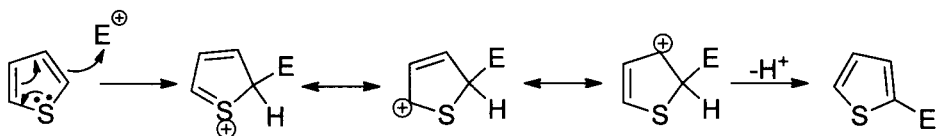


Electrophilic Substitution

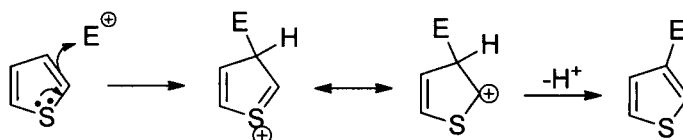
Electrophilic substitution of the thiophene ring occurs predominately at the C2 position. As seen below, this is facilitated by the lone pairs on the sulfur atom.

Preferred C2-electrophilic substitution:



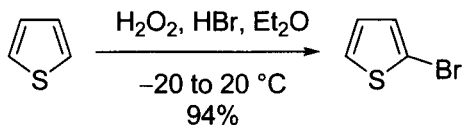
Addition at the C3 position of the thiophene is also possible, although unlikely unless the C2 position is already substituted. The electron-rich thiophene ring prefers electrophilic substitution at the C2 position because the intermediate has greater charge delocalization and, therefore, more stabilization in comparison to the less-favored C3 position.

Less-favored C3-electrophilic substitution:



Halogenation (Bromination)

Monobromination of thiophene at the C2 position can be achieved in excellent yields by the slow addition of hydrobromic acid in the presence of hydrogen peroxide under reduced temperatures.⁷⁵



Bromination at both C2 and C5 is also possible with the addition of excess bromine.⁷⁵