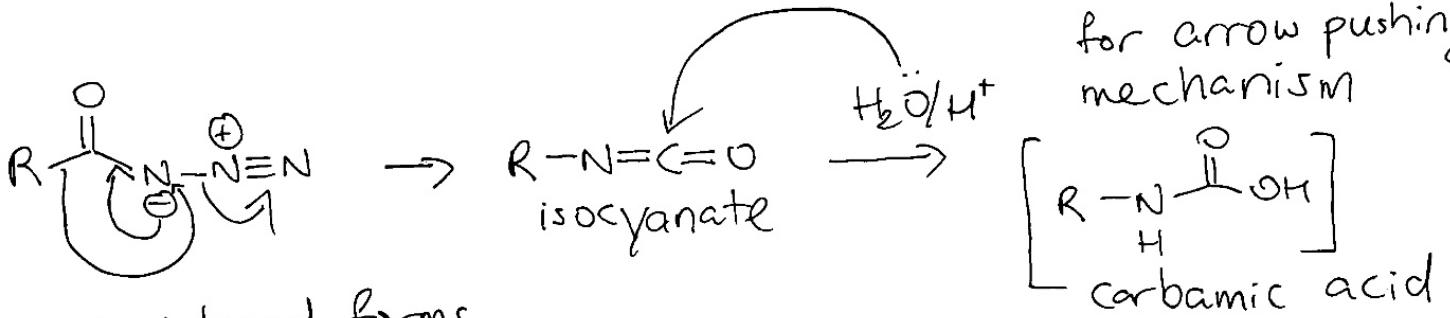
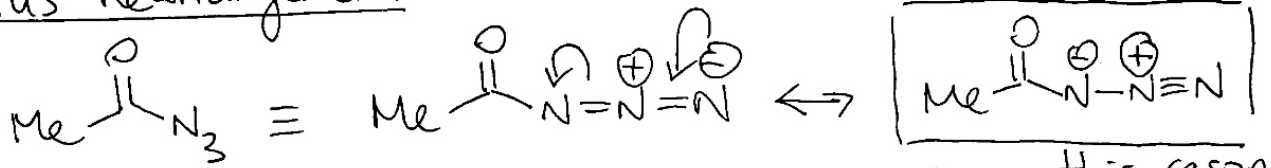
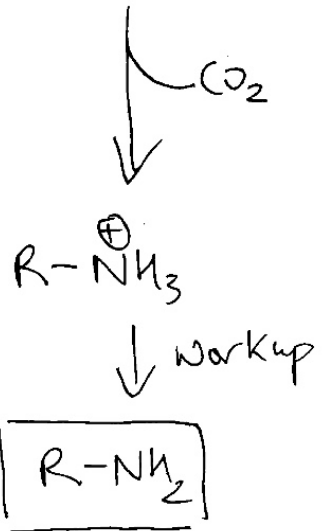


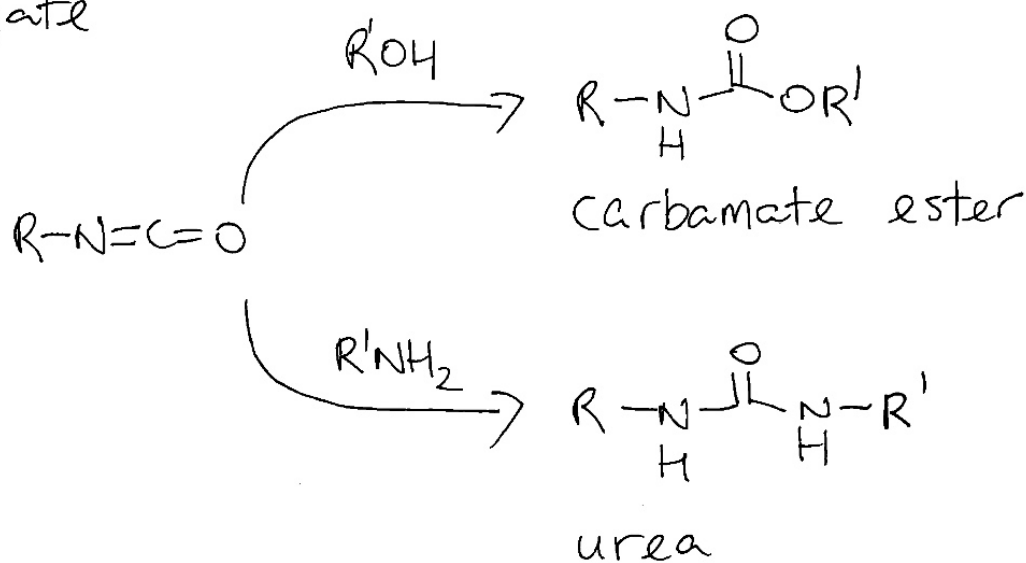
Curtius Rearrangement



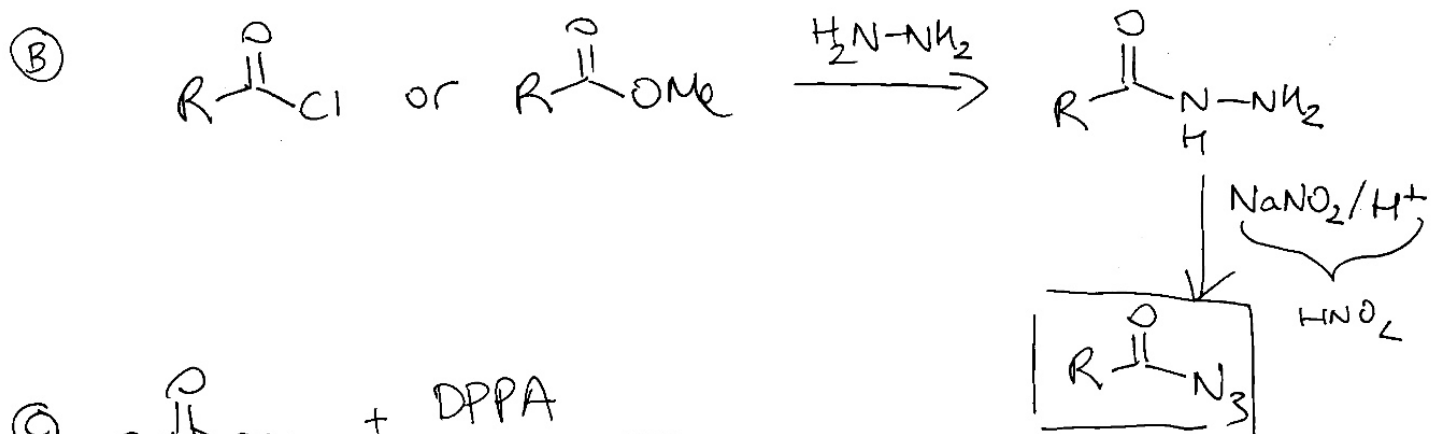
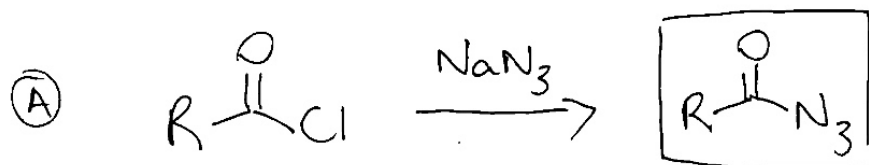
- C=N bond forms
- R group shifts from carbonyl to nitrogen
- $\text{N}_2(\text{g})$ departs as the leaving group



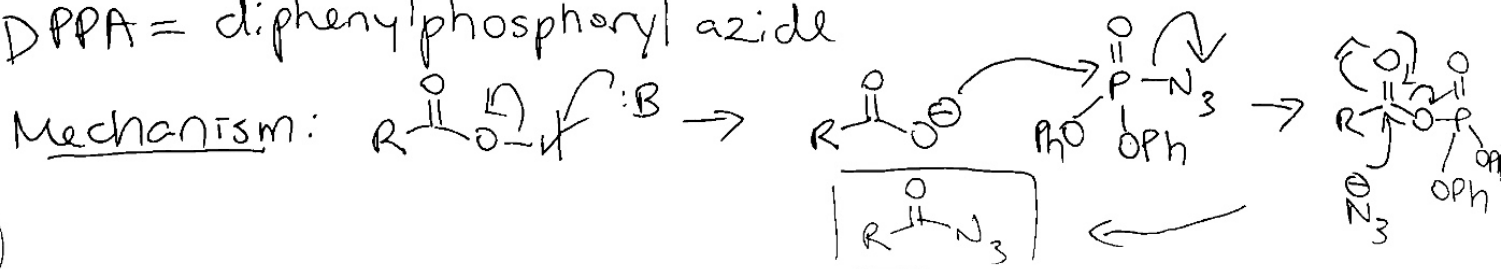
- besides H_2O , other nucleophiles can attack the isocyanate



Q How do we make acyl azides required for the Curtius?



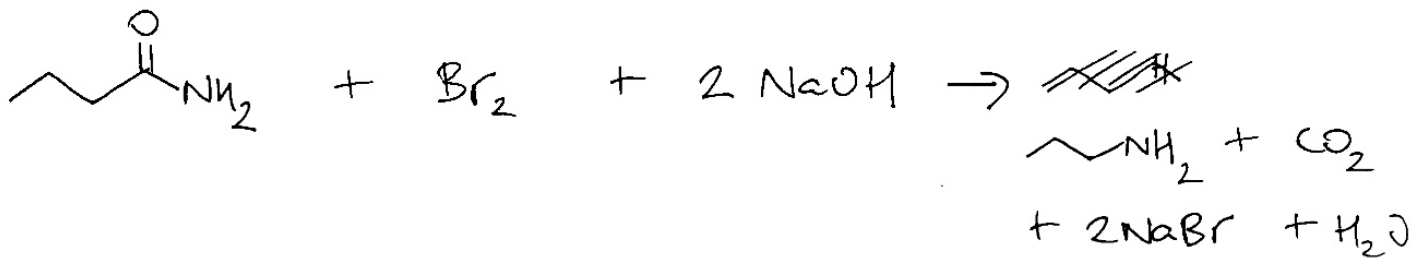
DPPA = diphenylphosphoryl azide



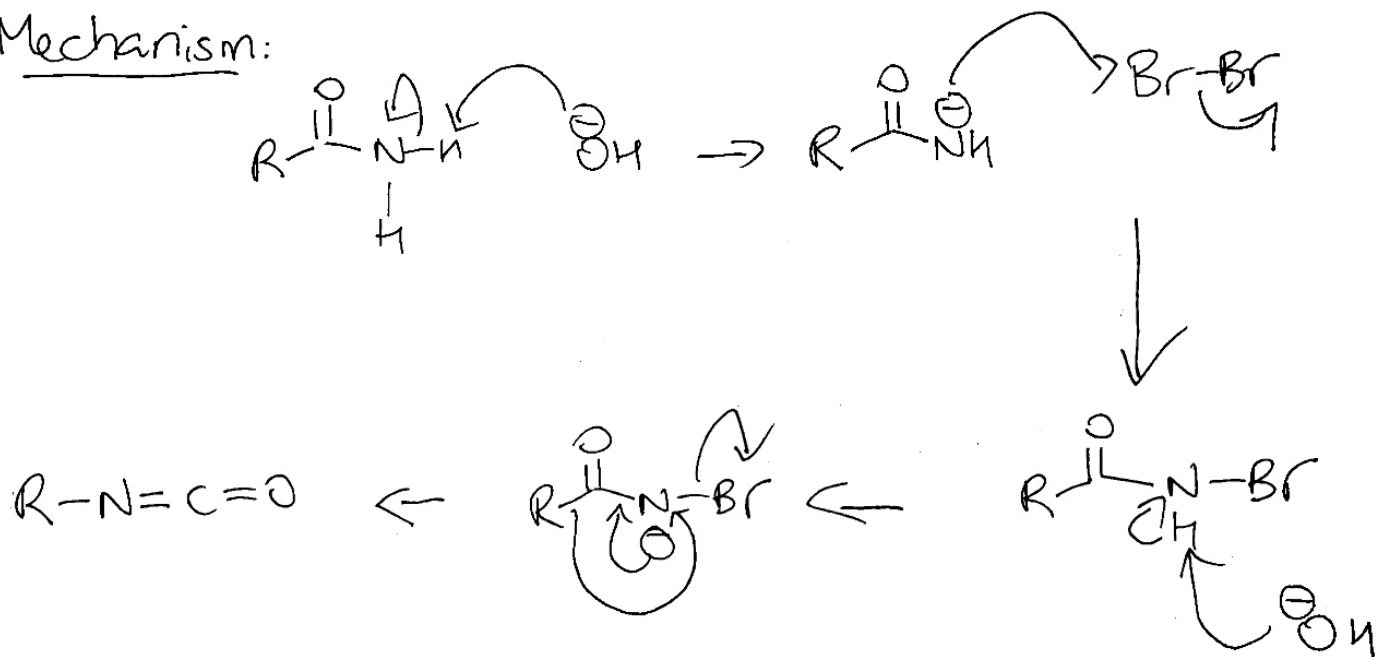
②

Hofmann Rearrangement

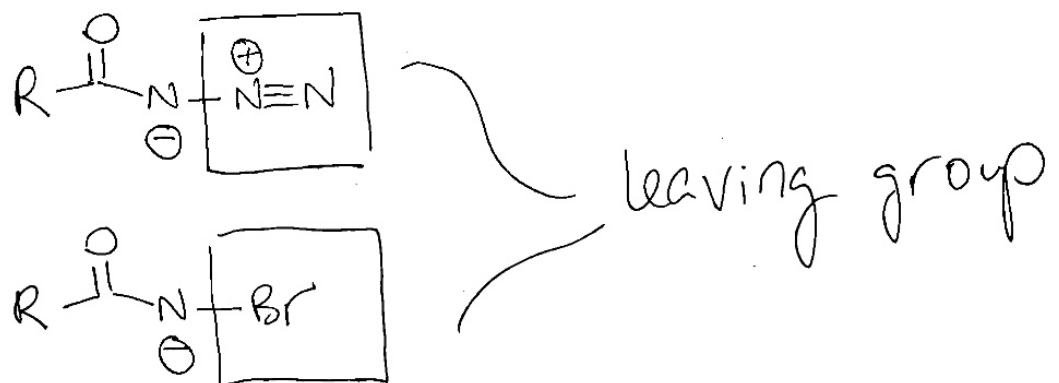
* also proceeds via isocyanate intermediate

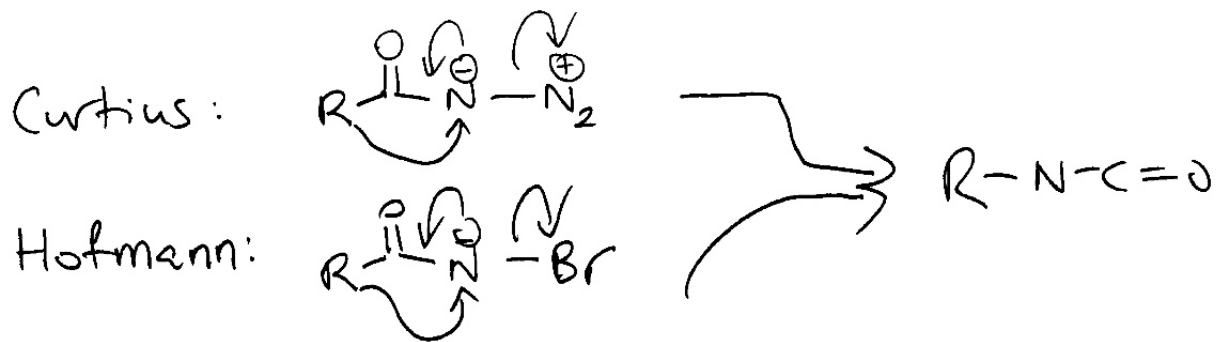


Mechanism:

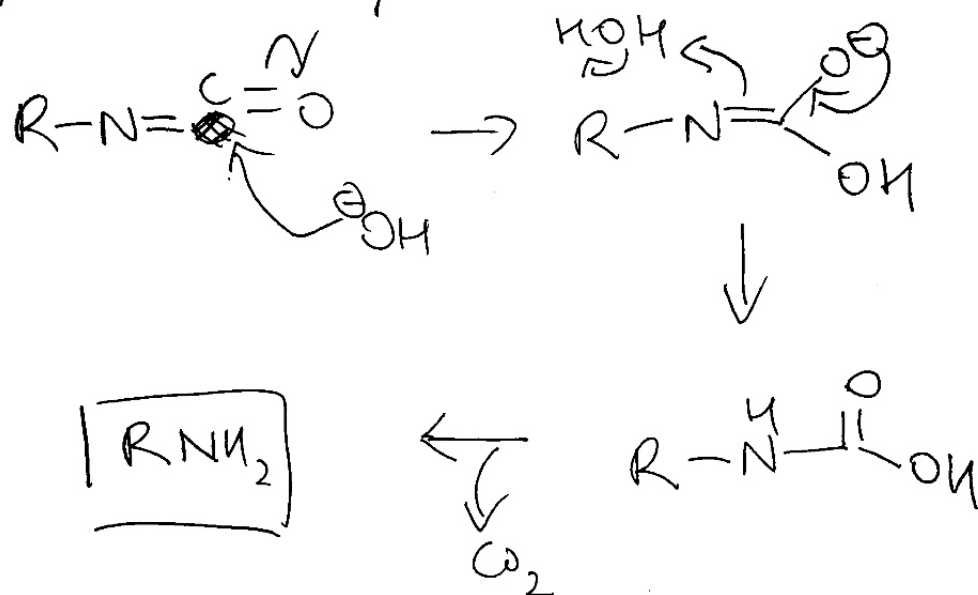


* notice the similarity with the Curtius

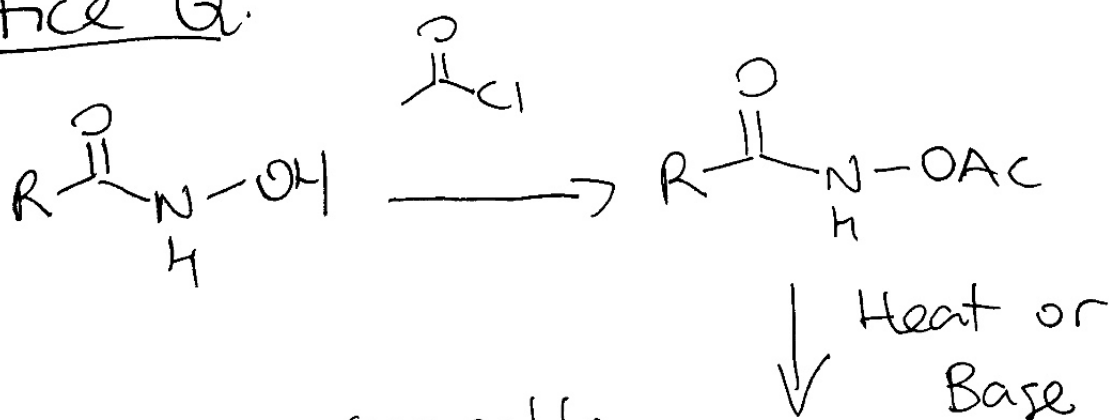




- bcs Hofmann is conducted in aq. base, the isocyanate cannot be isolated and it spontaneously converts to the amine



Practice Q:



* propose a reasonable mechanism for the above rxn!!

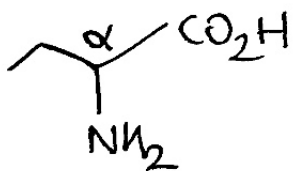


Final note on these rearrangements
→ they are stereospecific

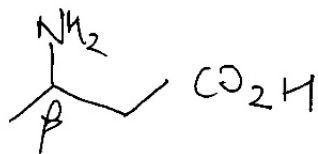


Chapter 27 - Amino Acids, Peptides and Proteins

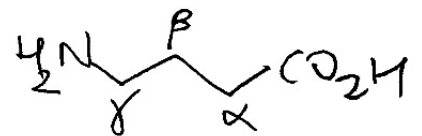
Amino acids = AA contain both an amine and acid group



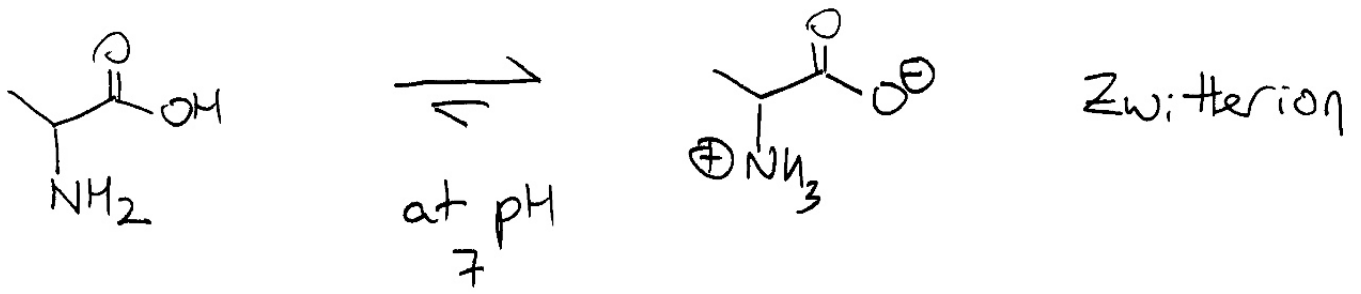
α-AA



β-AA

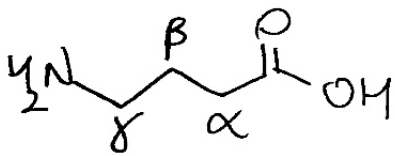


γ-AA

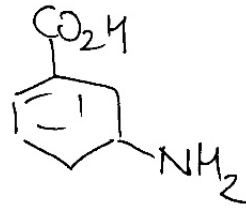


- when several AA are connected through amide (aka peptide) bonds they form peptides (fewer than 20-30 AA) and proteins

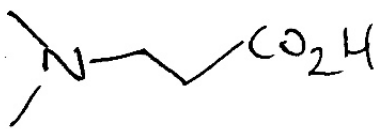
Nomenclature



γ -aminobutanoic acid
 4-aminobutanoic acid



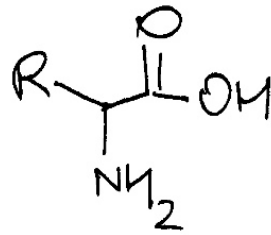
3-amino
 benzoic acid



3-(dimethylamino) propanoic
 acid

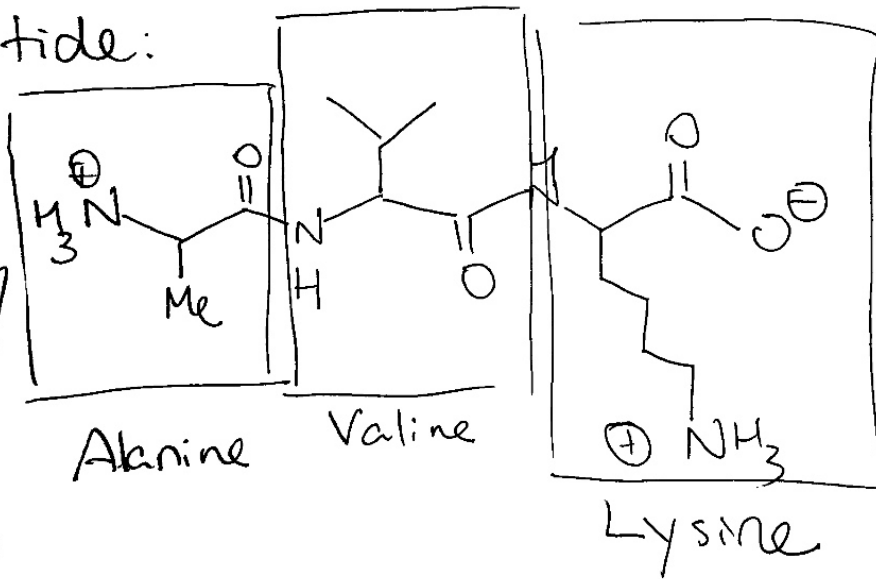
- the twenty α -amino acids are commonly known by their traditional names

- general formula:



- you do not have to memorize structures for the R groups

Peptide:



carboxy end or carboxy terminus

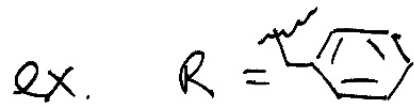
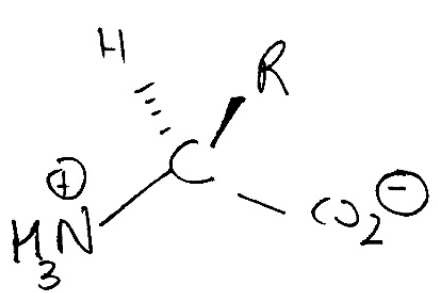
amino end or amino terminus

- should be able to recognize different AA connected together

name from Amino to Carboxy End
Ala-Val-Lys or A-V-K

Stereochemistry of AA

- with the exception of glycine, all common naturally occurring AAs are chiral

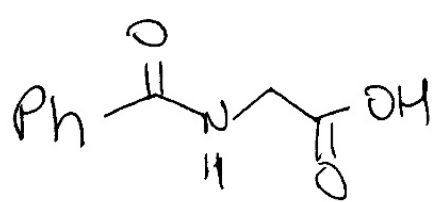


→ gives S configuration

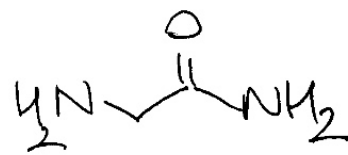
Q: What about Cysteine?

Acid-Base Properties of AAs

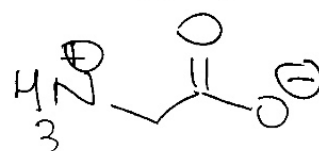
- as mentioned earlier, usually exists as zwitterions
- not soluble in a polar aprotic solvents
- very high MP!!



MP 190°C

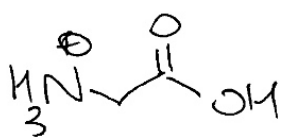


67°C

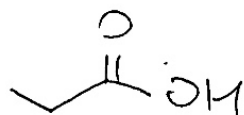


262°C

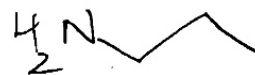
-large Dipole Moment



14D



1.7 D



1.4 D



because of charge separation