A.A idrofobici Gly (G), Ala (A), Val (V), Leu (L), *Ile (I), Met (M), §Pro (P)

Phe (F), Trp (W), Tyr (Y) aromatici

A.A polari Ser (S), *Thr (T), &Cys (C)

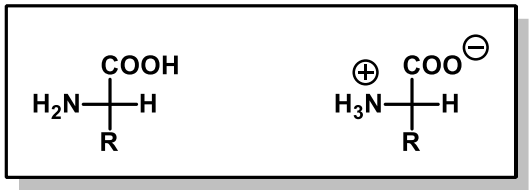
& configurazione assoluta R

* due centri stereogenici

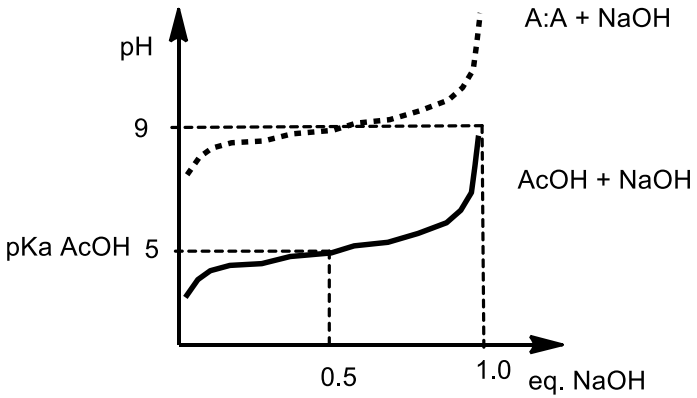
§ ammina secondaria

A.A acidi Asp (D), Glu (E)
ASN (N), Gln (Q)

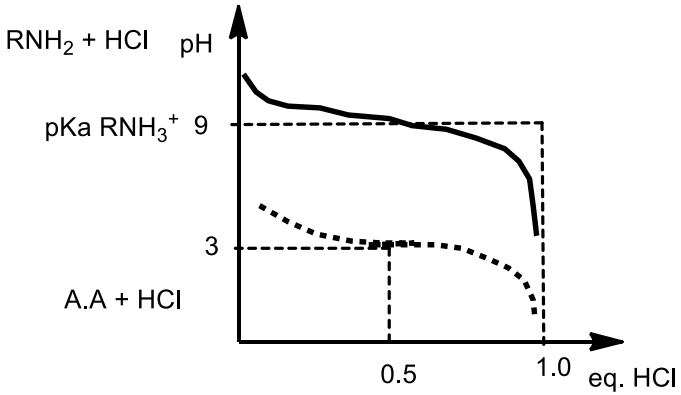
A.A basici Lys (K), Arg (R) His (H)

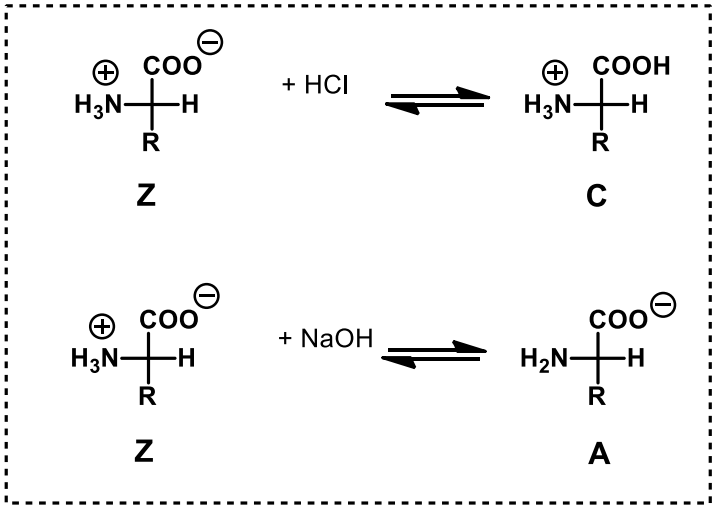


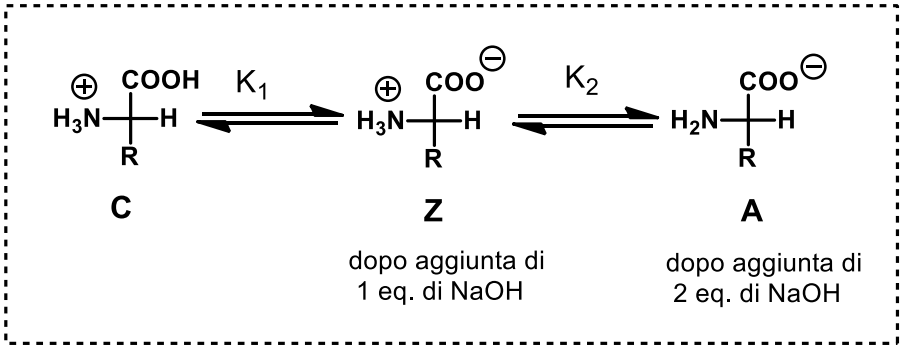
l'A.A è molto meno acido di AcOH

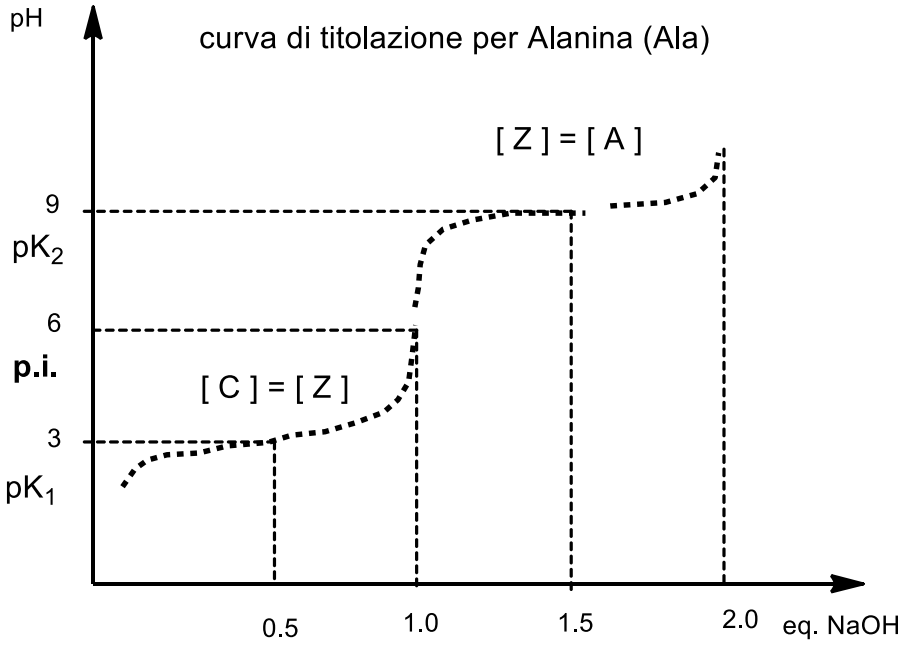


l'A.A è molto meno basico di un'ammina









Henderson-Hasselbach

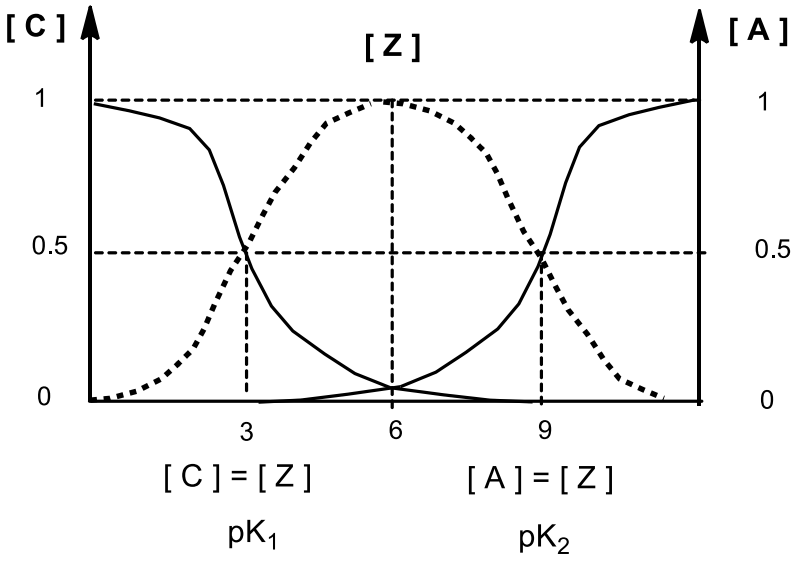
$$pH = pK + \lg \frac{[A^-]}{[HA]}$$

dopo 0.5 eq. NaOH $\quad pH = pK_1 + \lg \frac{[Z]}{[C]} = 3$

dopo 1.5 eq. NaOH $\quad pH = pK_2 + \lg \frac{[A]}{[Z]} = 9$

$$[C] + H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} [Z] + [H_3O^+] \qquad \frac{[Z] \cdot [H_3O^+]}{[C]} = K_1$$

$$[Z] + H_2O \overset{K_2}{\rightleftharpoons} [A] + [H_3O^+] \qquad \frac{[A] \cdot [H_3O^+]}{[Z]} = K_2$$



$$\frac{K_1 \cdot [C]}{[H_3O^+]} = [Z] \qquad \frac{[A] \cdot [H_3O^+]}{K_2} = [Z]$$

$$\frac{K_1 \cdot [C]}{[H_3O^+]} = \frac{[A] \cdot [H_3O^+]}{K_2}$$

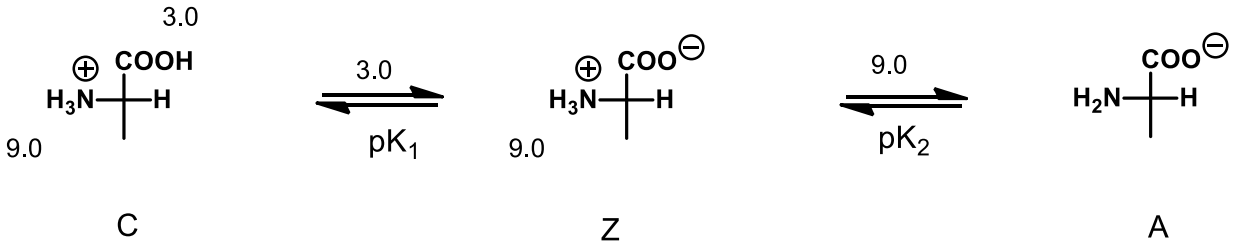
$$\boxed{\frac{[C]}{[A]} = \frac{[H_3O^+]^2}{K_1 \cdot K_2}}$$

$$\frac{[C]}{[A]} = \frac{[H_3O^+]^2}{K_1 \cdot K_2}$$

al p.i. $\frac{[C]}{[A]} = 1 = \frac{[H_3O^+]^2}{K_1 \cdot K_2}$ $\quad [H_3O^+]^2 = K_1 \cdot K_2$

$2\lg [H_3O^+] = \lg K_1 + \lg K_2$ $\quad \lg [H_3O^+] = \frac{\lg K_1 + \lg K_2}{2}$ $\quad p.i = \frac{pK_1 + pK_2}{2}$

Ala

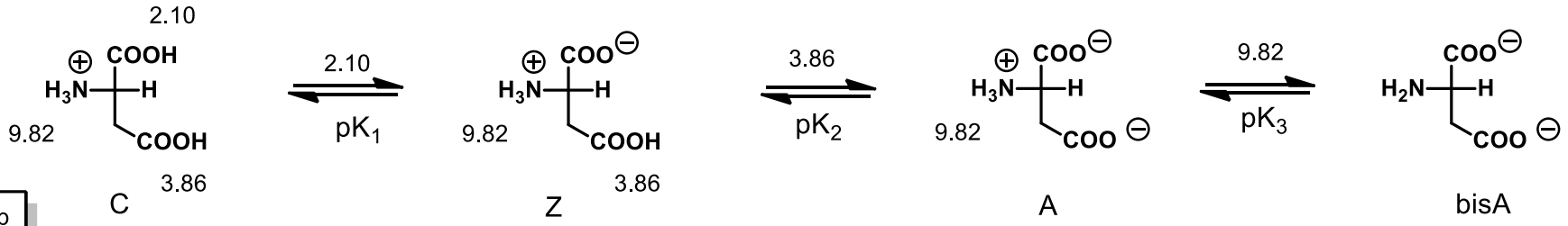


C Z A

$$p.i = \frac{pK_1 + pK_2}{2} = \frac{3 + 9}{2} = 6$$

$$\frac{[C]}{[A]} = \frac{[H_3O^+]^2}{K_1 \cdot K_2} = \frac{[10^{-6}]^2}{10^{-3}.10^{-9}} = \frac{10^{-12}}{10^{-12}} = 1$$

$[C] = [A]$ Ala se il pH è 6

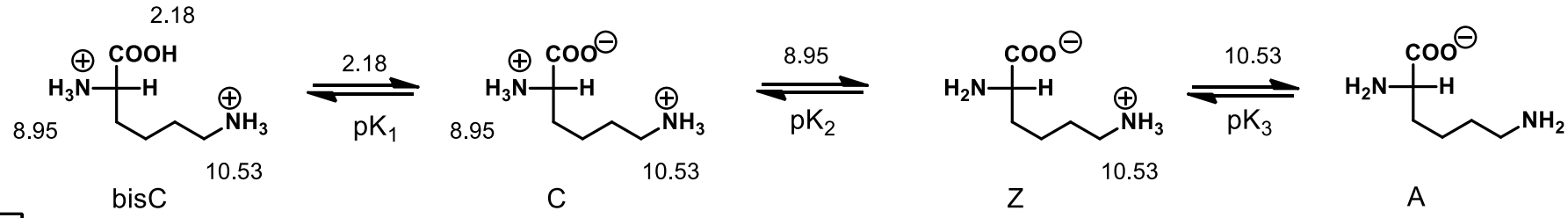


Asp

$$p.i = \frac{pK_1 + pK_2}{2} = \frac{2.10 + 3.86}{2} = 2.98$$

$$\frac{[C]}{[A]} = \frac{[H_3O^+]^2}{K_1 \cdot K_2} = \frac{[10^{-6}]^2}{10^{-2}.10^{-4}} = \frac{10^{-12}}{10^{-6}} = 10^{-6}$$

$[C] = 10^{-6} [A]$ Asp se il pH è 6

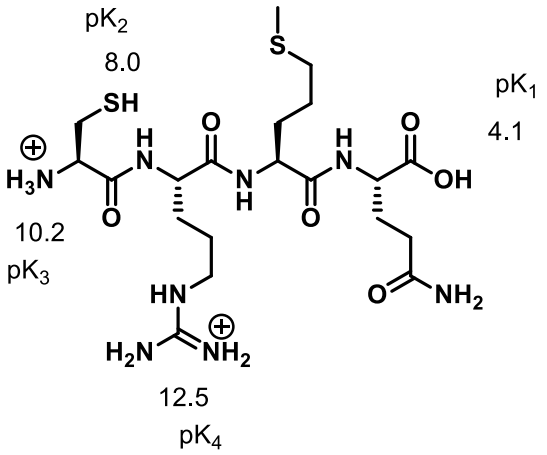


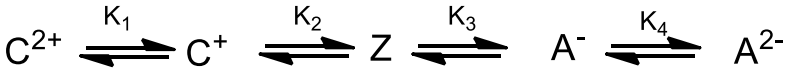
Lys

$$p.i = \frac{pK_2 + pK_3}{2} = \frac{8.95 + 10.53}{2} = 9.74$$

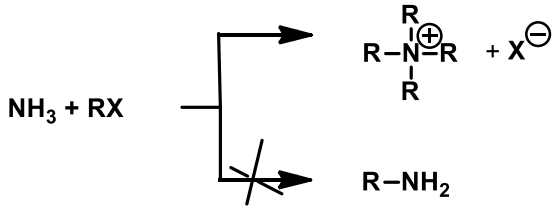
$$\frac{[C]}{[A]} = \frac{[H_3O^+]^2}{K_2 \cdot K_3} = \frac{[10^{-6}]^2}{10^{-9}.10^{-10}} = \frac{10^{-12}}{10^{-19}} = 10^{7}$$

$[C] = 10^{7} [A]$ Lys se il pH è 6





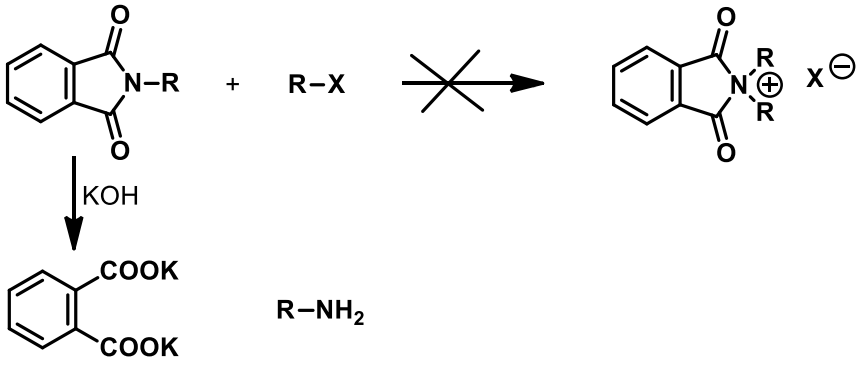
$$p.i = \frac{pK_2 + pK_3}{2} = \frac{8 + 10.2}{2} = 9.1$$



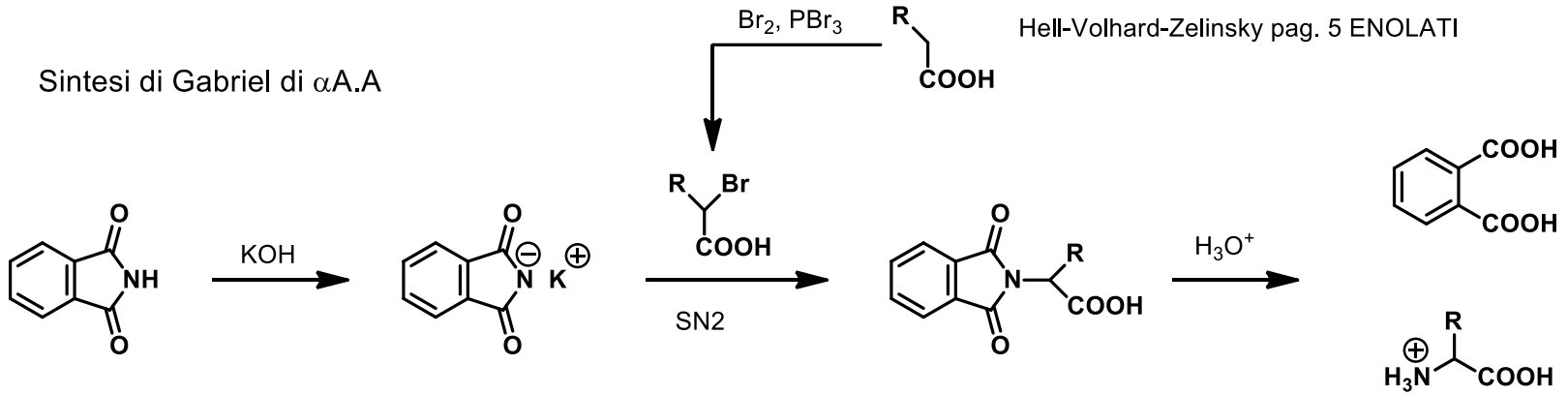
Siegmund Gabriel
7 November 1851 - 22 March 1924
German, b. Berlin, Germany

Gabriel synthesis

Gabriel, S., Chem. Ber. 1887, 20, 2224



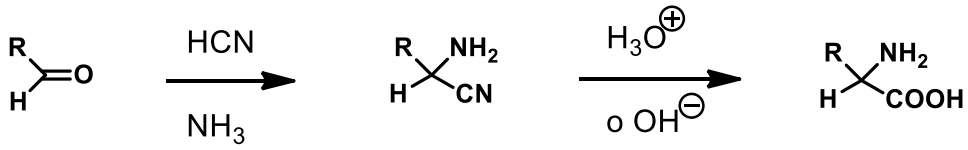
Sintesi di Gabriel di αA.A

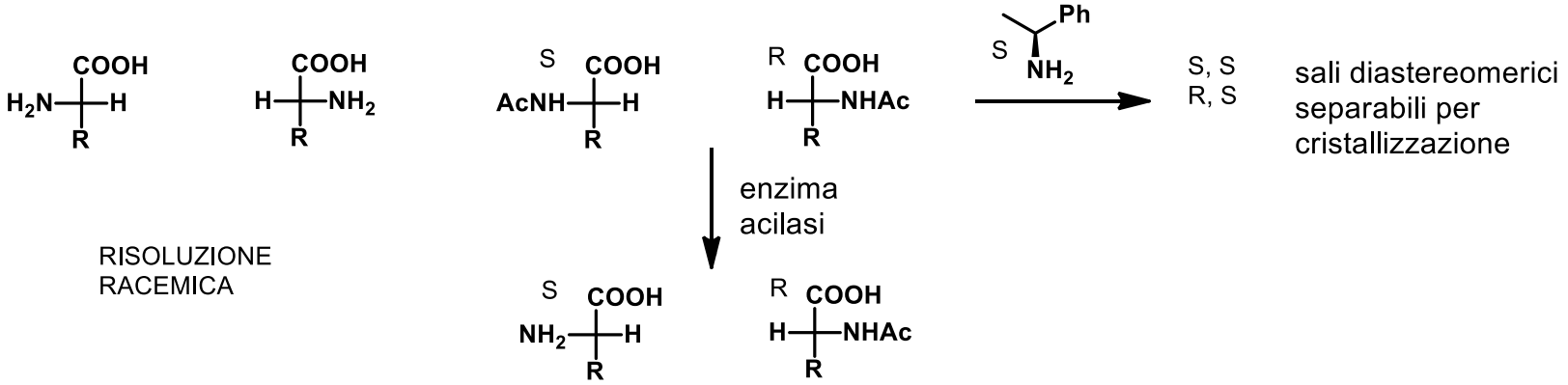


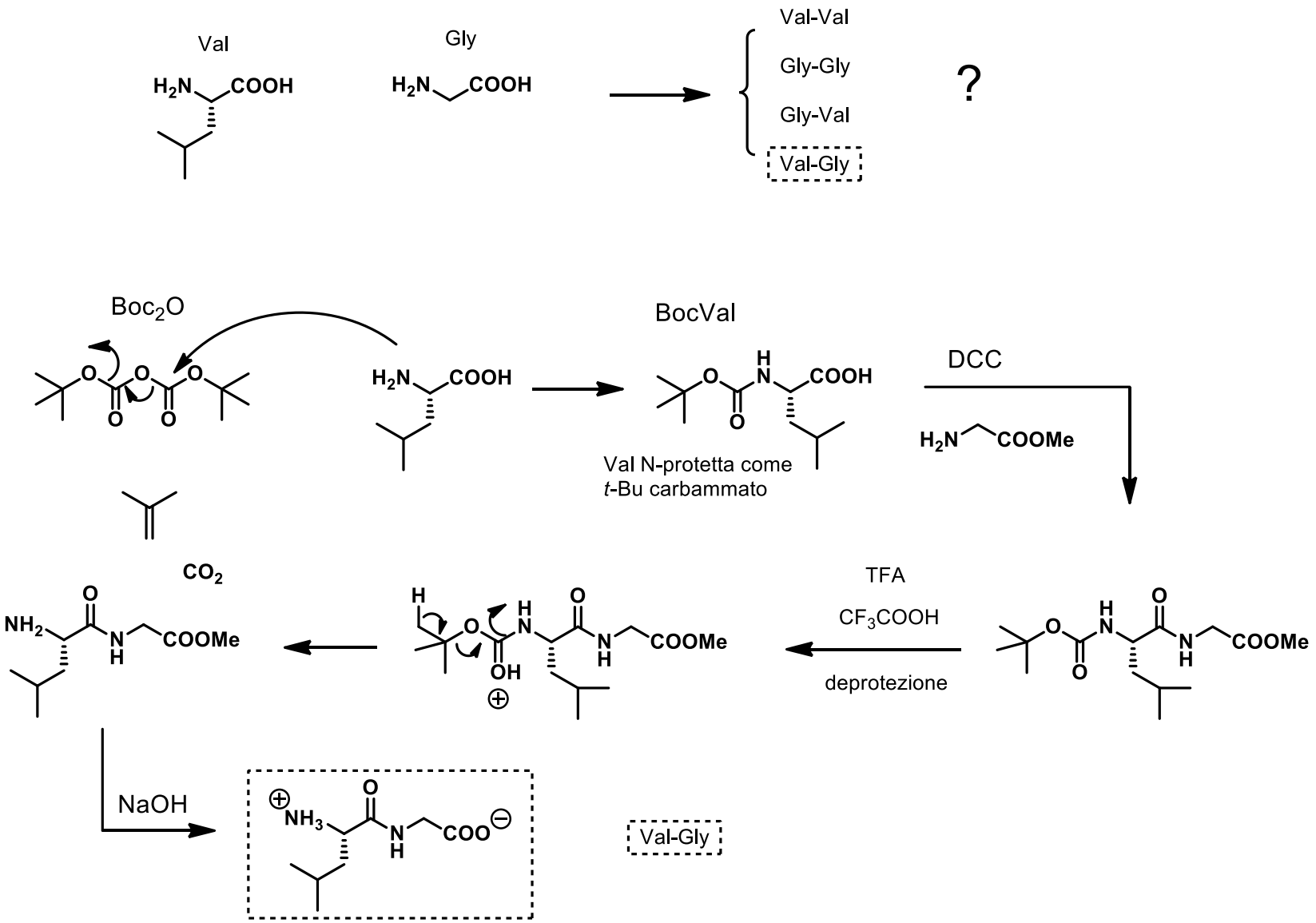
Adolf Friedrich Ludwig Strecker
21 October 1822 - 7 November 1871
German, b. Darmstadt, Germany

Strecker synthesis

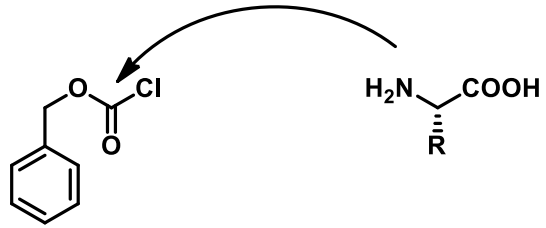
Strecker, A., Ann. Chem. 1850, 75, 27



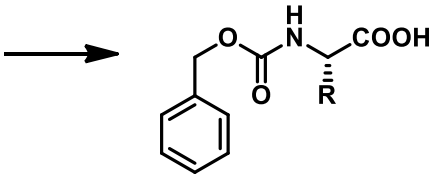



Val
Gly
Val-Val
Gly-Gly
Gly-Val
Val-Gly
?
Boc2O
BocVal
Val N-protetta come
t-Bu carbammato
DCC
TFA
CF3COOH
deprotezione
CO2
NaOH
Val-Gly

benzilossicarbonilcloruro



Z-amminoacido

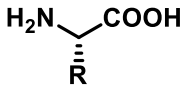


H_2, cat.

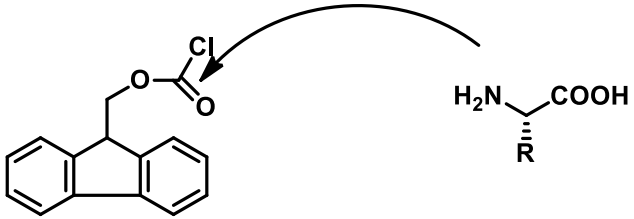
deprotezione

toluene

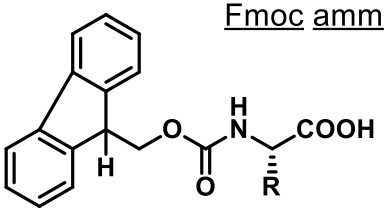
CO_2



fluorenilmetossicarbonilcloruro



Fmoc amminoacido

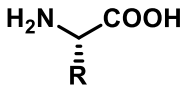


piperidina

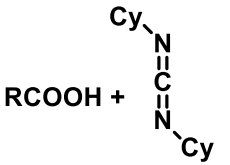
deprotezione

N-fluorenilmetilpiperidina

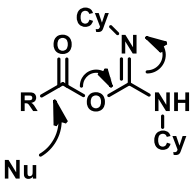
CO_2



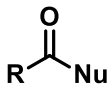
DCC



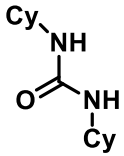
carbossile attivato



L'attivazione di α-a.a via RCOCl porta alla formazione di aza-lattone e conseguente rischio racemizzazione (vedi cap. enolati)!!



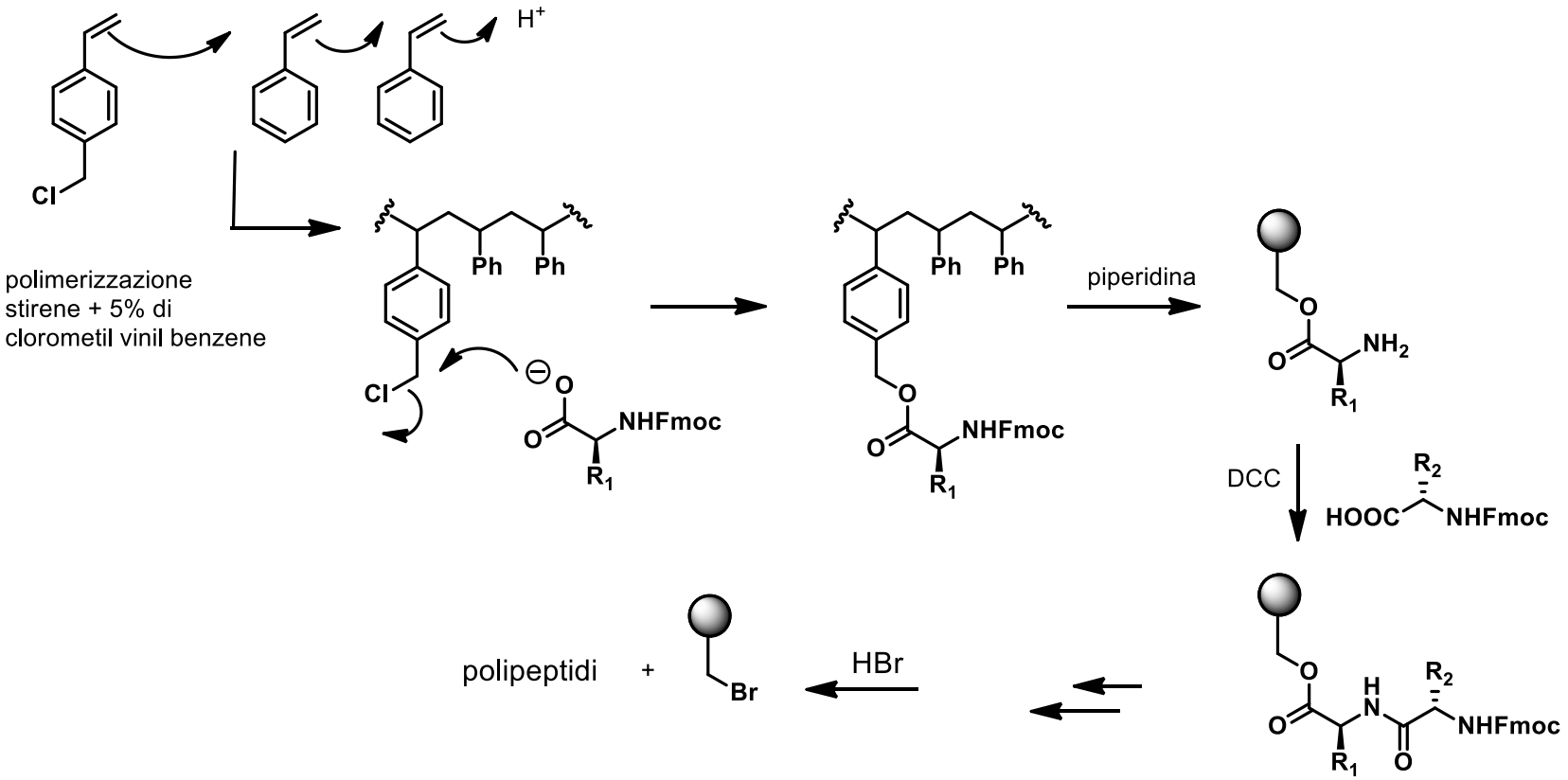
+



DCU
dicicloesilurea

Robert Bruce Merrifield
15 July 1921 – 14 May 2006
American, b. Fort Worth, Texas, USA
Nobel Prize Chemistry 1984

Merrifield solid-phase synthesis of peptides
Merrifield, R.B., J. Am. Chem. Soc. 1963, 85, 2149



semplici "lavaggi" consentono di rimuovere i reagenti in eccesso e i sottoprodotti di reazione

poichè ad ogni passaggio la resa < 100% alla fine si ottiene un peptide principale in una miscela di polipetidi
Diventa necessaria una difficile separazione cromatografica!

TRIGLICERIDI

NaOH

saponi

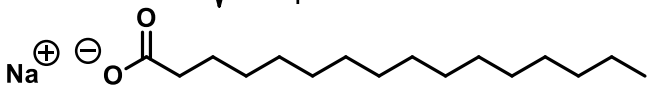
Acidi grassi

a) N° pari di C
b) Geom. cis
c) non coniugati

Saturi

H_2 cat.

Insaturi

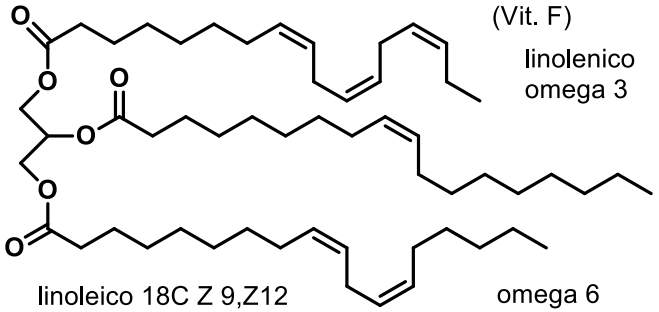


sali di Ca e Mg insolubili in acqua

ac. grasso Essenziale
(Vit. F)

linolenico
omega 3

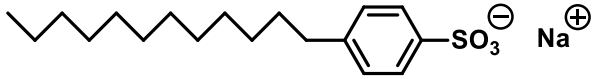
oleico



linoleico 18C Z 9,Z12

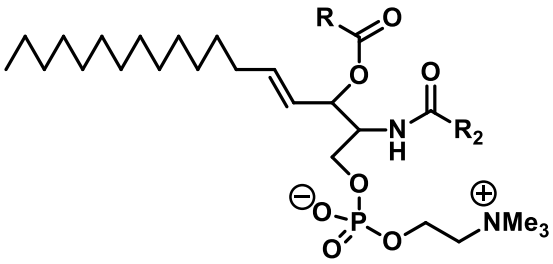
omega 6

sodio 4-dodecilbenzensolfonato

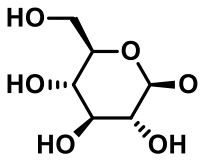


i sali di Ca e Mg sono solubili in acqua

SFINGOLIPIDI

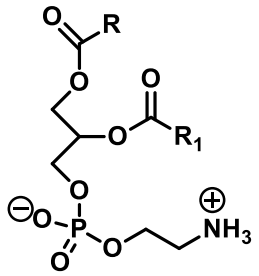


sfingomielina

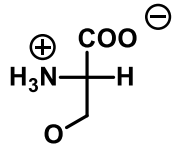


glucocerebroside

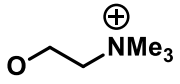
FOSFOLIPIDI



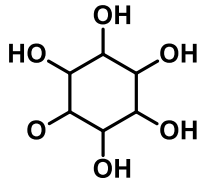
fosfatidiletanolammina (Cefalina)



fosfatidil serina



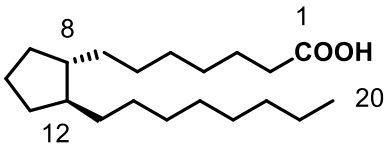
fosfatidil colina (Lecitina)



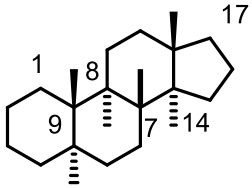
fosfatidil inositolo

PROSTAGLANDINE

ac prostanoico



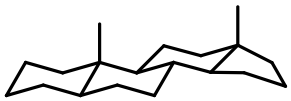
STEROIDI



Me C9 e H C8

trans-anti-*trans*-anti-*trans*

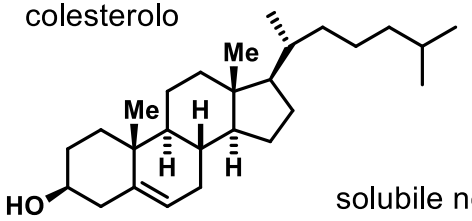
H C7e H C14



LDL colesterolo cattivo
trasportano dal fegato al circolo

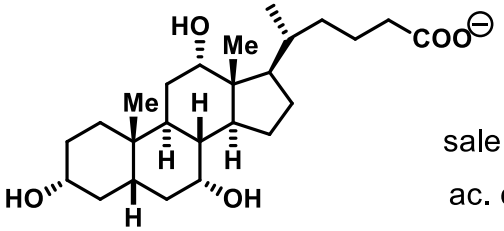
HDL colesterolo buono
trasportano dal circolo al fegato

colesterolo



insolubile nel plasma

solubile nel plasma se veicolato a proteine



sale biliare

ac. colico

emulsionante dei lipidi