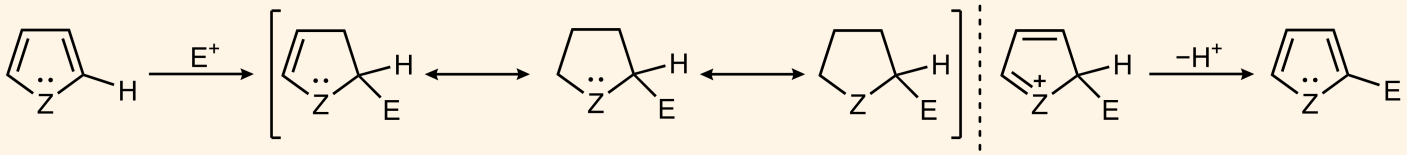
CONCEPT: REACTIONS OF PYRROLE, FURAN, AND THIOPHENE

● Pyrrole, furan, and thiophene undergo _____ reactions like benzene.

EAS Reaction: 5-Membered Heterocycles



Z = __, __, __

● Due to charge stabilization by the heteroatom, pyrrole, furan, and thiophene are _____ reactive than benzene.

□ Require _____ conditions for EAS.

□ **Reactivity Order:** Pyrrole __ Furan __ Thiophene

EXAMPLE: Furan can be acetylated using acetic anhydride and a Lewis acid catalyst (BF_3) while pyrrole can be acetylated directly without a catalyst. Why is pyrrole more reactive than furan?

a) Pyrrole is more reactive because it is basic. Basic aromatic heterocycles are always more reactive.

b) O is less electronegative and makes the aromatic ring electron deficient and decreases its reactivity.

c) The large atomic size of O and poor orbital overlap with the aromatic pi system makes furan less reactive.

d) N is less electronegative than O, takes up a + charge more easily, and better stabilizes the intermediate carbocation.

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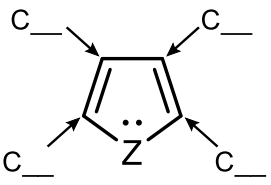
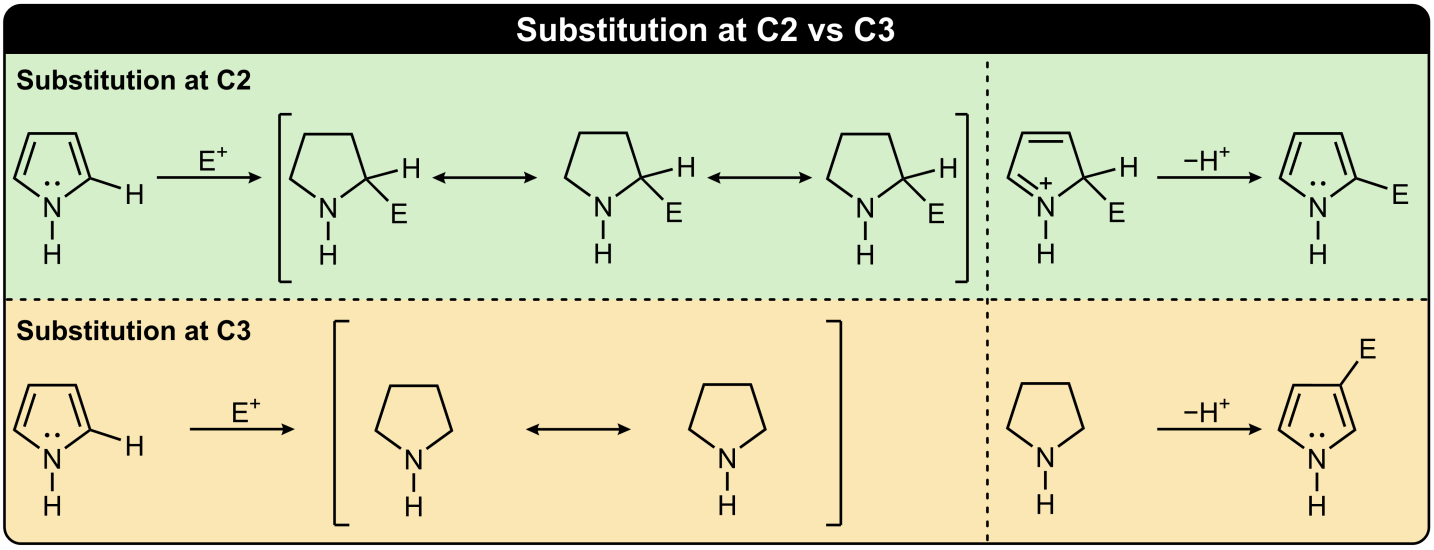
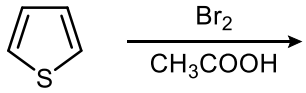


Substitution at C2 vs C3

- EAS reactions of pyrrole, furan, and thiophene give major products by substitution at ____.
  - □ Substitution at ____ produces minor products.



EXAMPLE: Thiophene is highly reactive in comparison to benzene and undergoes bromination without a Lewis acid catalyst. Draw the major and minor products of the following bromination reaction.



PRACTICE: Furan undergoes nitration under milder conditions than benzene. Draw a mechanism for the formation of the major product when furan reacts with concentrated nitric acid.