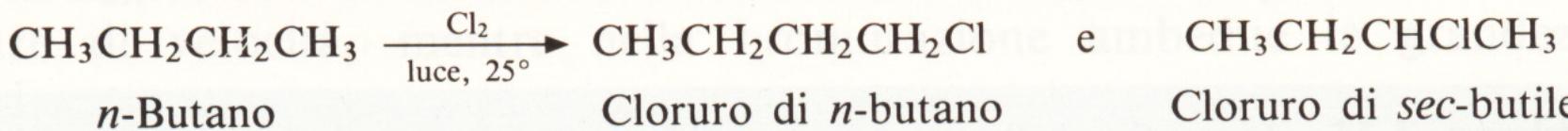
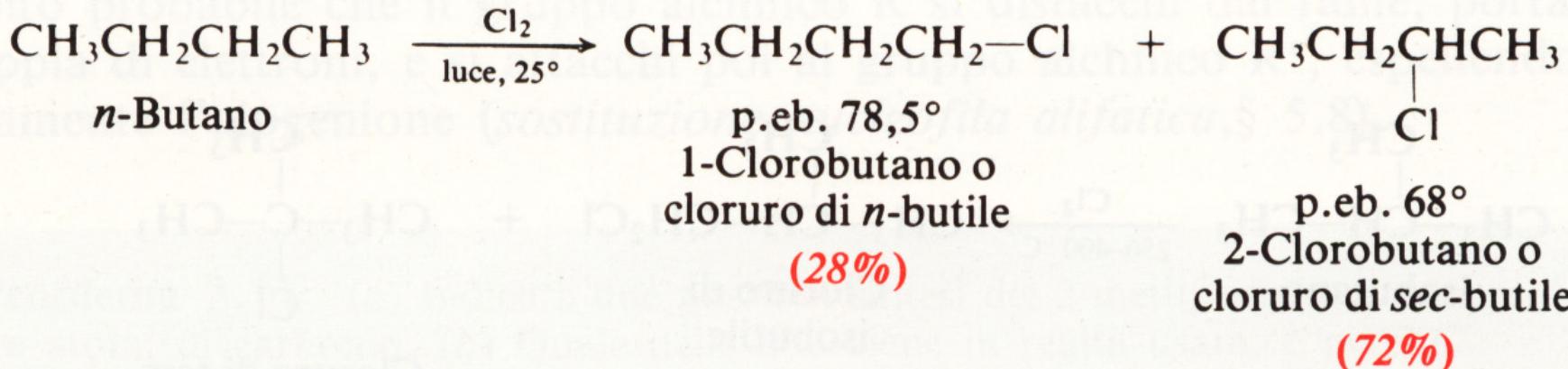
Nucleofili: reagenti che **attaccano** zone molecolari con residui di carica (+). Esempi: basi di Broensted e Lewis (H_2O , NH_3 , OH^- ...)

Elettrofili: reagenti che **attaccano** zone molecolari con residui di **carica negativa**. Esempi: acidi Lewis, cationi (BF_3 , Fe^{3+} , H^+ ...)



Per gli alcani (\approx apolari): solo reazioni radicaliche:
i radicali sono specie molto reattive e poco selettive.
 Le reazioni avvengono ad alta T o in presenza di luce.

Clorurazione n-butano

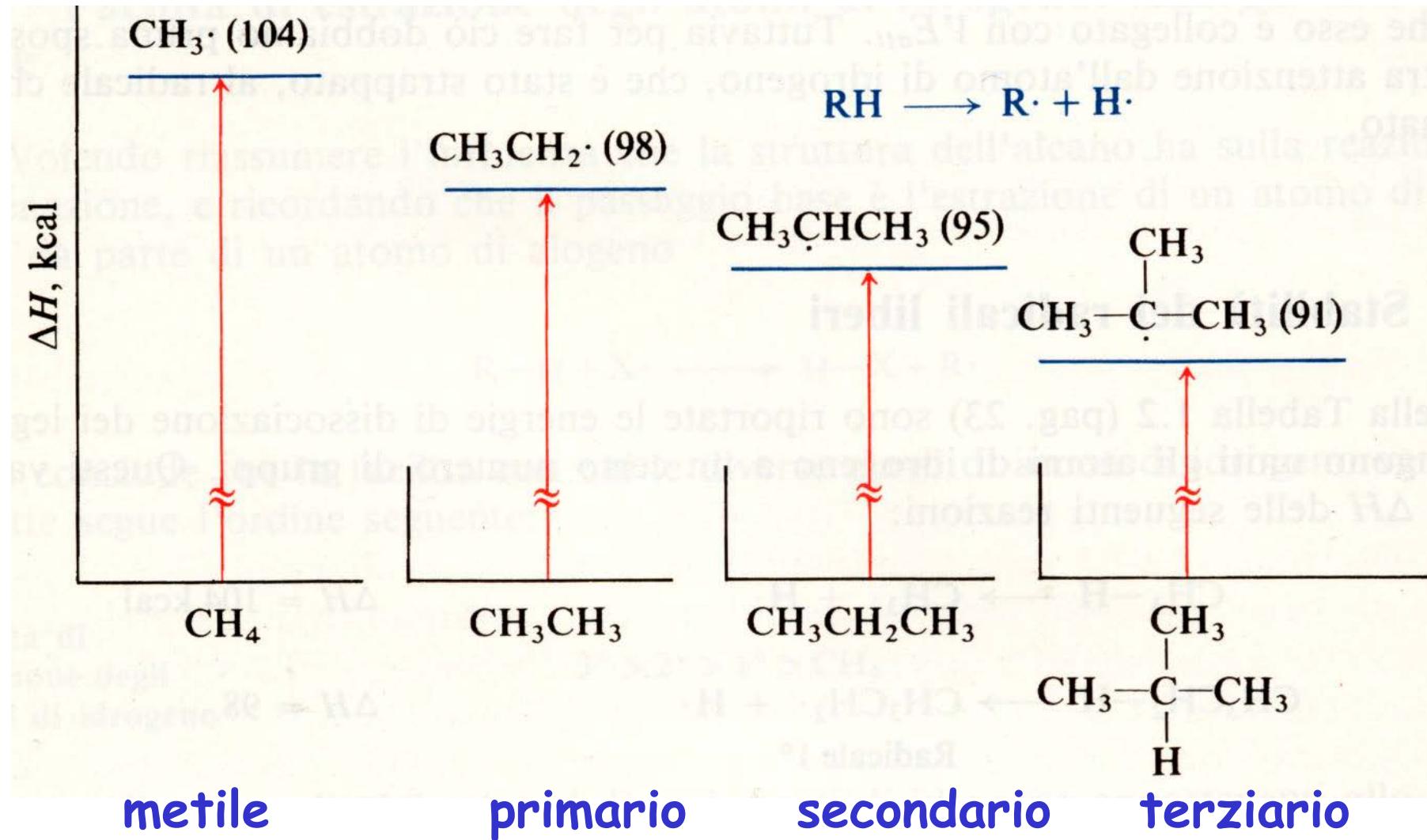


$$\frac{\text{cloruro di } n\text{-butile}}{\text{cloruro di sec-butile}} = \frac{n^\circ \text{ di H } 1^\circ}{n^\circ \text{ di H } 2^\circ} \times \frac{\text{reattività degli H } 1^\circ}{\text{reattività degli H } 2^\circ}$$

$$= \frac{6}{4} \times \frac{1,0}{3,8}$$

$$= \frac{6}{15,2} \quad \text{pari a} \quad \frac{28\%}{72\%}$$

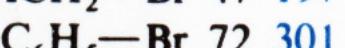
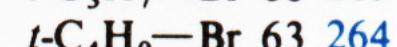
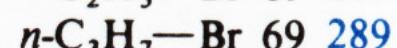
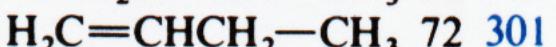
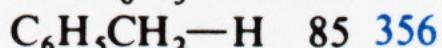
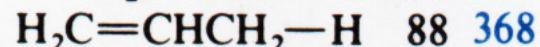
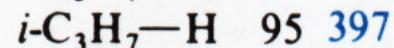
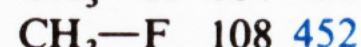
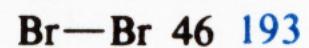
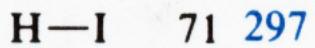
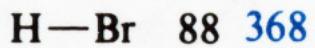
Stabilità relativa radicali alchilici



ENERGIE DI DISSOCIAZIONE OMOLITICA DI LEGAME IN KCAL/MOLE*

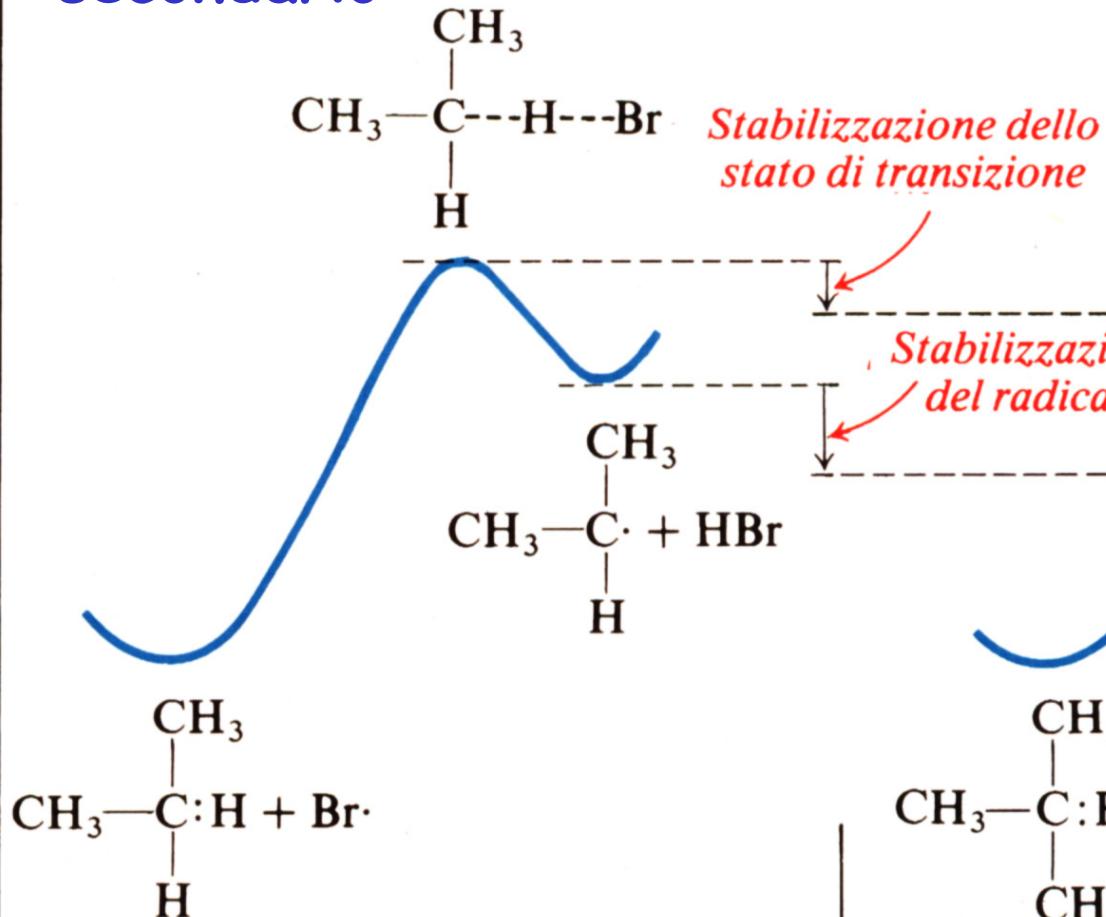


ΔH = Energia di dissociazione omolitica del legame o $D(A-B)$

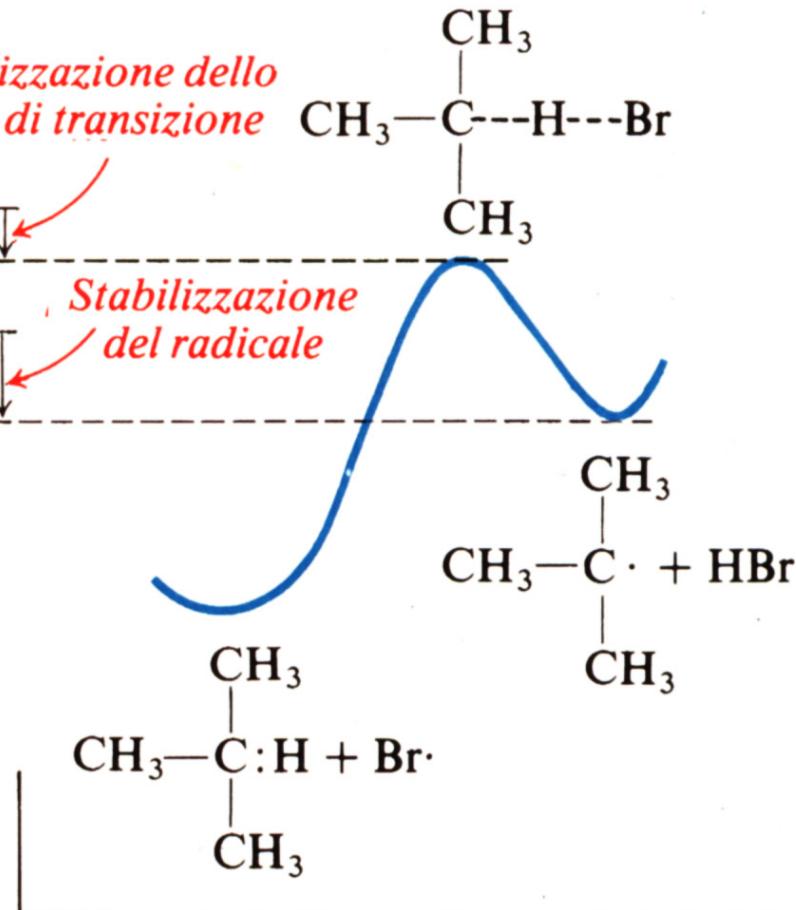


* $(\text{blu } \text{kJ mol}^{-1})$

secondario

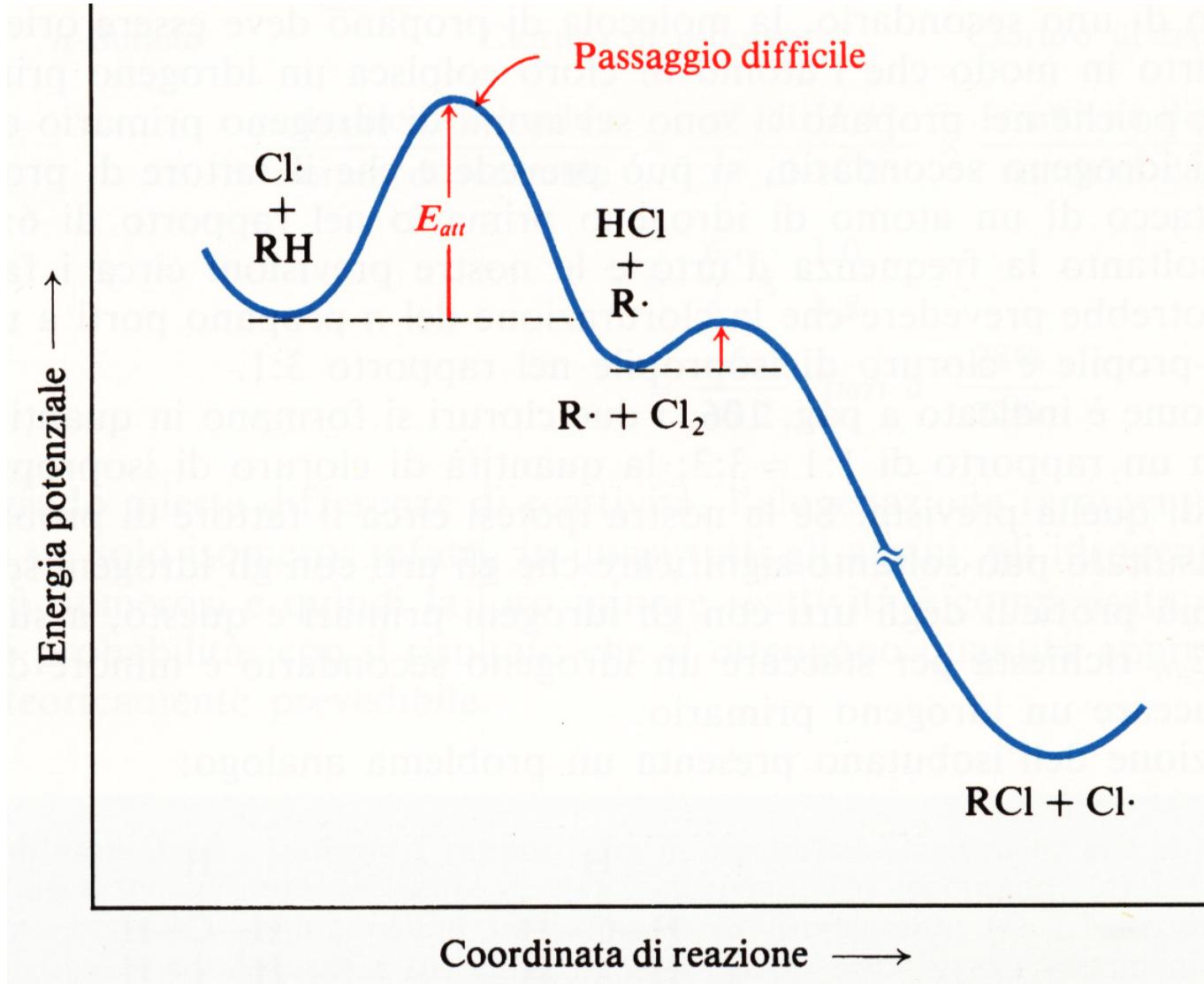


terziario

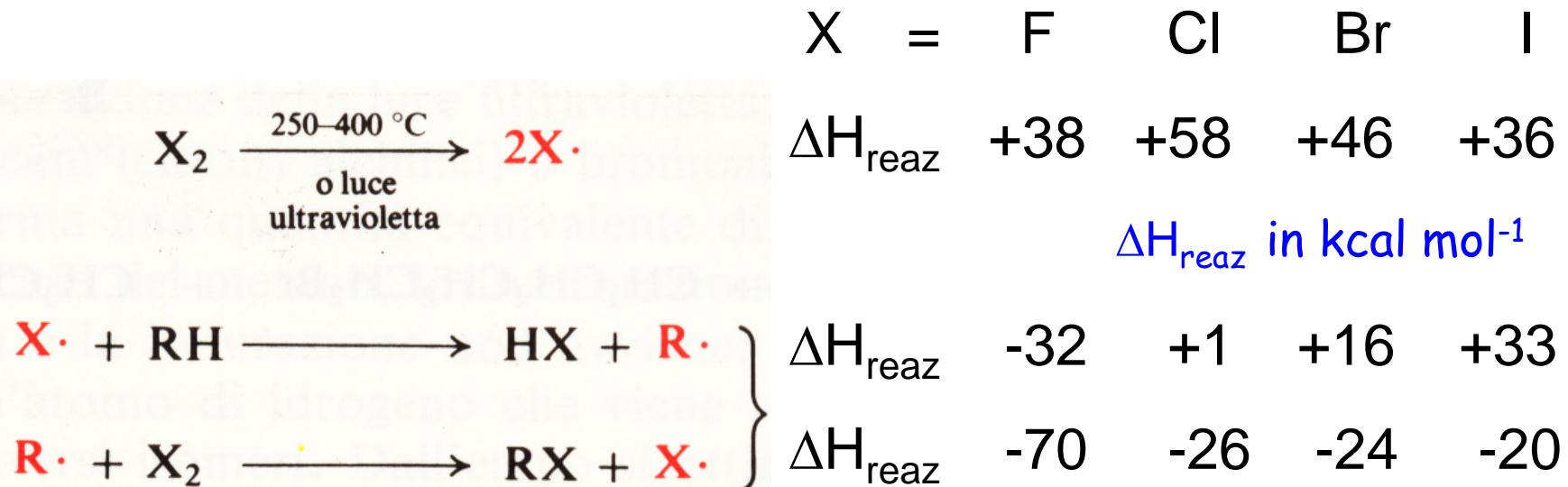


Coordinata di reazione →

Ipotesi: lo stato di transizione è tanto più stabilitizzato quanto più stabile è il radicale alchilico intermedio ! Ragionevole.



Meccanismo alogenazione alcani



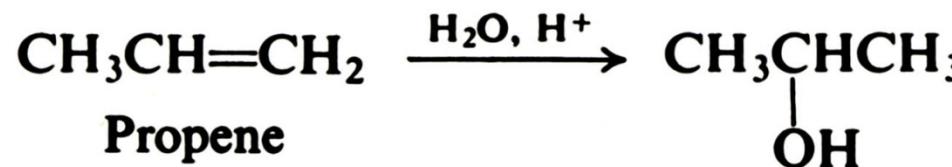
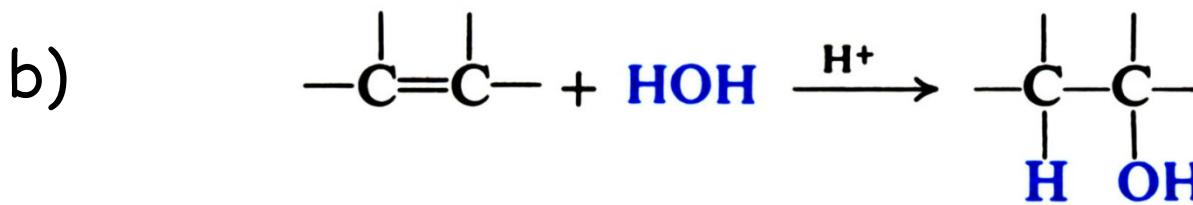
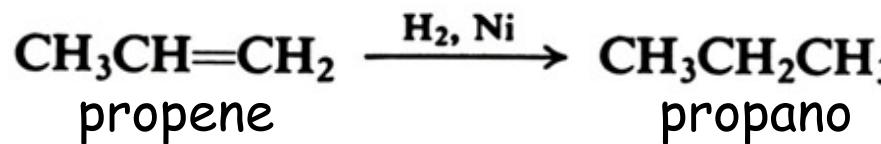
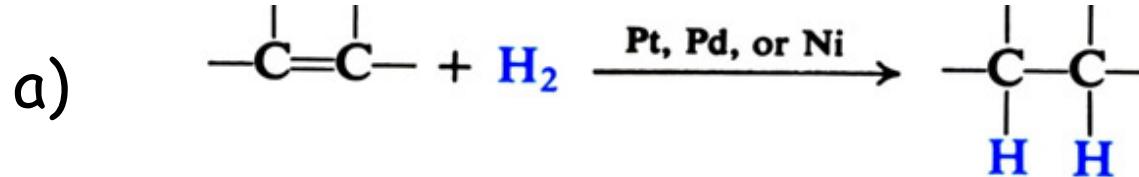
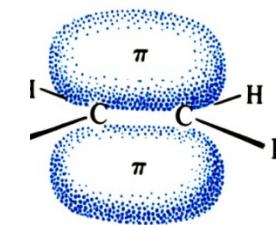
poi (2), (3), (2), (3) ecc. fino a che la catena termina (§ 2.13)

Si capisce perché la reazione con F è simile ad una combustione violentissima, quella con Cl è una reazione veloce, quella con I praticamente non va.

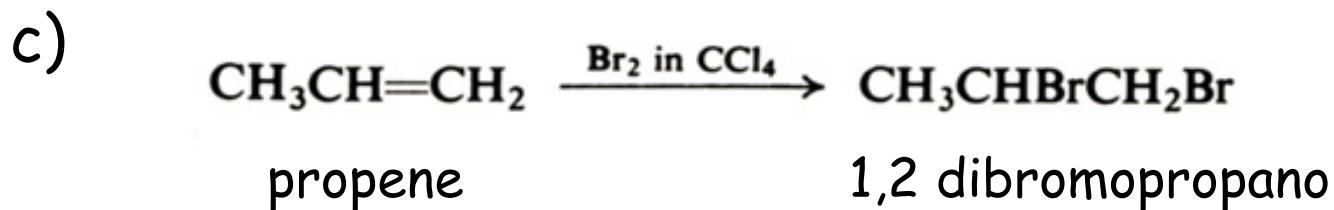
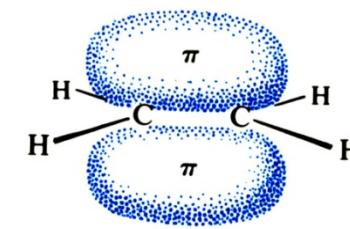
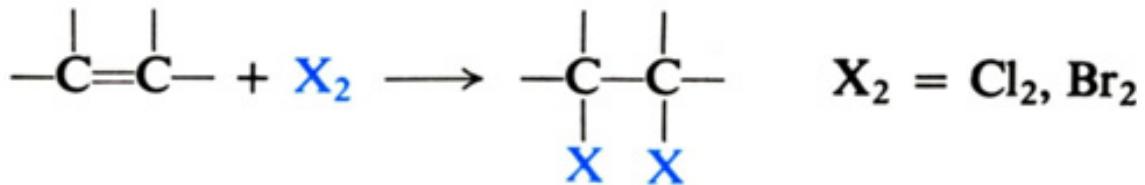
Entalpie di legame medie (kJ mol⁻¹)

	H	C	N	O	F	Cl	Br	I	S	P	Si
H	436										
C	412	348 s 612 d 837 t 538 a									
N	388	305 s 613 d 890 t	163s 409 d 946 t	157s 607 d							
O	463	360 s 743 d 1072 t	157s 607 d	146 s 490 d							
F	565	484	270	185	155						
Cl	431	338	200	203	254	242					
Br	366	276				219	193				
I	299	238			275	210	178	151			
S	338	259 s 573 d	464	523 sd	343	250	212		264 s 424 d		
P	322	264		350 s 544 d	490	326	264	184	335 d	201 s 480 dt	
Si	318	307	333	466 s 642 d	584	400			293		226

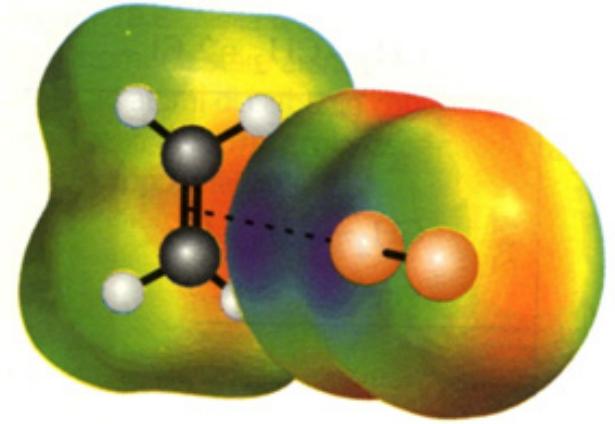
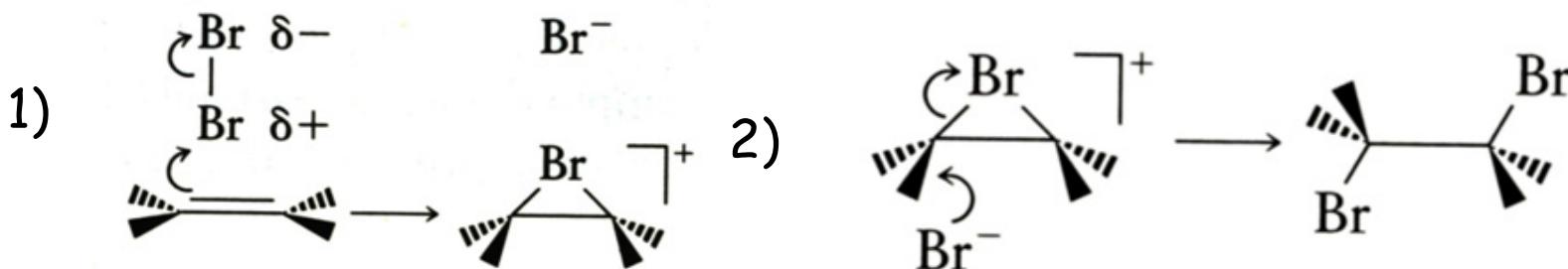
Le reazioni caratteristiche di alcheni e alchini (+ reattivi degli alcani), oltre le radicaliche, sono le **addizioni elettronofile al legame multiplo**: legami π sostituiti da legami σ più stabili



addizione elettrofila al doppio legame



meccanismo:

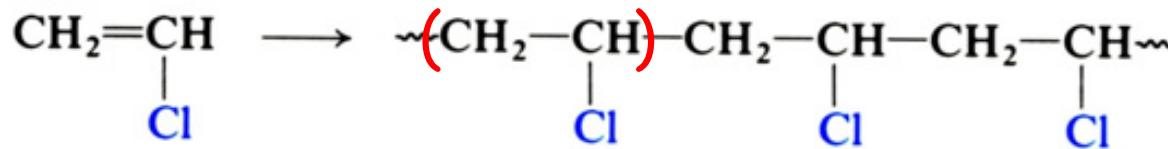


L'addizione elettrofila avviene per la minore stabilità del legame π rispetto ai σ . Gli elettroni π negli alcheni sono quelli a energia più elevata

polimerizzazione alcheni: poliaddizione

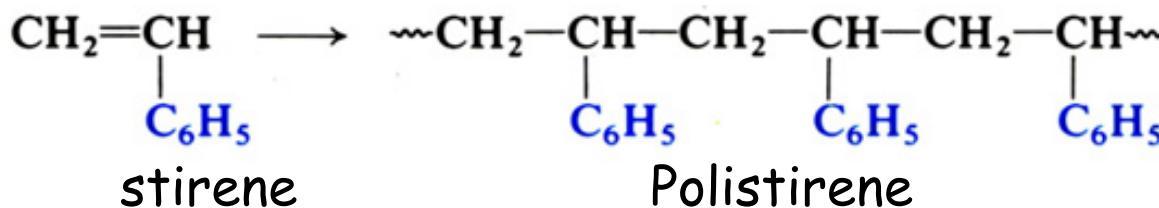
a) radicalica

cru = unità ripetitiva chimica



Vinil cloruro
(monomero)

Polivinilcloruro
(polimero)



stirene

Polistirene

meccanismo radicalico:

(1)

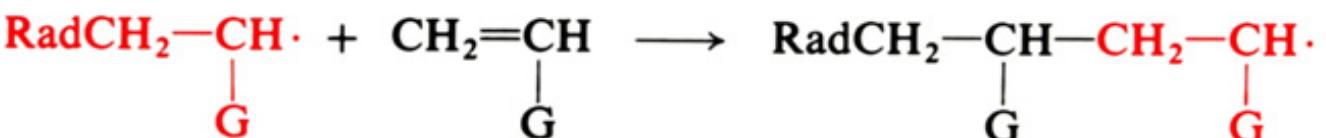
Peroxide \longrightarrow Rad.

(2)



Chain-initiating steps

(3)

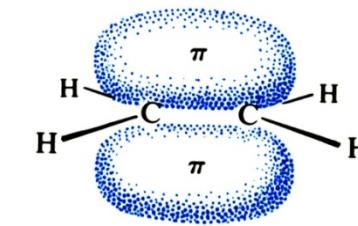


Chain-propagating steps

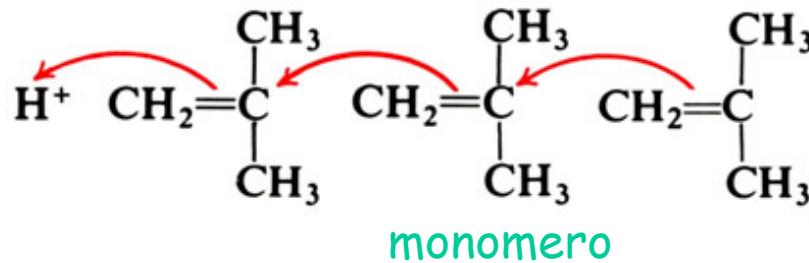
then steps like (3) repeated, until finally:

polimerizzazione alcheni: poliaddizione

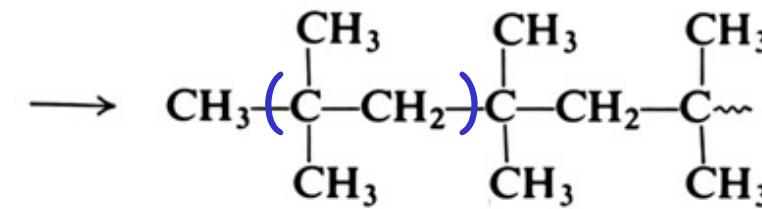
b) cationica \Rightarrow forma carbocationi molto instabili



isobutene



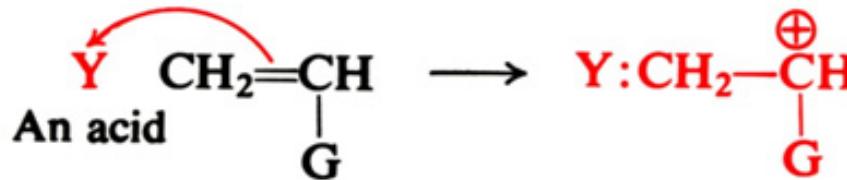
Poliisobutene



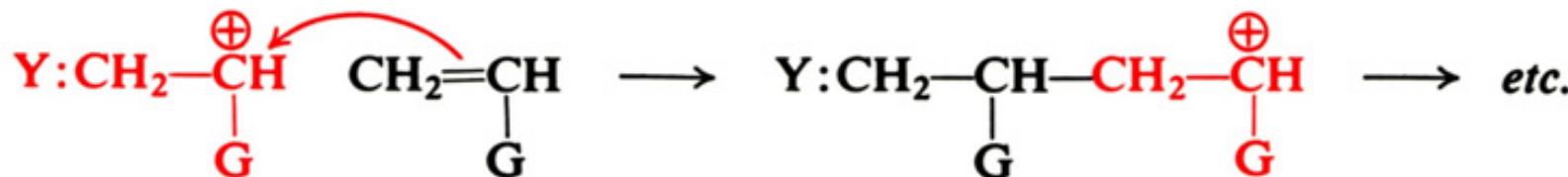
cru = unità ripetitiva chimica

meccanismo ionico:

L'acido è un acido di Lewis (elettrofilo) come BF_3 o AlCl_3

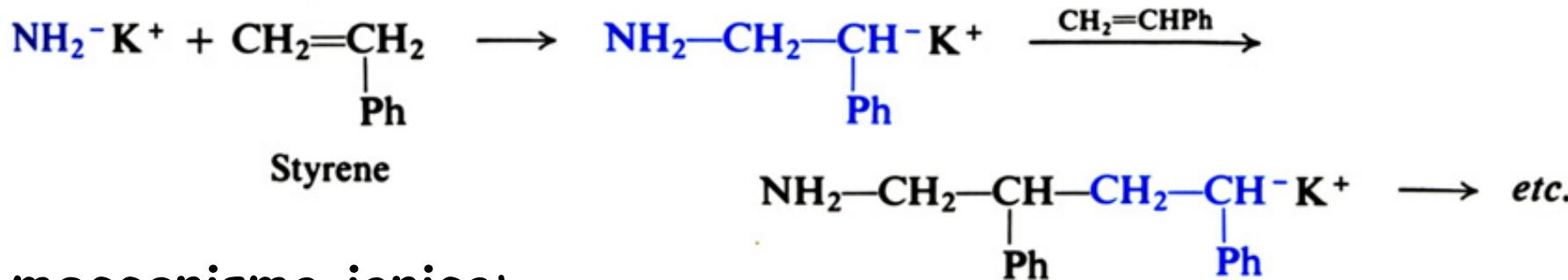
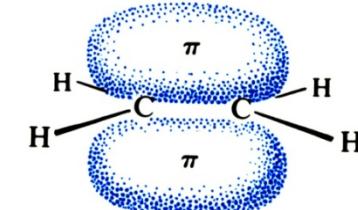


2) A carbocation



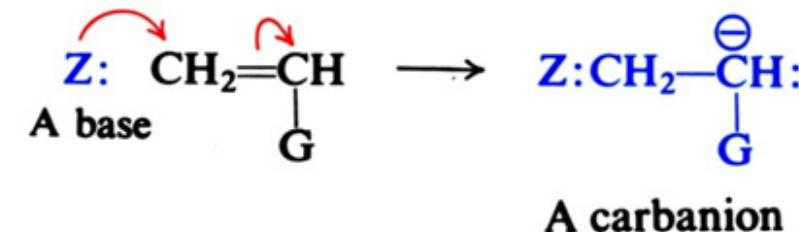
polimerizzazione alcheni: poliaddizione

c) È possibile anche la polimerizzazione anionica, che forma carbanioni, molto instabili:

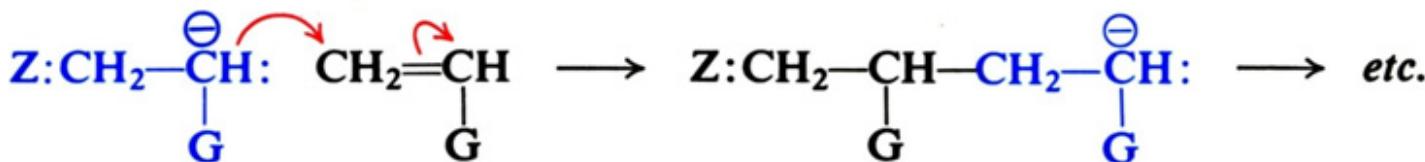


meccanismo ionico:

La base è un nucleofilo, spesso un composto organo-metallico come n-BuLi, che polarizza il doppio legame e lo attacca:



A carbanion



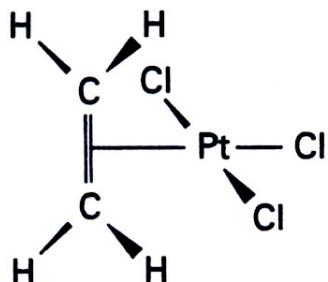
polimerizzazione alcheni:

d) Stereospecifica Ziegler-Natta

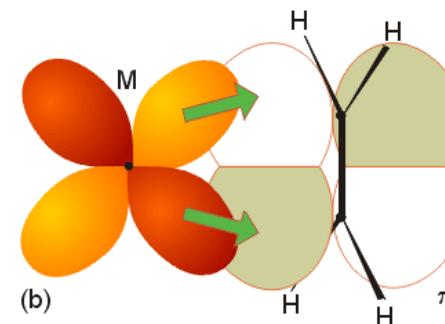
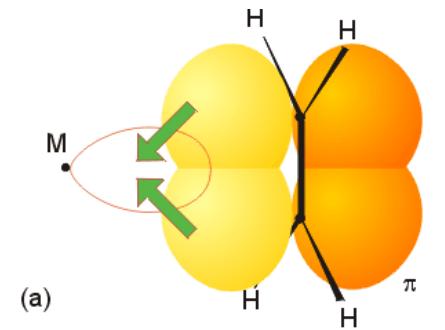
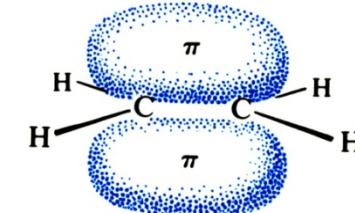
Gli alcheni sono tendenzialmente nucleofili e possono legarsi a ioni metallici di molti metalli di transizione:

Alchene = Base di Lewis; M^{n+} = acido di Lewis

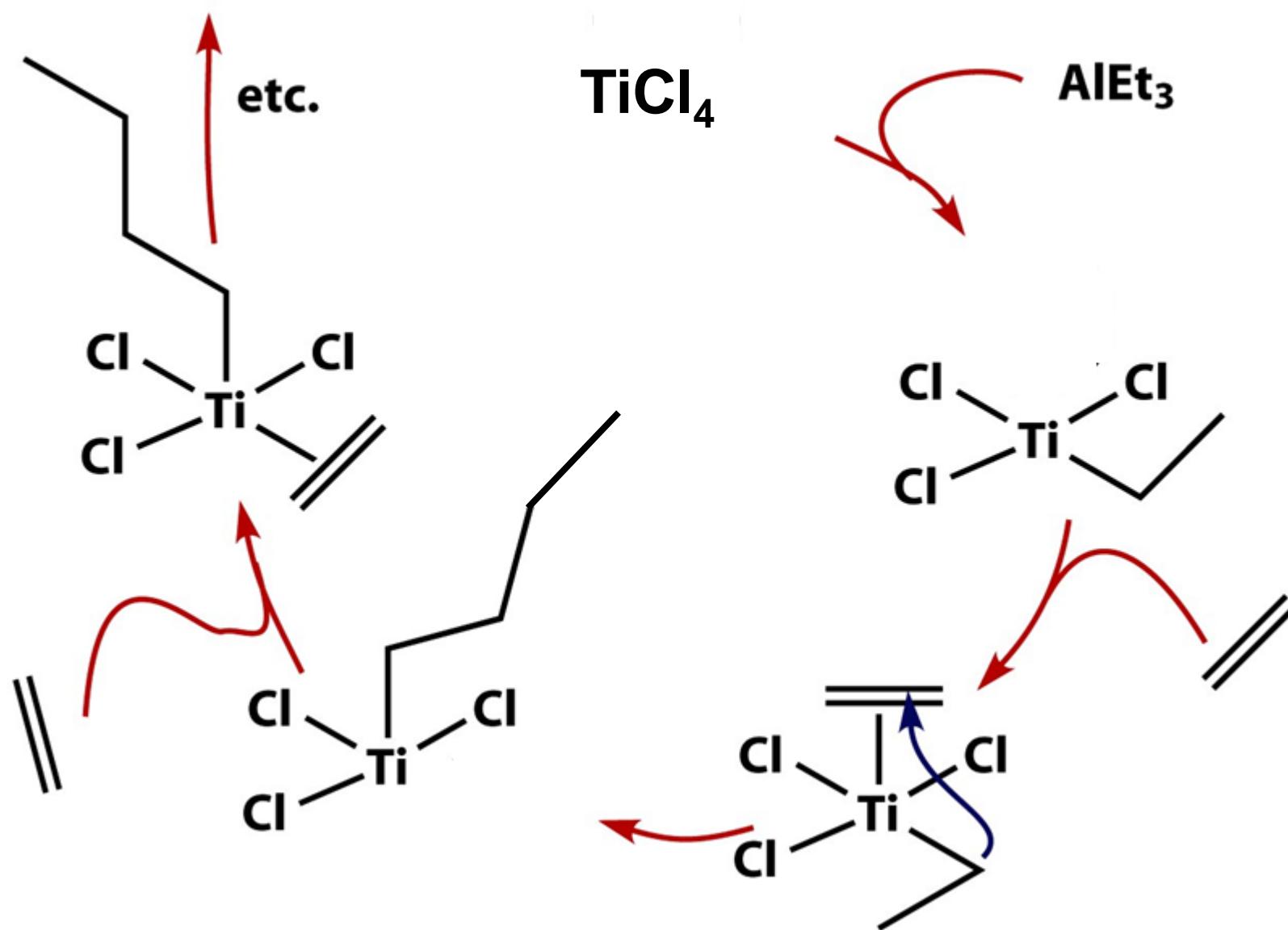
Esempio: sale di Zeise, stabile!



1 $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$



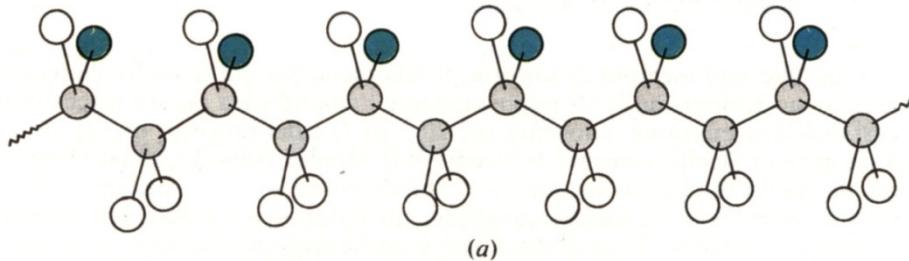
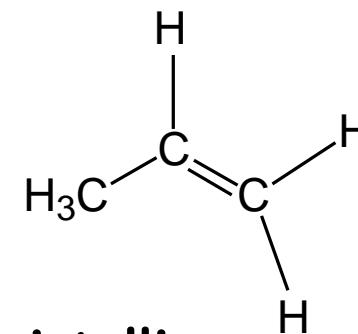
Meccanismo per polimerizzazione Ziegler-Natta



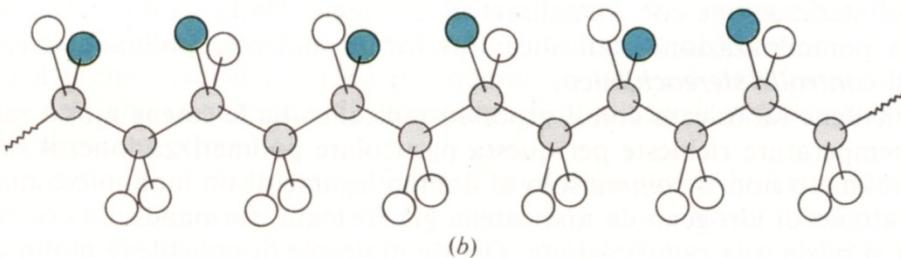
Polimerizzazione Ziegler-Natta del propene

(Natta 1955, Nobel Chimica 1963)

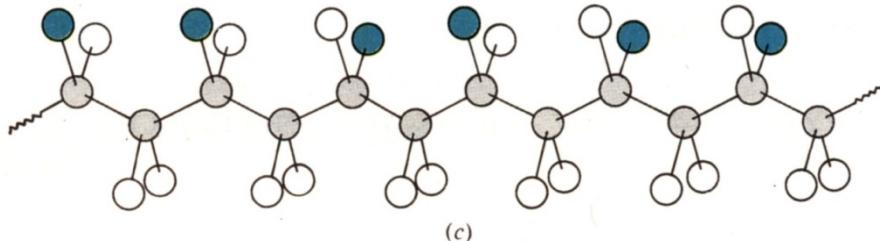
Con catalizzatori di Ziegler, Natta ottenne polipropilene (e altri polimeri) **stereoregolari**



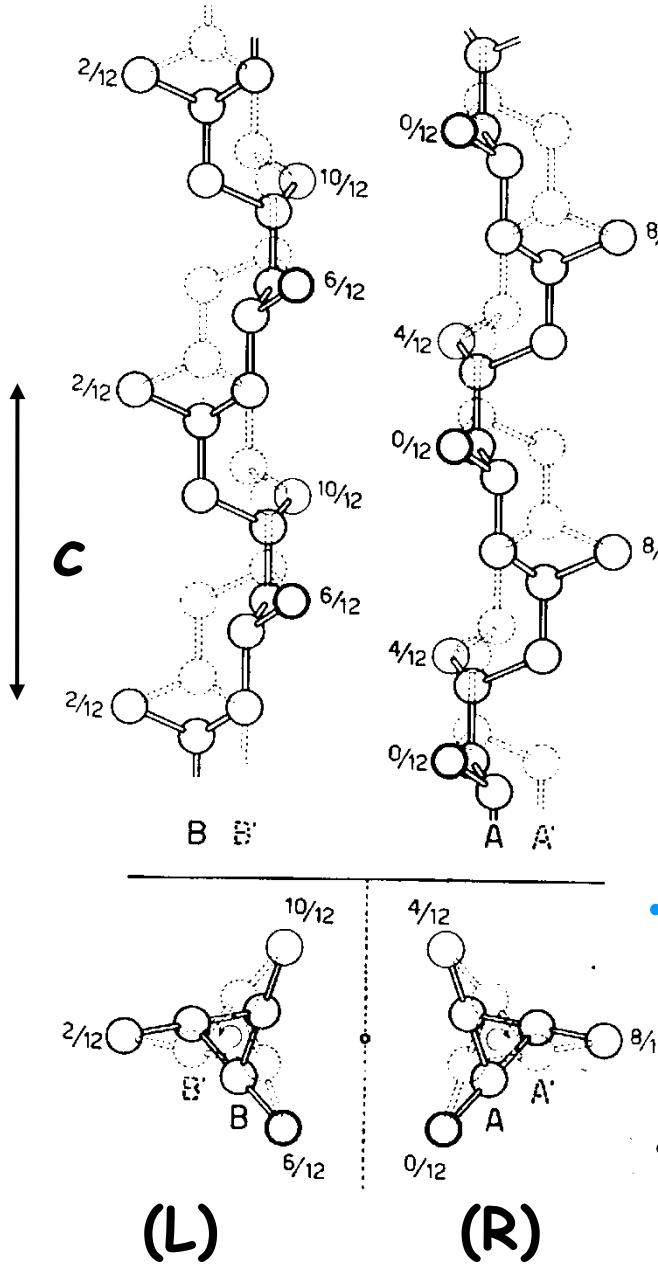
isotattico \Rightarrow cristallino:
pt. fus. $\sim 160^\circ\text{C}$
buone proprietà meccaniche



sindiotattico \Rightarrow cristallino:
pt. fus. $\sim 150^\circ\text{C}$
buone proprietà meccaniche



**atattico \Rightarrow cera amorfa
(\sim "liquido")**
proprietà meccaniche scarse



da Natta e Corradini, 1957



Paolo Corradini al Poli con Natta dal '52 al '60

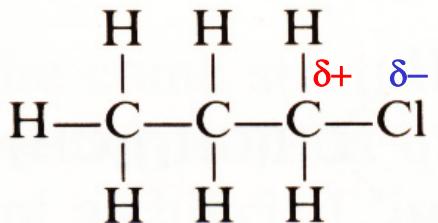
• **Polimeri stereoregolari cristallizzano ed hanno buone proprietà meccaniche.**

- PP cristallino ha conformazione regolare con periodo di ripetizione $c \approx 6.5 \text{ \AA}$, da diffrazione di **PP cristallino**
- 3 monomeri in $c \Rightarrow$ eliche 3_1 (3 unità per spira) destre (R) e sinistre (L)
 $a =$ energia
- dall'analisi di **modelli molecolari** con questi dati solo l'**ipotesi polimero isotattico ha senso (bassa energia)**

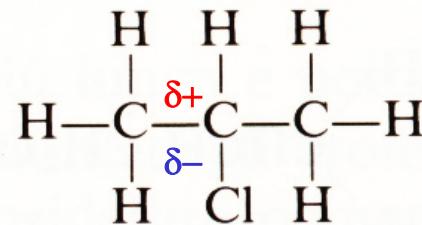
Principali gruppi funzionali organici

-OH	alcol, fenolo
-N\	ammina
-CHO	aldeide
-CO-	chetone
-COOH	acido carbossilico
-COOR	estere
-CO-N\	ammide
-O-	etero
-X	alogenuro (X = F, Cl, Br o I)

Alogenuri alchilici



I
Cloruro di *n*-propile



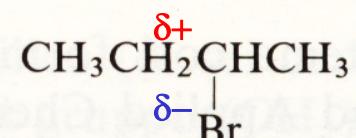
II
Cloruro di isopropile



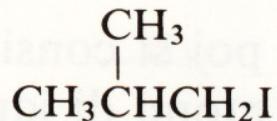
1-Cloroetano



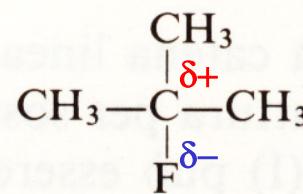
1-Bromopropano



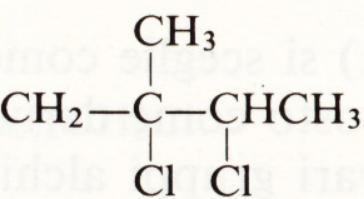
2-Bromobutano



1-Iodo-2-metilpropano



2-Fluoro-2-metilpropano

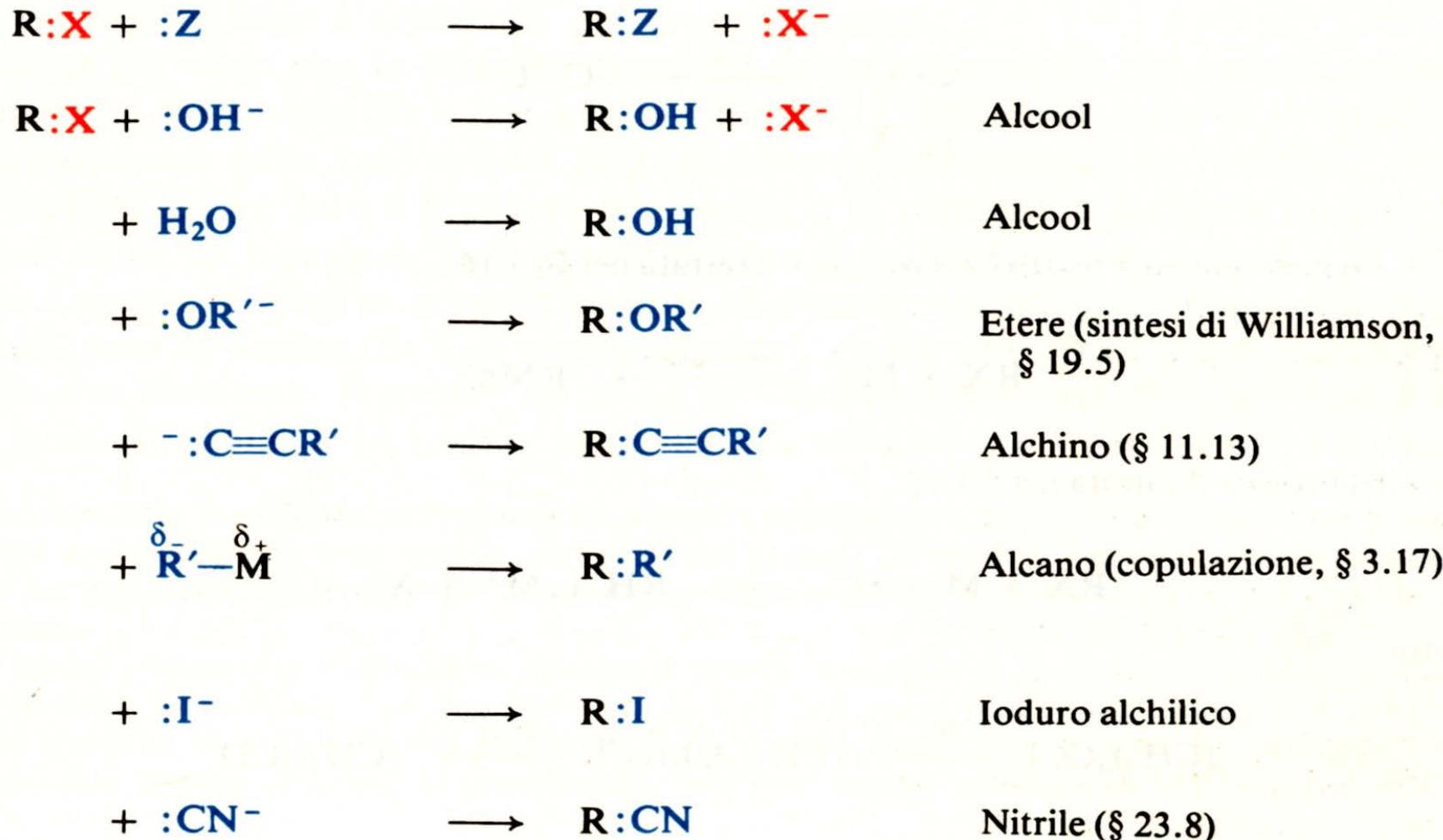


2,3-Dicloro-3-metilpentano

Negli alogenuri alchilici il legame $C-X$ è polare con un $\delta+$ sul C ed un $\delta-$ sull'atomo di cloro X . L'attacco di reagenti è quindi in genere un attacco nucleofilo sul $C^{\delta+}$ legato all'atomo di cloro.

Reazioni alogenuri alchilici

1. Sostituzione nucleofila



Sostituzione nucleofila alifatica

Gruppo alchilico



Substrato

Gruppo uscente



Nucleofilo

*Gruppo
uscente*



Ione
ossidrilico

Alcool



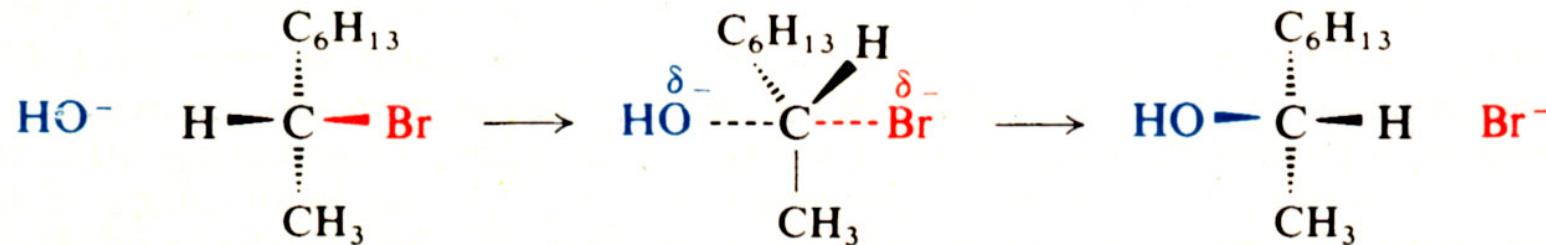
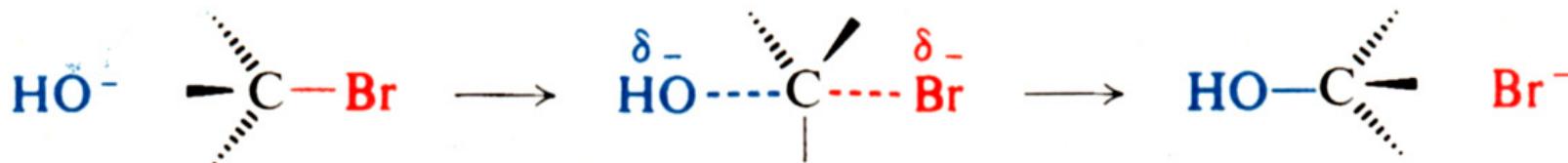
Ione metossilico
(Ione alcossilico)

Etere

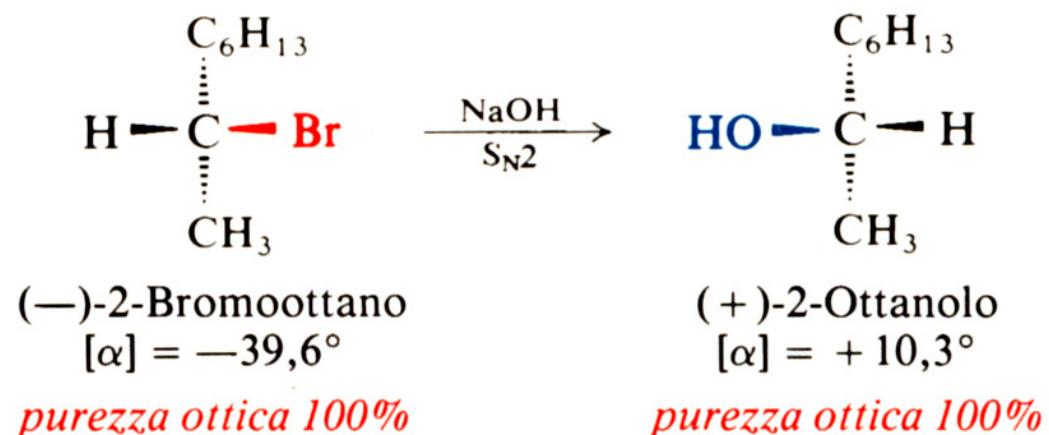


Alcool
protonato

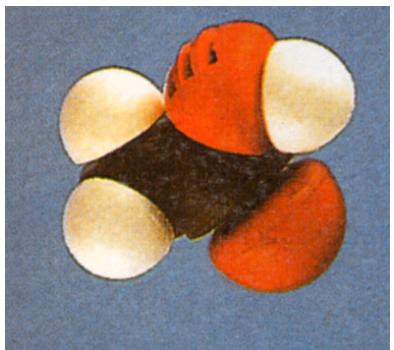
Meccanismi Sostituzione Nucleofila: Stereochimica S_N2



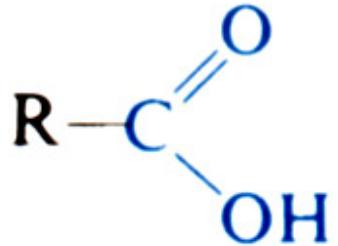
S_N2 : inversione completa



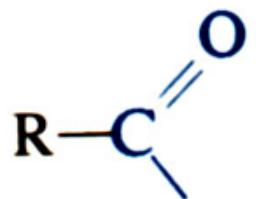
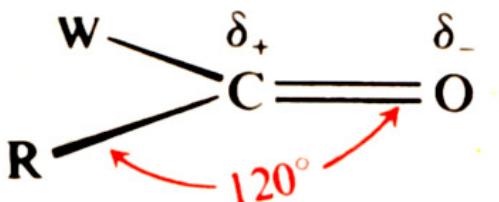
Acidi carbossilici



Acido acetico



Gruppo carbossilico
 C sp^2 , planare

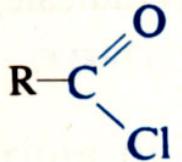


Gruppo acilico

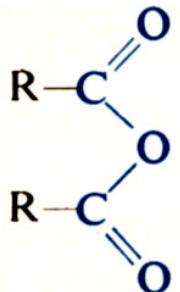
Gruppo acilico C sp^2 , planare

Il C acilico (e.g. con $\text{W} = \text{OH}$) ha un $\delta+$ maggiore che il C del C carbonilico

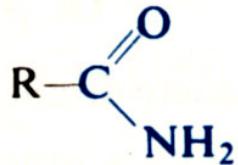
Derivati acidi carbossilici



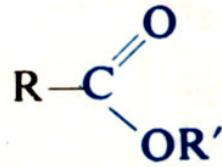
Cloruro acilico



Anidride

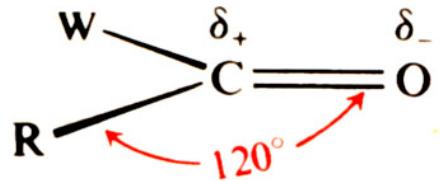


Ammide

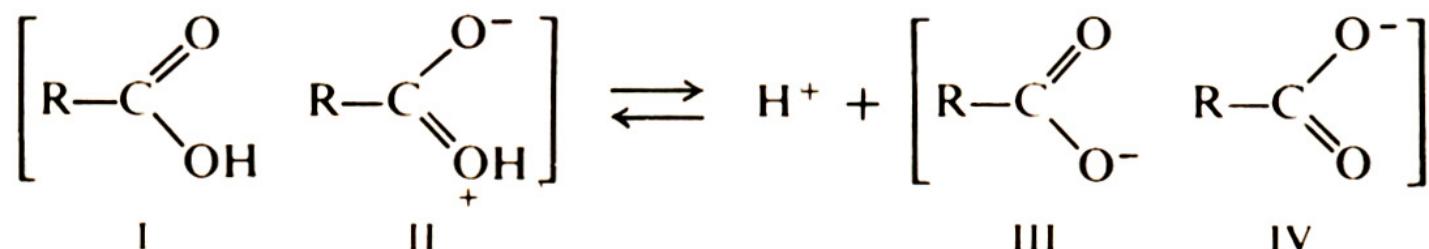
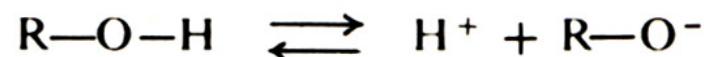


Estere

R può essere
alchilico o
arilico



Reazioni di acidi carbossilici: dissociazione e salificazione

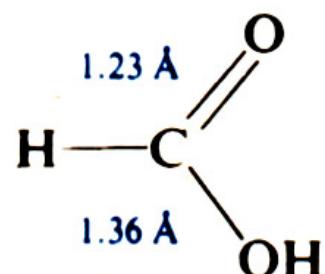


Non equivalenti:

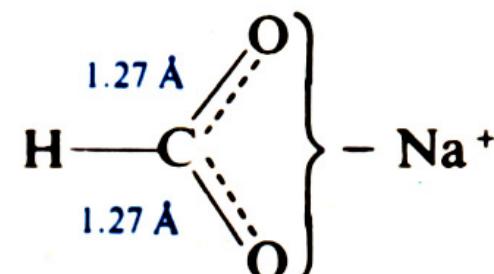
*la risonanza
è meno importante*

Equivalenti

*la risonanza
è più importante*



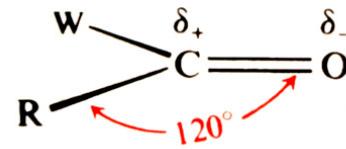
Acido formico



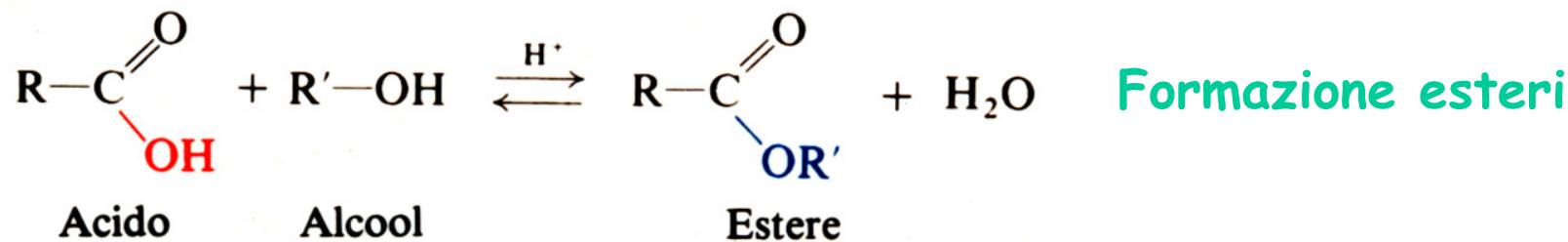
Formiato sodico

Gli acidi carbossilici sono molto più acidi degli alcol

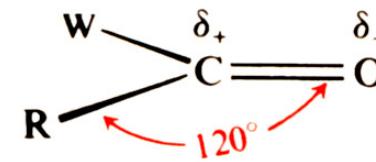
Sostituzione nucleofila acilica



Negli acidi carbossilici e nei loro derivati, l'attacco di reagenti nucleofilici è sul $C^{\delta+}$ acilico, legato a $=O$ e ad un altro gruppo W molto elettronegativo.

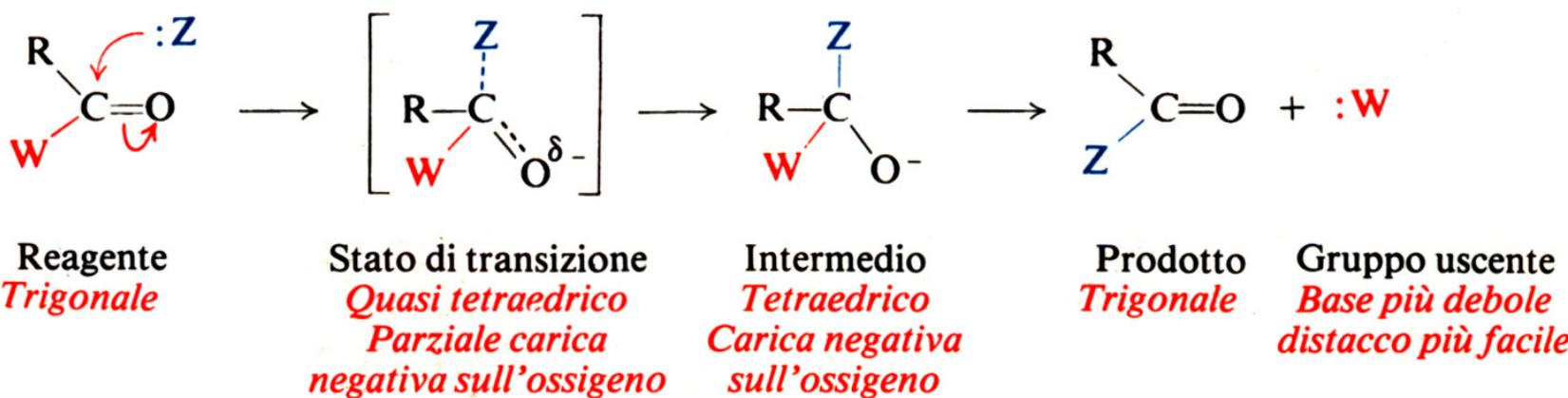


Sostituzione nucleofila acilica



Formazione ammidi

Meccanismo sostituzione nucleofila acilica



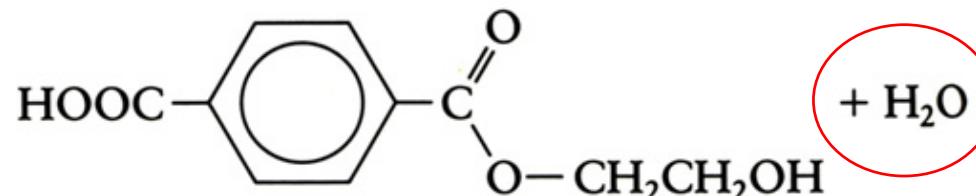
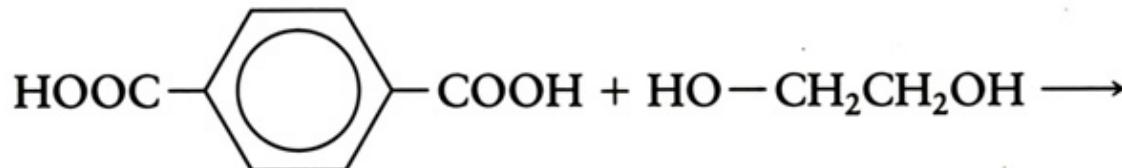
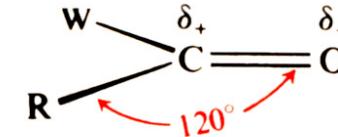
Negli acidi carbossilici e nei loro derivati, l'attacco di reagenti nucleofilici Z^- è sul $C^{δ+}$ acilico, legato a $=O$ e ad un altro gruppo W molto elettronegativo.

Reazioni di acidi carbossilici: policondensazioni

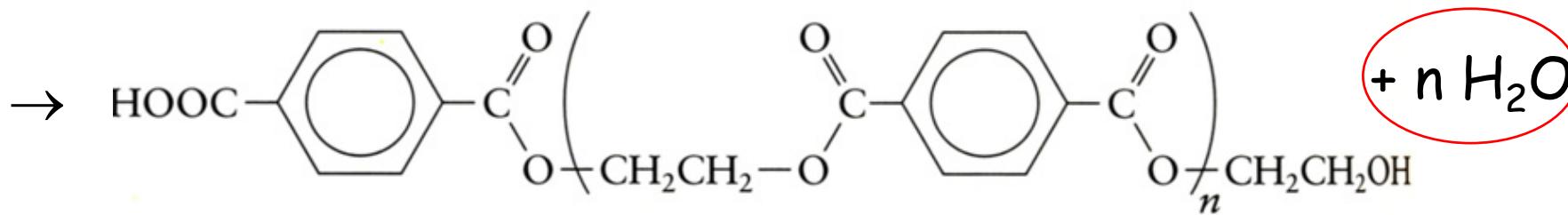
Diacido + dialcol → poliestere

Acido tereftalico

glicol etilenico (dialcol)



+ H₂O



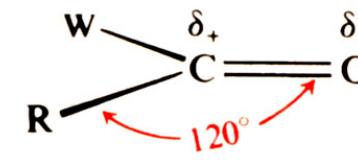
+ n H₂O

unità ripetitiva chimica del polimero

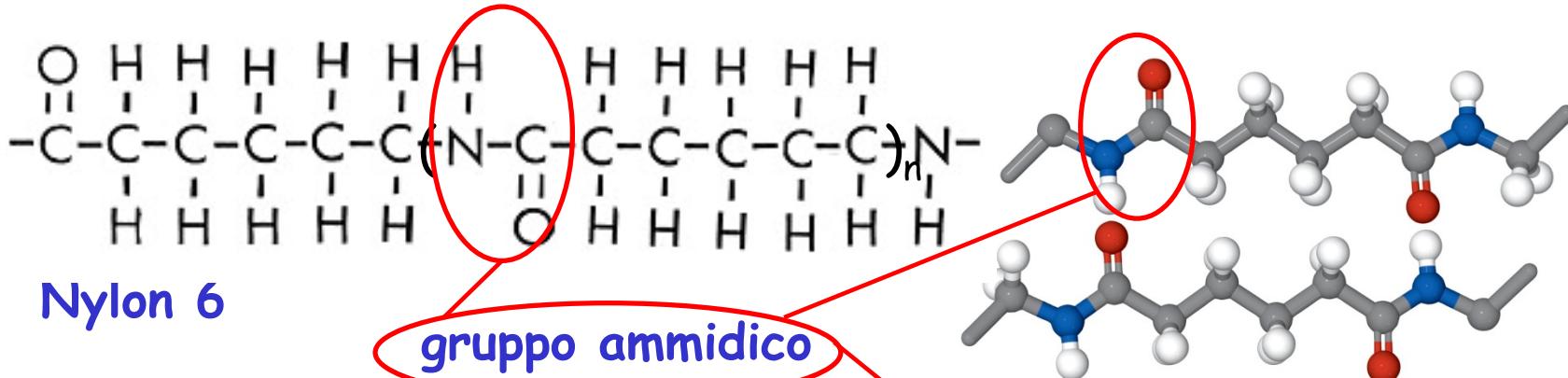
Polietilenterftalato = PET

Nelle reazioni di policondensazione si forma, oltre al polimero, anche H₂O (o un'altra piccola molecola) spesso volatile. Possono procedere quindi ad alta temperatura **perdendo H₂O**.

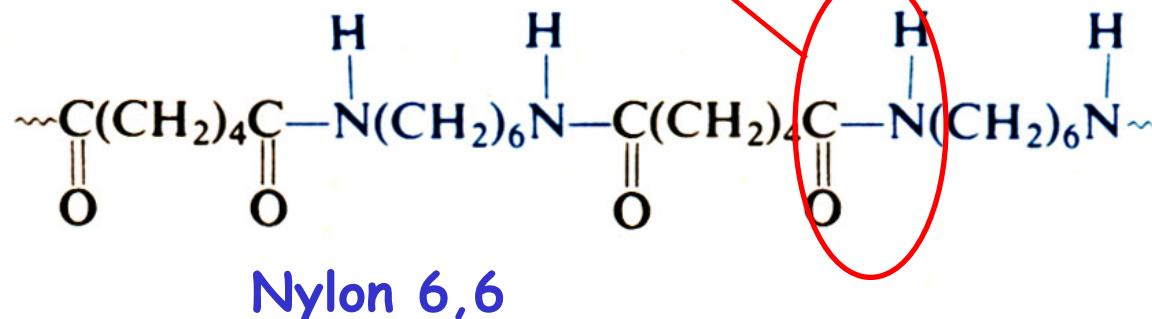
Reazioni di acidi carbossilici: policondensazioni



Diacidi + diammine → poliammidi = Nylons, polimeri con legami idrogeno intermolecolari:



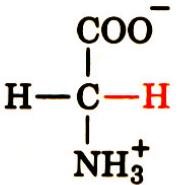
Il **gruppo ammidico**
caratterizza
anche le proteine



α -amminoacidi: sono quasi tutti chirali

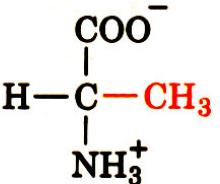
Glicina

Gly G



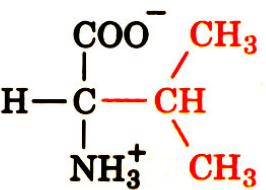
Alanina

Ala A



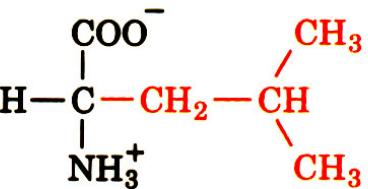
Valina

Val V



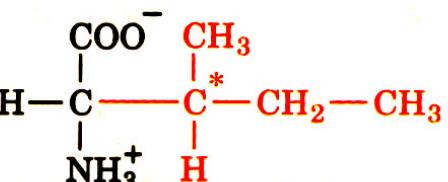
Leucina

Leu L



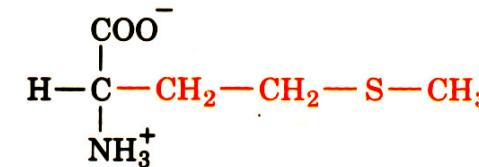
Isoleucina

Ile I



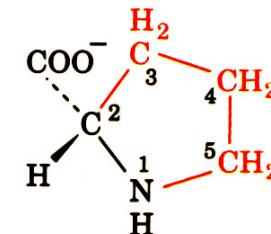
Metionina

Met M



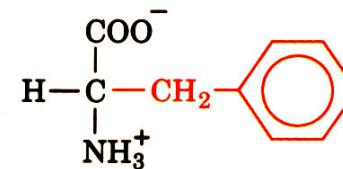
Prolina

Pro P



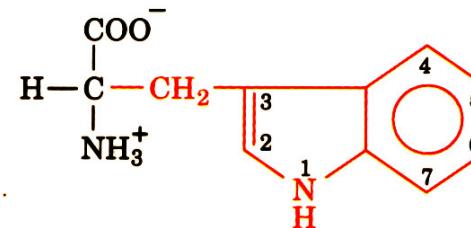
Fenilalanina

Phe F

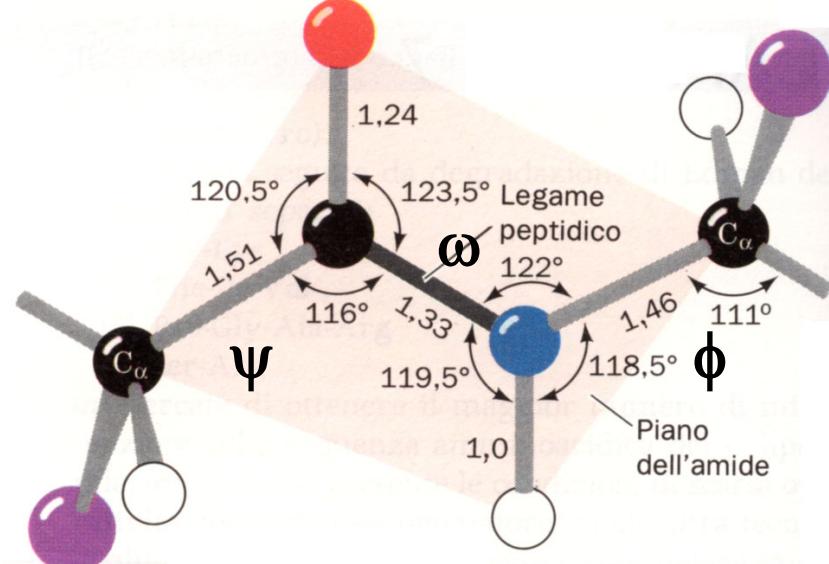
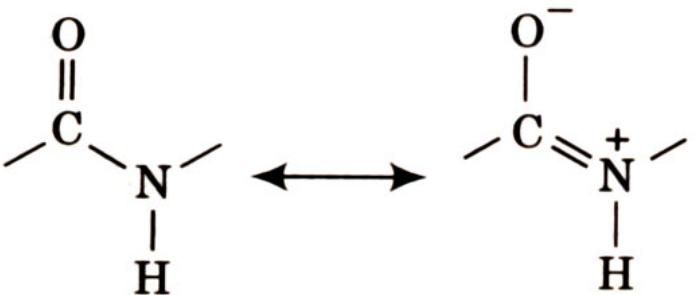


Triptofano

Trp W



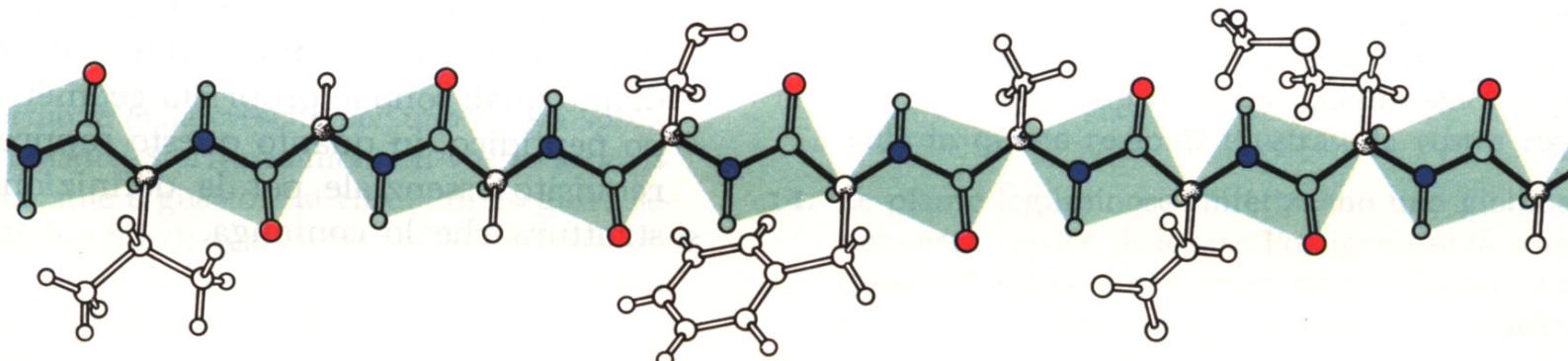
Legame peptidico: il gruppo ammidico



Le ammidi hanno normalmente conformazione planare (energia di risonanza ca. 85 kJ/mol)

distanza C-N più corta del valore atteso

distanza C-O più lunga



catena polipeptide