CHAPTER-8

CARBON-CARBON DOUBLE BOND AS SUBSTITUENT

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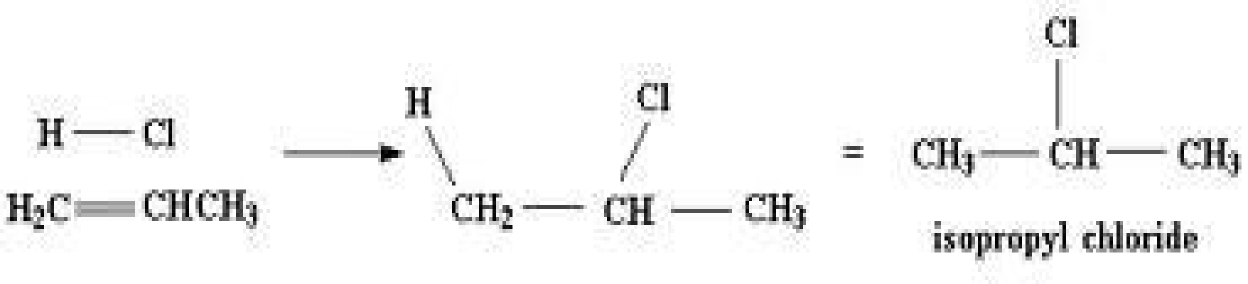
Alkene, propylene contains carbon-carbon double bond, where the same addition reactions that are characteristics of ethylene take place. With hydrogen chloride, for example, propylene

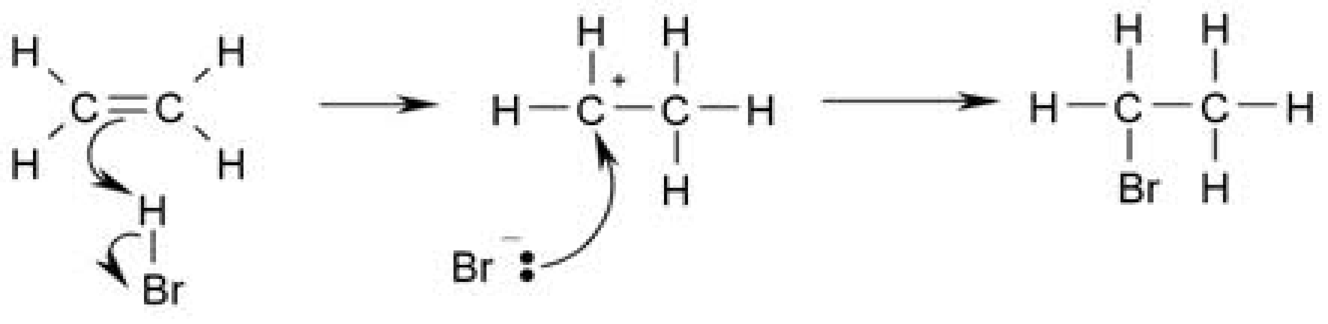
$CH_2{=}CH—CH_3$

propylene

undergoes electrophilic addition; with hydrogen bromide in the presence of peroxides, it undergoes free- radical addition.



Because of the methly group, the electrophilic addition takes place faster than with ethylene itself, and gives exclusively isopropyl chloride.



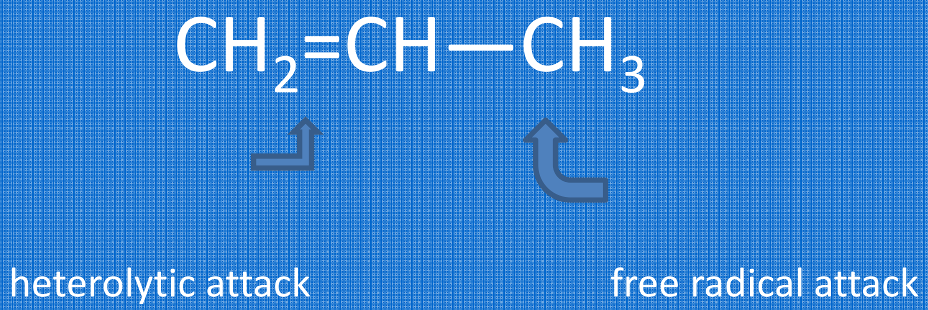
Because of methyl group the free-radical addition takes place faster than the ethylene, and gives exclusively n-propyl bromide.

$CH_2{=}CH{-}CH_3$

alkene like

alkane like

The propylene molecule has two sites where the halogen can attack, the double bond and the methyl group.



$CH_2{=}CH{-}CH_3$

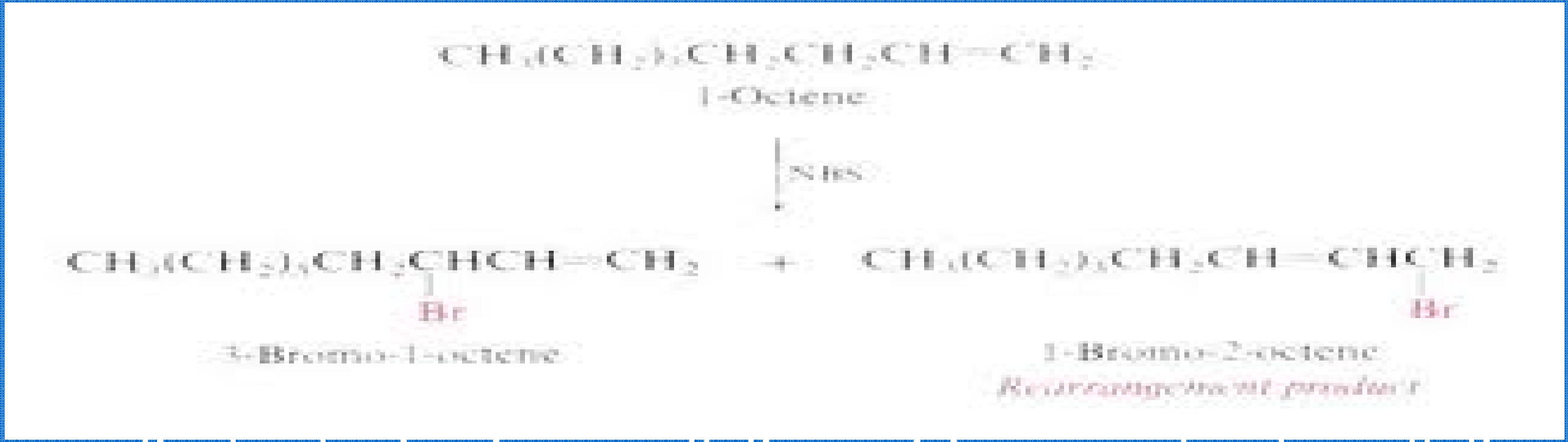
heterolytic attack

free radical attack

- Alkanes undergo substitution by halogen at high temperatures and generally in the gas phase conditions favor to form free radicals.
- Alkenes undergo addition of halogen at low temperatures and generally in liquid phase conditions favor to form heterolytic reactions.

The compound N-bromosuccinimide(NBS) is a reagent used for the specific purpose of brominating alkenes at the allylic position; NBS functions simply by providing a constant, low concentration of bromine. As each molecule of HBr is formed by the halogenation, NBS converts it into a molecule of Br

Free- radical substitution in alkenes: allylic rearrangement



Free-radical substitution at allylic positions can lead to allylic rearrangement:

When 1-octene, for example, is treated with N-bromosuccinimide, there is obtained not only the expected 3-bromo-1octene, but also– and in larger amounts—1-bromo 2-octene.

The allylic radical reacts to give two different products: one in which halogen has become attached to the carbon that lost the hydrogen ; and the other in which halogen has become attached to the carbon at the other end of three-carbonunit – the allylic system – that were presents as C=C—C

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