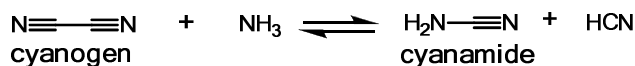


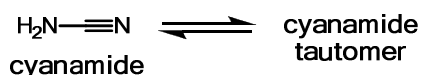
26-1. (a) In glycine polymerization reactions containing excess glycine and DAMN there is very little tripeptide or longer polypeptide products. In fact, very little diglycine is observed. Show the mechanism of formation of the major product.

(b) Why is this side reaction not a problem in laboratory and cellular syntheses of peptides?

26-2. (a) Cyanogen may be converted into cyanamide and hydrogen cyanide under prebiotic conditions in the presence of ammonia, Provide a mechanism for the transformation (you need not explicitly show proton transfers).

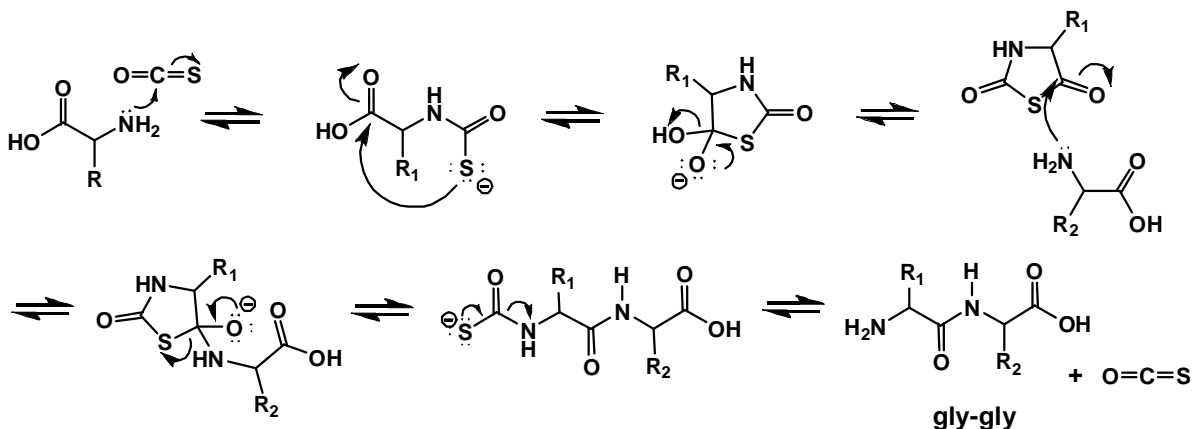


(b) A tautomer of cyanamide unveils its prebiotic potential. Draw this tautomer and explain why this molecule may be of prebiotic interest in terms of the chemistry it could facilitate (hint: it will look like something you have seen earlier in the term).

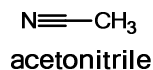


26-3. (a) Cellular peptides exist as a single enantiomer composed of stereochemically-pure amino acids. These peptides cannot arise from simple polymerization of Strecker Reaction products. Why not?

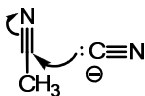
(b) Even if stereochemically pure amino acids were present, their mechanism of polymerization must also be considered. Consider the cyanide tautomer coupling reagent from 26-2b and another proposed coupling reagent, $\text{O}=\text{C}=\text{S}$, whose mechanism of coupling is outlined below. Which mechanism is likely to lead to a single enantiomer of peptide product?



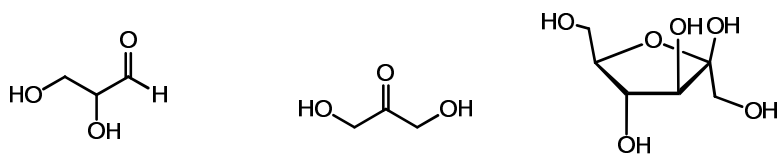
26-4. Propose a reasonable mechanism for the synthesis of asparagine from hydrogen cyanide, water and acetonitrile. You need not explicitly show proton transfer steps.



The first step:



26-5. 1,3-dihydroxyacetone and 2,3-dihydroxypropanal react to form fructose (shown below in its β -furanose form).



1,2-dihydroxypropanal 1,3-dihydroxyacetone β -fructofuranose

- (a) Circle the portion of fructose that comes from 1,3-dihydroxyacetone.
- (b) How many other furano-ketoses could potentially form in the reaction of 1,3-dihydroxyacetone with racemic 2,3-dihydroxypropanal?