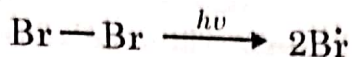


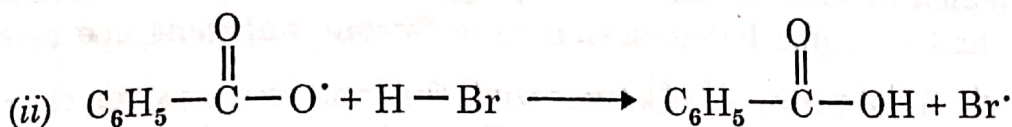
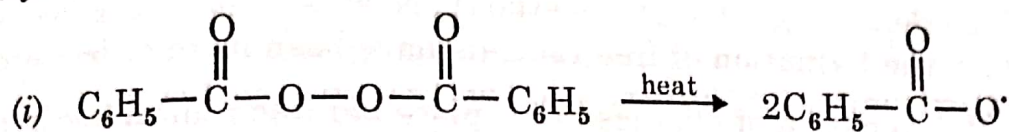
6.8 Mechanism of Free Radical Reactions

The mechanism of free radical reactions involves three steps, *initiation*, *propagation* and *termination*. Each of these steps, in turn, may involve two or more steps.

Initiation Step : This step involves the generation of free radicals *in situ* by irradiation or heating the reagent or by carrying out the reaction in the presence of an initiator such as benzoyl peroxide. The initiation step involving the formation of free radical may be one or two step process. For example, the formation of bromine radical from bromine during substitution reaction is a one-step process.

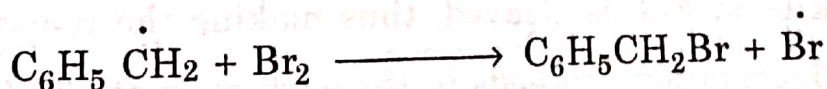
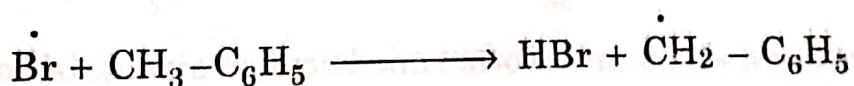


On the other hand, a two-step process is involved in the formation of bromine radical from hydrogen bromide during addition of HBr on propylene in the presence of benzoyl peroxide.

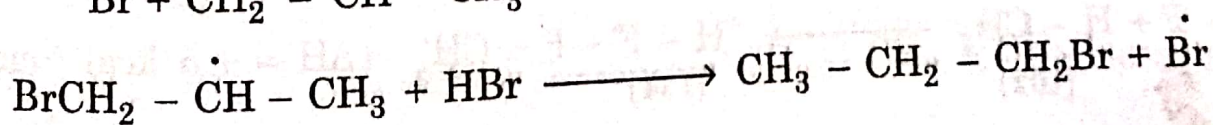
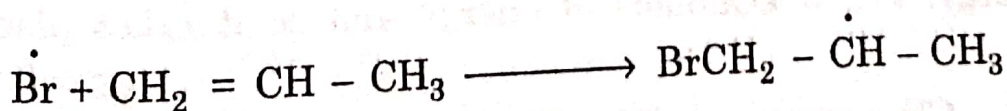


The initiation step initiates the formation of free radicals. Therefore, it is an essential step for all free radical reactions.

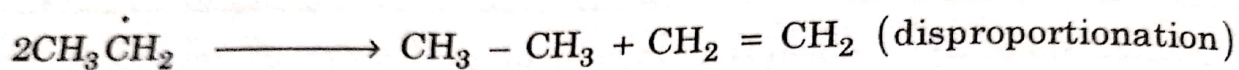
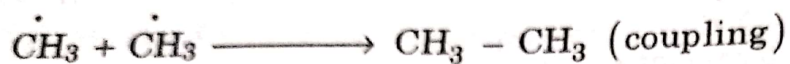
Propagation Step : In this step, the free-radical formed in the first step may generate a new free radical by abstracting a hydrogen atom (an easy target, having no screening electrons to repel the free-radical) from the substrate. The new free radical, in turn, may further undergo reactions with other molecules or free-radicals, to form new free radicals. This process may continue in an indefinite number of ways until there occurs an end of the chain of propagation somehow.



Alternatively, the free-radical obtained in the initiation step may add to an ethylenic carbon atom forming new free-radical which in turn may undergo reaction with the fresh molecule of alkene or reagent (HBr) forming still new free radical. In this way the chain of free radical gets propagated.

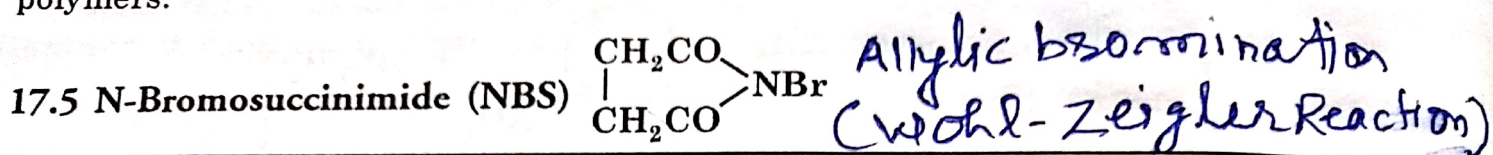


Termination Step : In this step, there occurs destruction of free-radicals either by combination of two free-radicals (same or different) or by disproportionation.

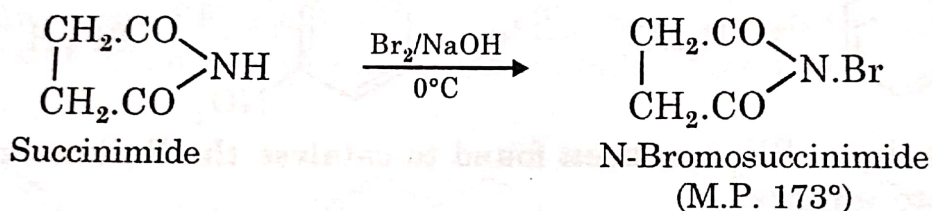


It is also possible to terminate chain reaction of free-radicals by adding free-radical inhibitors like benzoquinone, phenols, amines, thiols, nitric oxide, etc.

polymers.

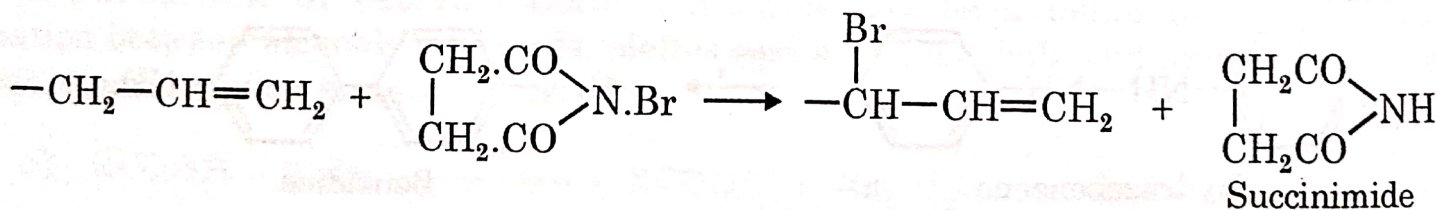


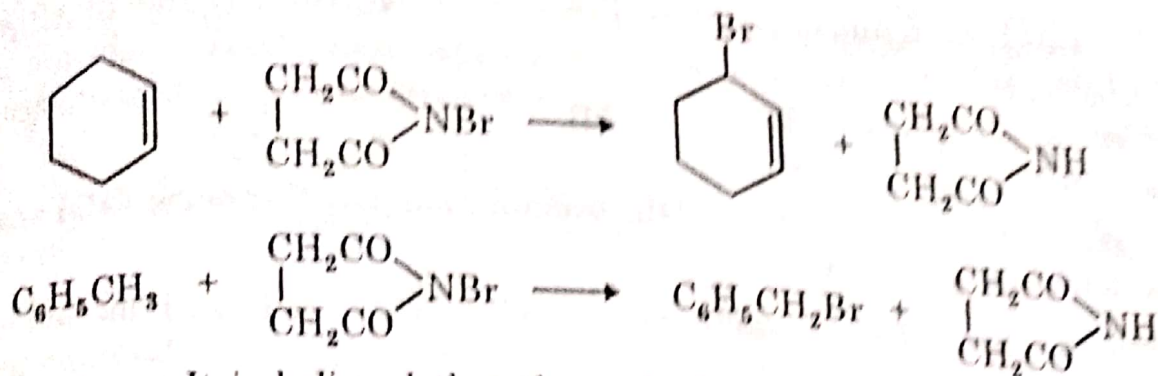
Preparation : It is a very important derivative of succinimide and can be conveniently prepared by adding bromine to an ice-cooled solution of succinimide in alkali. A precipitate of N-bromosuccinimide is immediately obtained.



Uses : Some uses of N-bromosuccinimide are as follows :

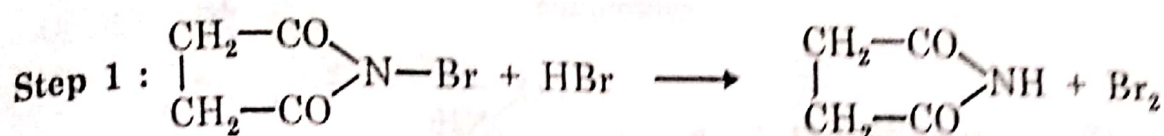
1. **As a brominating reagent :** NBS was introduced by Ziegler in 1942 as a selective brominating agent because it normally brominates the ethylenic compounds in the allylic position. It is also used for benzylic bromination. Some examples are as follows:



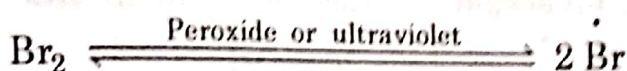


Mechanism : It is believed that the main function of NBS is to act simply as a bromine reservoir maintaining a lower concentration of molecular bromine by undergoing reaction with HBr which is initially formed in the side reactions.

Initiation :

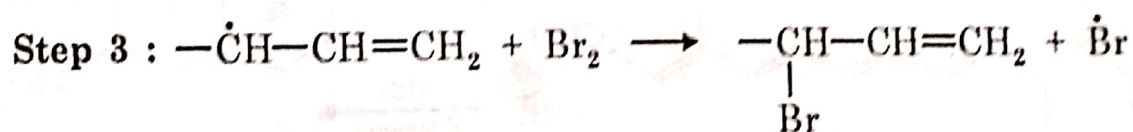
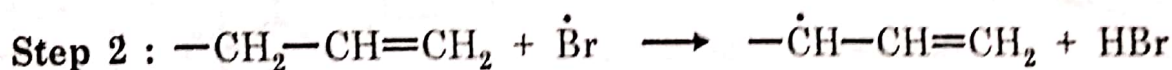


The bromine molecule then gets dissociated into bromine atoms in the presence of light or radical initiators. This explains the fact that bromination by NBS is initiated by a peroxide or ultraviolet light.



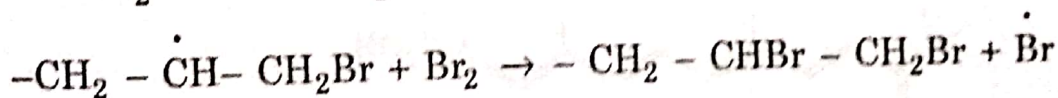
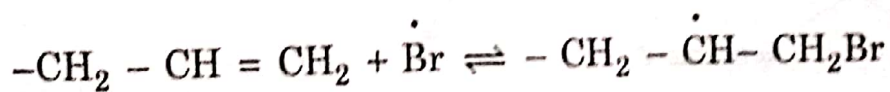
Bromine atom then abstracts hydrogen forming an allylic radical which then reacts with the molecular bromine to form the product. The preferential removal of the hydrogen atom adjacent to the double bond as shown in step 2 has been most probably occurring due to the greater stability of the resulting free radical on account of electron delocalisation.

Propagation



The free bromine radical produced in step 3 will continue the chain reaction.

An interesting factor is to be mentioned that the allylic bromination is preferred over addition to the double bond by a low concentration of bromine because the addition of bromine atoms to the double bond is a reversible process.

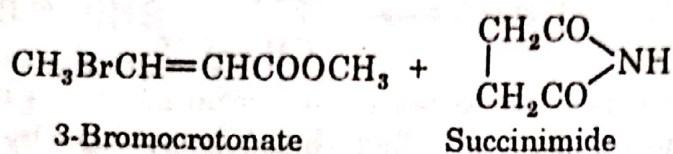
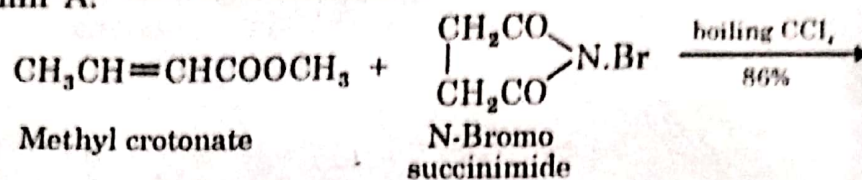


It implies that if the concentration of bromine is low, then the radical formed due to addition of bromine to the double bond will get reverted to the alkene because it is a reversible reaction. On the other hand, the allylic bromination is favoured by a low

bromine concentration because an allylic radical will wait till it is able to get a bromine molecule (the hydrogen abstraction reaction is irreversible). This conclusion is further supported by the observation that it is possible to carry out allylic bromination by slow photolysis of molecular bromine.

In synthetic organic chemistry, allylic bromination may find some valid applications which are described as follows :

- (i) **Preparation of bromoacid ester** : When NBS reacts with methyl crotonate, there occurs the formation of 3-bromocrotonate (by allylic bromination) which as a synthetic reagent finds use in Reformatsky reaction, *e.g.*, in the synthesis of vitamin A.



- (ii) **Conversion of vitamin A₁ to vitamin A₂** : NBS has been found to be of immense help in the conversion of vitamin A₁ into vitamin A₂.

