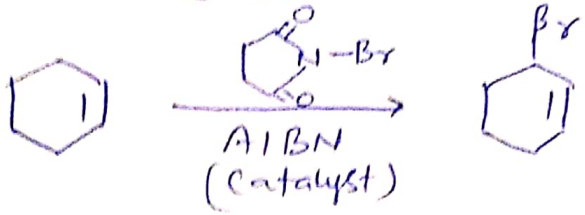
Paper-CC(VIII) (ORGANIC CHEMISTRY)

## Free radical Reaction

**Allylic halogenation (NBS)** - The substitution of allylic H-atom of olefins by halogen (Br) is called allylic halogenation. Allylic bromination is a chemoselective substitution of olefins which succeeds only according to Wohl-Ziegler process with N-bromo-succinimide (NBS)

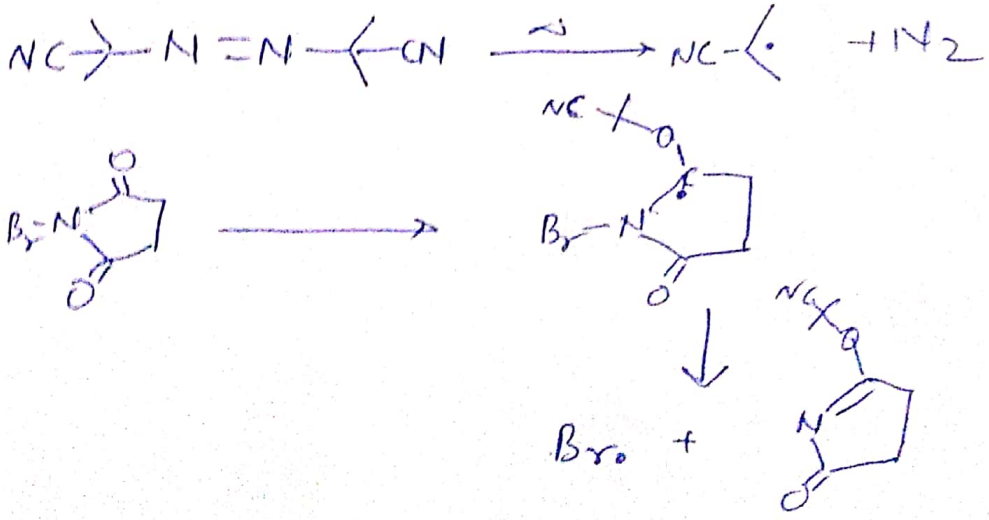
Example



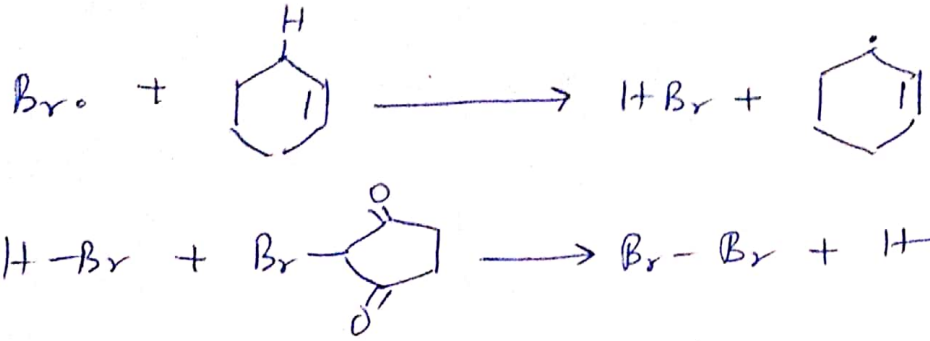

NBS - is used in this reaction in stoichiometric amount and radical initiator AIBN is used in a catalytic amount.

- The formation of Br· as initiating free radical involves several reactions in chain

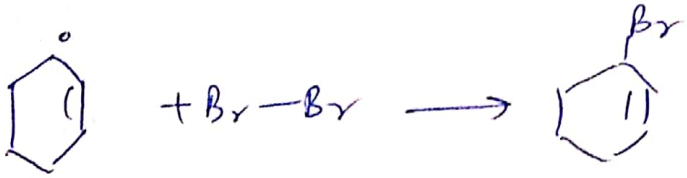
Initiation step:



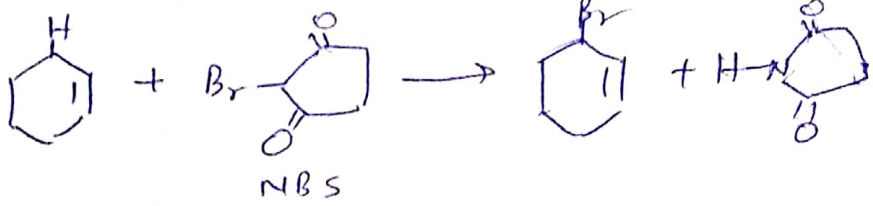
Propagation Step - involves formation of allylic bromo product.





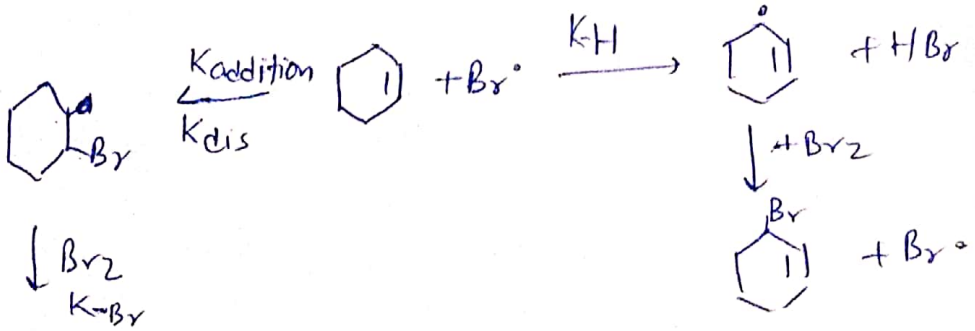


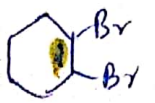
Net propagation



NBS

In propagation Step The $[Br_2]$ is low hence addition product is supposed to form.





The Kinetic Expression for chemoselectivity is

$$\frac{d\left(\text{Br-C}_6\text{H}_5\right)}{d\left(\text{Br-C}_6\text{H}_4\text{-Br}\right)} = \frac{K_{-H} \cdot K_{dis}}{K_{add} \cdot K_{-Br}} \frac{1}{[Br_2]}$$

Hence high $[Br_2]$ favours addition product while Low $[Br_2]$ favours Allylic Bromination.