P 1060 # Ch. 28. Biomolecules : Heterocycles and Nucleic Acids

Heterocycles only ; Ch. 28.1 ~ 28.7.

28.1. Five-Membered Unsaturated Heterocycles.


Pyrrole


Furan


Thiophene.

 ⇒ Some unique chemistry.

↳ both amine and conjugated diene ; but chemical properties are different from typical amine and conjugated diene.

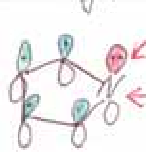
① Although amine, pyrrol is not basic

② Although conjugated diene, pyrrol undergoes electrophilic aromatic substitution rather than electrophilic addition

P1062 ## 28.2. Structures of Pyrrole, Furan, and Thiophene.

- Pyrrole, Furan, Thiophene
  - $6\pi e^-$ in cyclic conjugated system ⇒ aromatic

 pKa=0.4



less e^- rich,
less basic, less nucleophilic

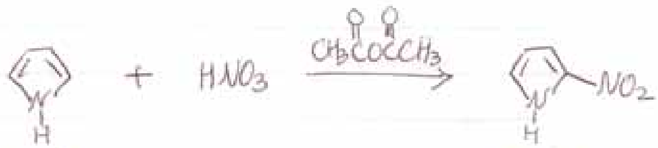
↳ In pyrrole nitrogen, [3 e^- are used in forming 3 σ bonds
2 lone-pair e^- are involved in aromatic π bonding ⇒ protonation destroy aromaticity

28.3. Electrophilic Substitution Rxns of Pyrrole, Furan, and Thiophene

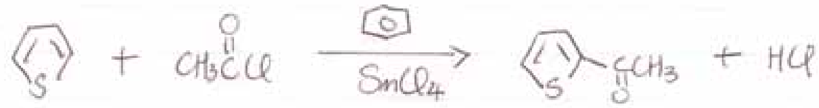
- Chemistry of pyrrole, furan, thiophene
  - aromatic system ; similar to chemistry of activated benzene.
  - heterocyclic aromatic system : more reactive than (benzene)
    - ↳ low temp to control the rxns.
    - ↳ halogenation, nitration, sulfonation, F-C acylation
  - reactivity order ;

  - occur only at C2 position.

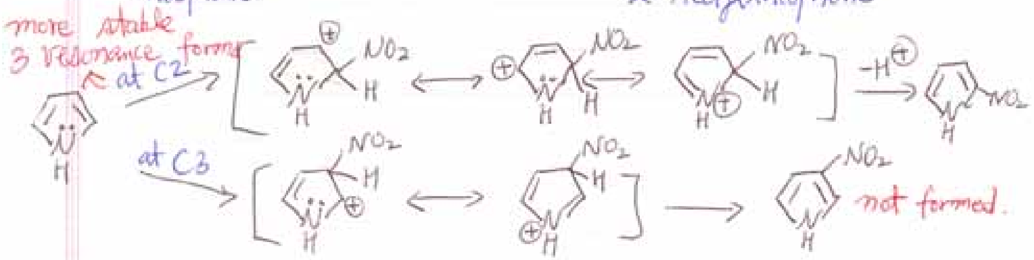
Furan — 2-Bromofuran



Pyrrole — 2-Nitropyrrole

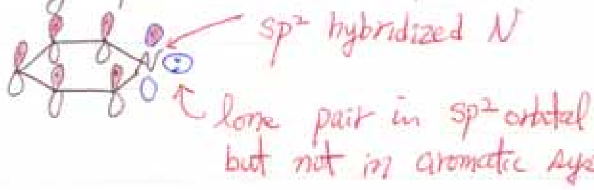


Thiophene — 2-Acetylthiophene

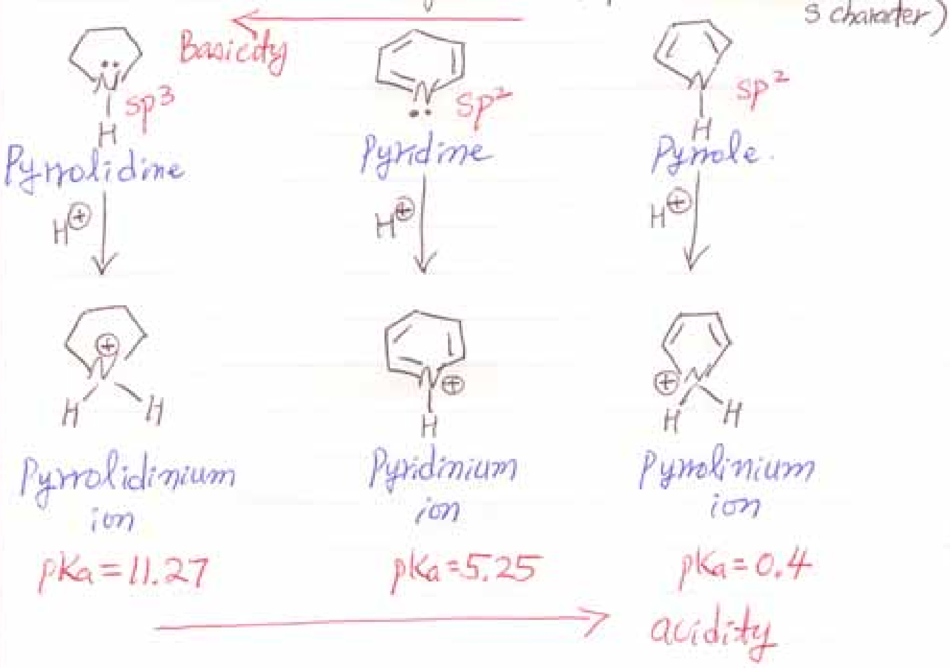


28.4. Pyridine, Six-Membered Heterocycles

- Pyridine
  - Heterocyclic analog of benzene; aromatic
  -



  - stronger base than 
  - weaker base than alkylamine. (sp³ N has 25% s character)



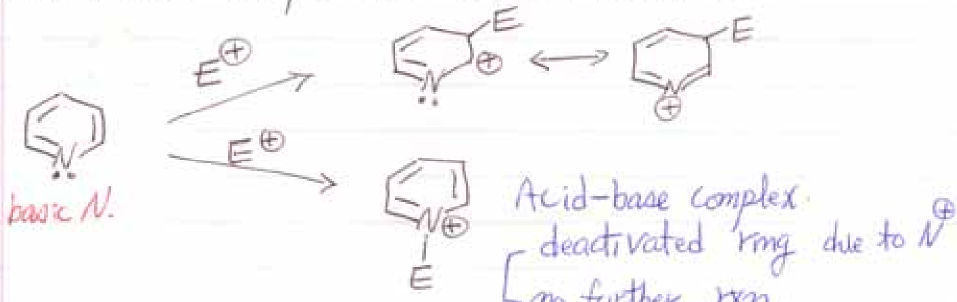
  - Pyridine N has sp² N hybridization (33% s character)
    ↳ lone pair e⁻ more tightly bound to nuclei

P1065 28.5. Electrophilic Substitution of Pyridine

- Electrophilic aromatic substitution of pyridine
  - very difficult.
  - low yield at C3 position under drastic condition

Reasons

① Acid-base complexation between N and $E^{\oplus}$

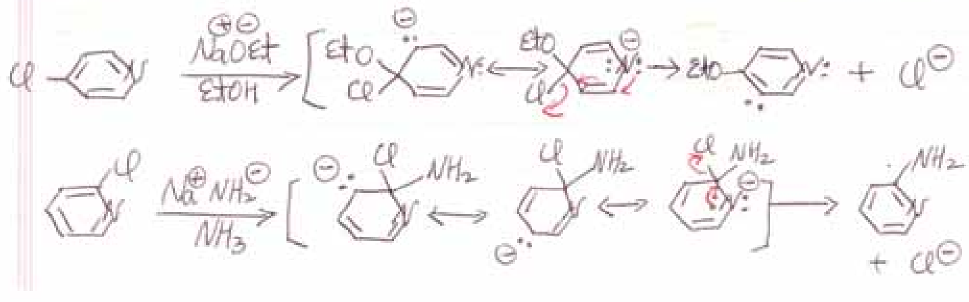


② e-w inductive effect of EN nitrogen atom.

EN nitrogen atom decrease e^- density in the ring ⇒ makes rxn w/ electrophile difficult

P1066 28.6. Nucleophilic Substitution of Pyridine

- Easy nucleophilic aromatic substitution at C2 and C4.



P1159 # Ch.31. Synthetic Polymers

- Polymer is a large molecule built up by repetitive bonding together of many smaller units. (monomers)

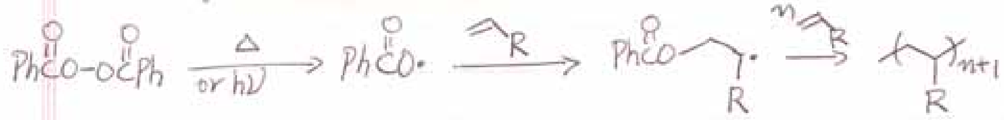
Styrene Polystyrene

P1160 ## 31.1. Chain-Growth Polymers.

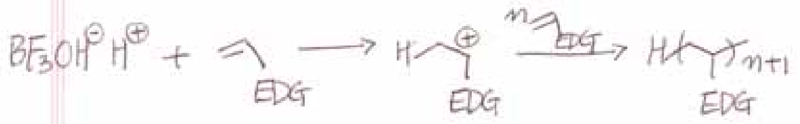
- Synthetic polymers ; classified by their method of synthesis
  ① Chain-growth polymer ; Polyolefins (PE, PP, rubber)
  ② Step-growth polymer ; Polyester, Polyamide, polycarbonate

- Chain-growth polymers.
  - produced by chain-rxn polymerization of vinyl monomer
  - initiator ; radical, cation, anion, TM.

  ① Radical polymerization
  - For any vinyl monomer. => the most common

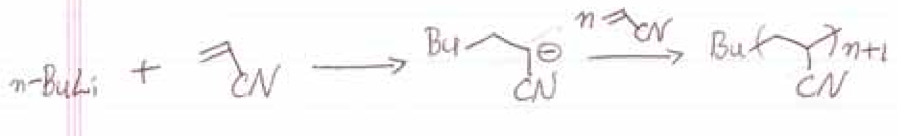


  ② Cationic polymerization.
  - Only for vinyl monomers that contain e-d group. capable of stabilizing carbocation intermediate



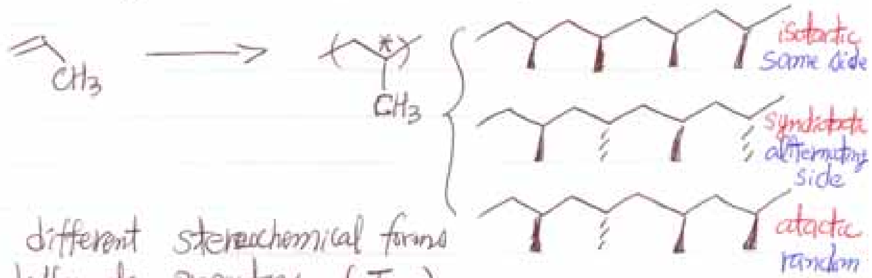
P1160 ③ Anionic polymerization

- Only for vinyl monomers that contain e-w group.



P1161 31.2. Stereochemistry of Polymerization
; Ziegler-Natta Catalysts.

- Polymerization of vinyl monomer can induce chirality centers on its polymer chain



- Three different stereochemical forms
  ⇒ different properties (Tm)
  ⇒ prepared by different polymerization catalyst

- Ziegler-Natta Catalyst (1963 Nobel Prize)
  - $(CH_3CH_2)_3Al$ + $TiCl_4$ ⟶ Z-N catalyst (precipitation)
  - Produce linear polyolefins w/o branching under mild conditions (2~5 atm, 50-70°C)
  - Crystalline polymers ⇒ iPP, HDPE (Plastics)
    isotactic ↙ ↳ no branching.

31.3. Copolymers

P 1163 • [Homopolymers ; polymers that consist of identical units
[Copolymers ; when 2 or more different monomers form polymer chain.

vinyl chloride   vinylidene chloride   "Saran"

• Copolymerization of monomer mixtures
- generate material w/ properties different from those of either corresponding homopolymer.
- offer great flexibility for new materials.

• Types of copolymers based on distribution of monomer

① -A-A-A-B-A-B-B-   random copolymer

② -A-B-A-B-A-B-   alternating copolymer

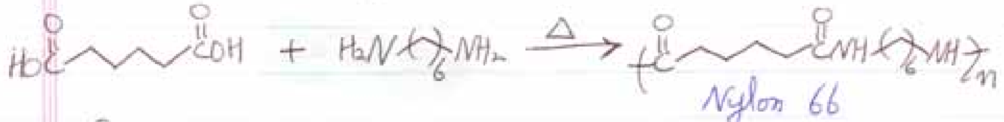
③ -A-A-A-B-B-B-   block copolymer

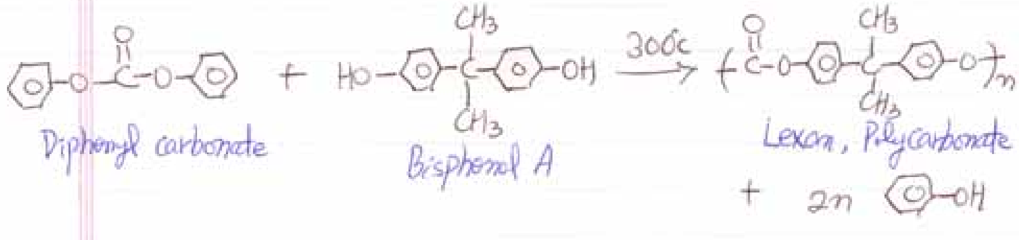
④ -A-A-A-A-A-A   graft copolymer

(branches on the second and fifth A: -B-B-B-)

31.4. Step-Growth Polymers

P1165 • Step-growth polymers
- produced by rxn between two difunctional reactants
  - single reactant w/ two different FGs





P.1167. 31.5. Polymer Structure and Physical Properties.
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