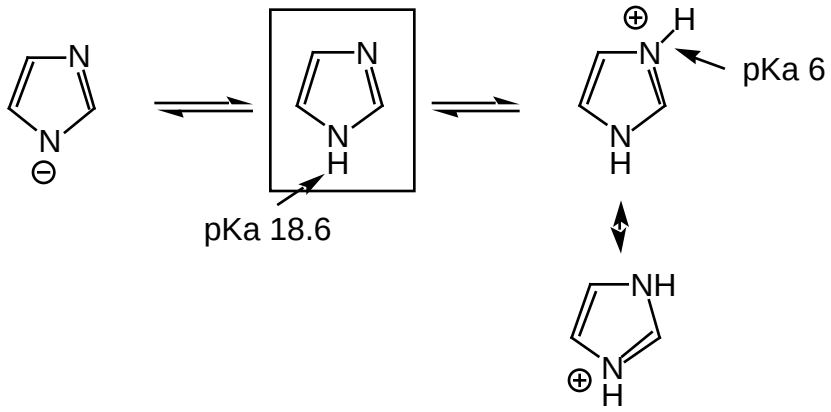
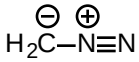
Correction:

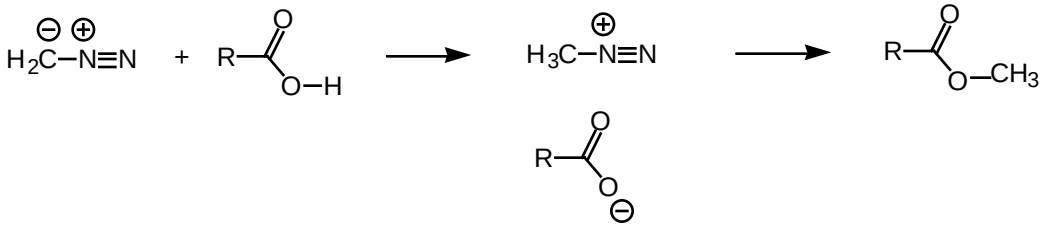


Diazoalkanes:

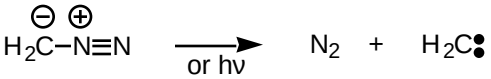
diazomethane



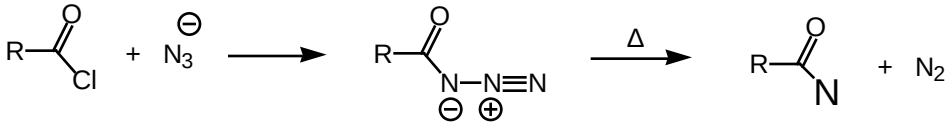
Powerful esterification reagent:



Source of carbenes: Divalent Carbon (Chapter 10, p 436. 303?)



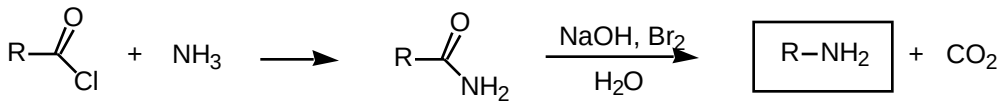
Special cases of divalent nitrogen:



Curtius Rearrangement

Related:

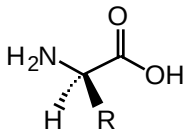
Hoffman Rearrangement



Amino acids, peptides, proteins

Proteins: structures [bone support, skin, muscle]
enzymes [catalysts]
transport [hemeoglobin, etc]
hormones [regulation, signaling]
antibodies [immune system]

Composed of **α–amino acids**

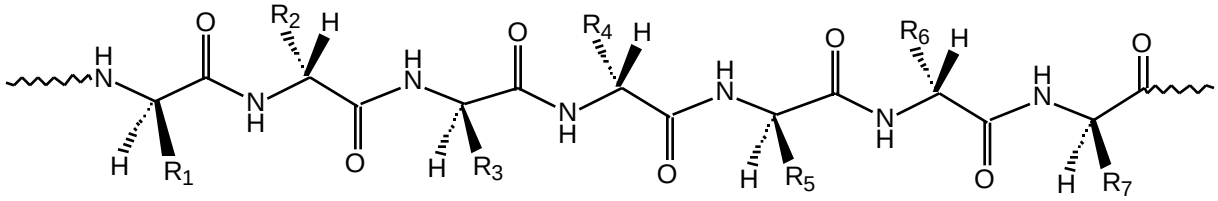


20 are genetically encoded by DNA for assembly into proteins: differ in **R**

150 total variations appear in proteins

Biosynthesis and chemical synthesis

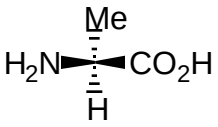
Proteins are polymers via the amide bond = this version is called the **peptide bond**



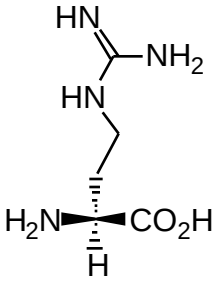
Biosynthesis and chemical synthesis

Structure: Primary structure--sequence of amino acids Chemical determination
Secondary structure--interactions between chains ribbons, helix
Tertiary structure-----folding of secondary structure
Quarternary structure--Separate proteins (subunits) associate together

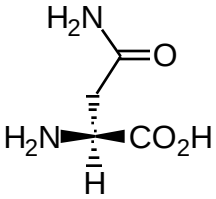
The 20 suspects:
side chains differ in: acid/base H-bonding van der Waals dipole-dipole charge/charge
(hydrophobic)



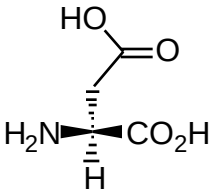
alanine
ala, A



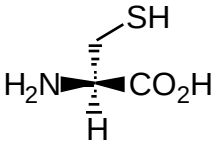
arginine
arg, R



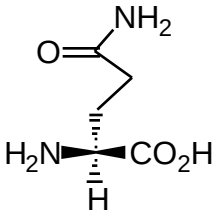
asparagine
asn, N



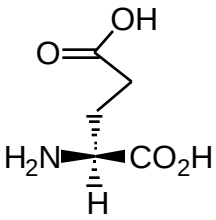
aspartic acid
asp, D



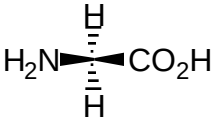
cysteine
cys, C



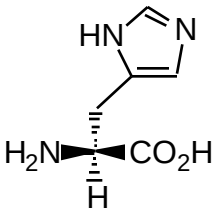
glutamine
gln, Q



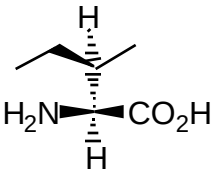
glutamic acid
glu, E



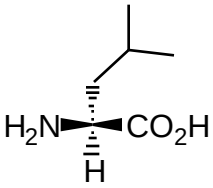
glycine
gly, G



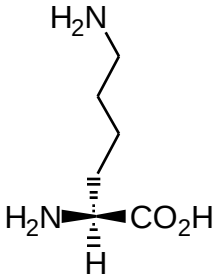
histidine
his, H



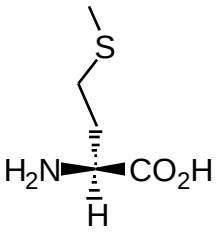
isoleucine
ile, I



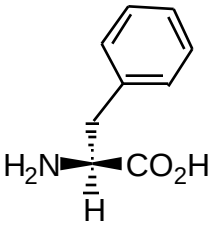
leucine
leu, L



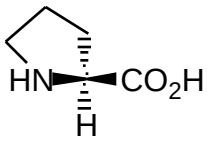
lysine
lys, K



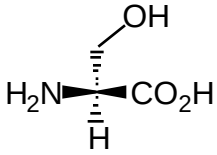
methionine
met, M



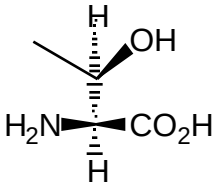
phenyl
alanine
phe, F



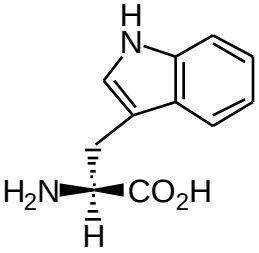
proline
pro, P



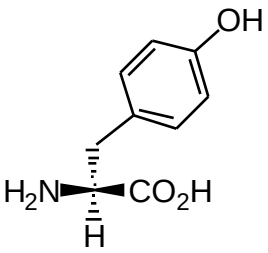
serine
ser, S



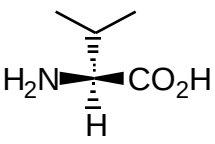
threonine
thr, W



tryptophane
trp, W



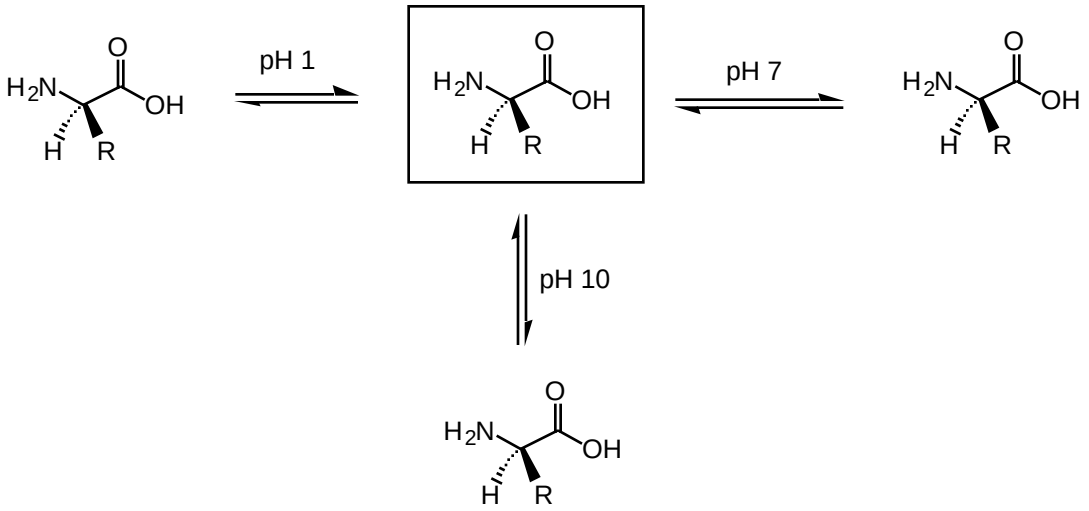
tyrosine
try, Y



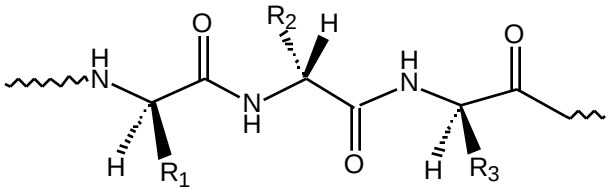
valine
val, V

Amino acids can be sorted according to the properties of the side chains, **R**

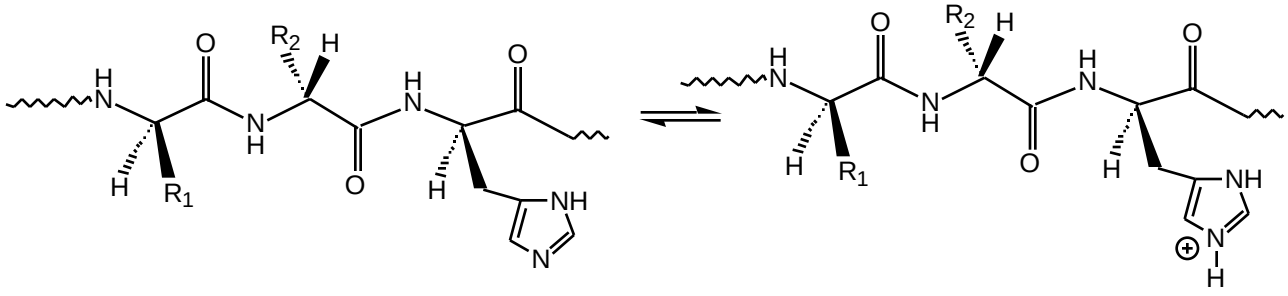
Nonpolar:	ala, val, leu, ile
Aromatic	phe, tyr, try
Cyclic	pro
Acidic	asp, glu
Basic	lys, arg, his
Neutral, polar	gly, ser, thr, cys, met, asn, gln



But, in polypeptides [proteins], the amino group is non-basic and the acidic group is non-acidic



More important: the side chains can be protonated and deprotonated



Henderson-Hasselbalch equation:

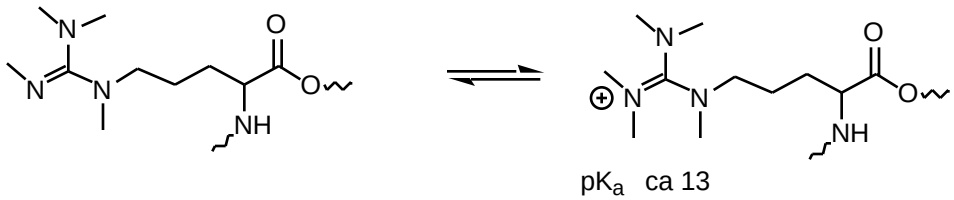
$$pH = pK_a + \log \frac{[A^-]}{[HA^-]} \qquad HA \rightleftharpoons H^+ + A^-$$

Check Table 25.3, Handout on amino acids. [Overhead]

Basic side chains: histidine--imidazole

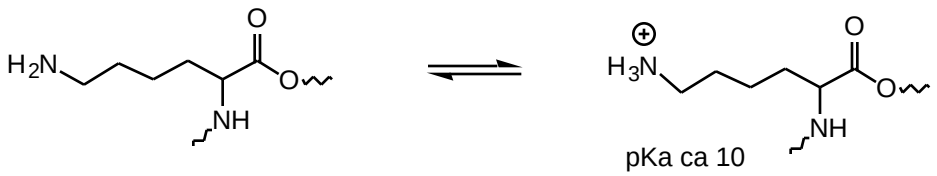
arginine:

[most basic]



pK_a ca 13

lysine



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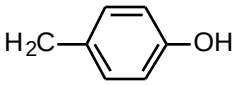
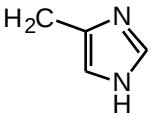
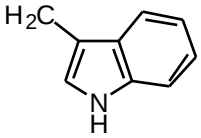
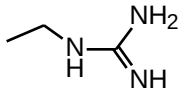
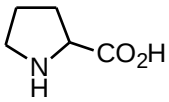
analysis of proteins involves determining the amino acid content: which amino acids are present
what is the sequence of the amino acids?

Separation of amino acids by **electrophoresis:**

Amino acids can be (+), (-), or neutral (zwitterion): when the net charge is zero, **isoelectric point in pH**

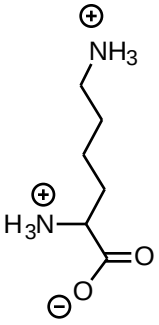
Each amino acid has a characteristic pH for the isoelectric point.

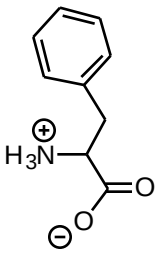
R	name	isoelectric point
H	glycine	6
CH_3	alanine	6
$CH(CH_3)_2$	valine	6
$CH_2CH(CH_3)_2$	leucine	6
$CHCH_3(CH_2CH_3)$	isoleucine	6
$-CH_2Ph$	phenyl alanine	5.9
	tyrosine	5.7
	histidine	7.6
	tryptophane	5.9
$-CH_2OH$	serine	5.7
$-CH(CH_3)OH$	threonine	5.6
$-CH_2SH$	cysteine	5.0
$-CH_2CH_2SCH_3$	threonine	5.6
$-CH_2CO_2H$	aspartic acid	2.9
$CH_2CH_2CO_2H$	glutamic acid	3.2
$-CH_2CONH_2$	asparagine	5.4
$-CH_2CH_2CONH_2$	glutamine	5.7

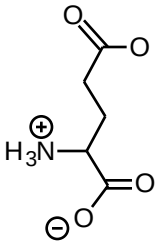
-$CH_2CH_2CH_2CH_2NH_2$	lysine	9.7
	arginine	10.8
	proline	6.1

Apparatus: Fig 26.11 in text [overhead]

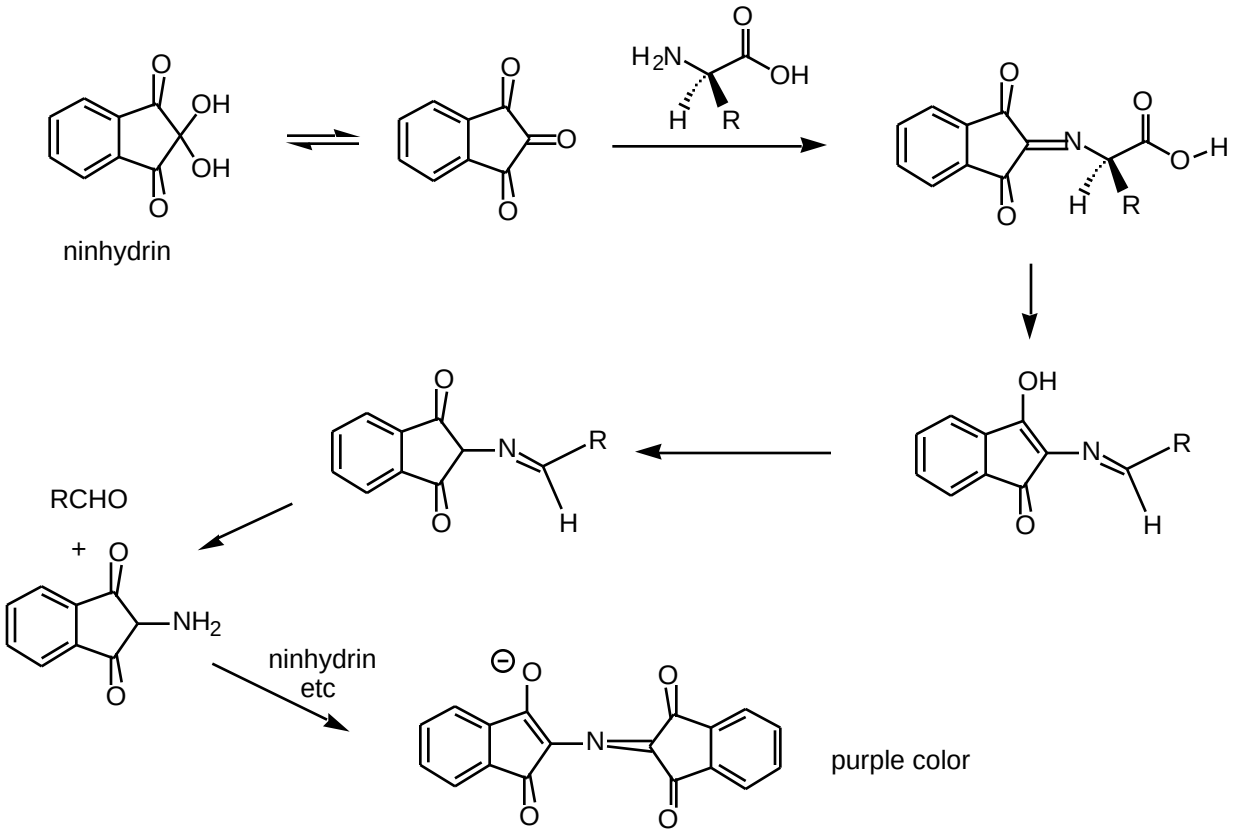
Assume pH 5.5


lys


phe


glu

Apply potential; allow migration. Then "visualize" Add ninhydrin Text 26.2C


ninhydrin
RCHO
+
ninhydrin
etc
purple color