B.Sc. I

Paper II Organic Chemistry

ADDITION REACTIONS
Electrophilic , Nucleophilic , Free radical

DR. VINITI GUPTA
ASSOCIATE PROFESSOR

ORGANIC CHEMISTRY

SRI TIKA RAM KANYA MAHAVIDYALAYA
ALIGARH

INTRODUCTION

Addition reaction is a chemical reaction wherein two or more reactants come together and combine together to form a larger single product/single compound (ADDUCT).
Chemical compounds containing multiple bond character can undergo addition reactions as a double or triple bond is usually broken to form the required single bonds.

Types of Addition Reactions

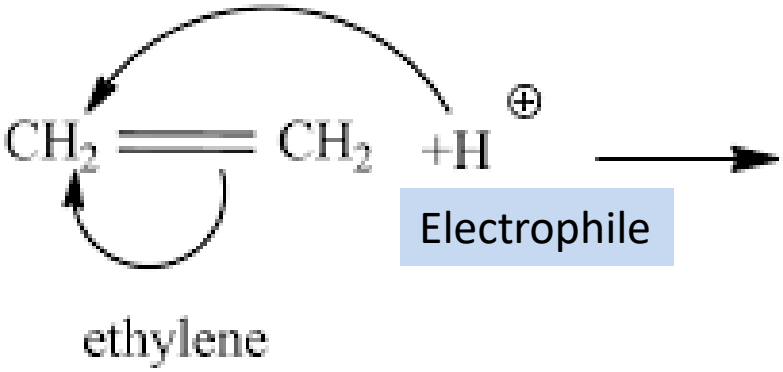
For polar addition reactions there are two classifications, namely:
1. Electrophilic Addition reactions
2. Nucleophilic Addition reactions

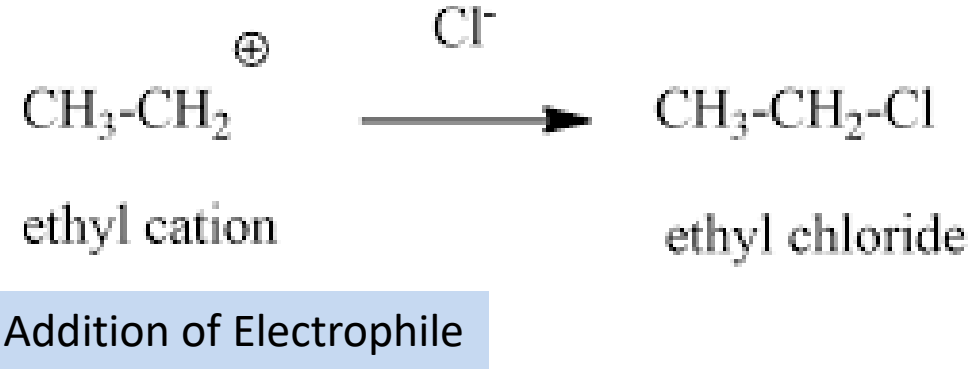
For non-polar addition reactions, we have two classifications, namely:
1. Free radical addition reactions
2. Cycloadditions reactions

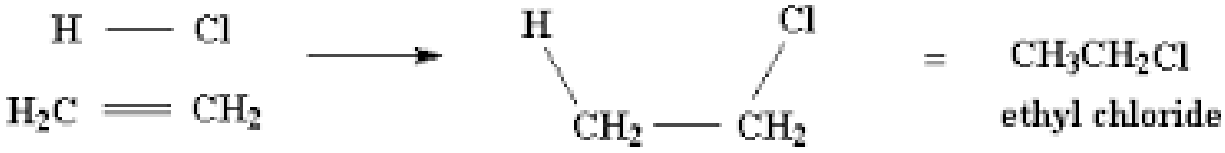
ELECTROPHILIC ADDITION
Halogenation of Alkenes

Addition bought about an electrophile. The addition reaction between hydrochloric acid (HCl) and ethylene (C_2H_4) yields chloroethane.

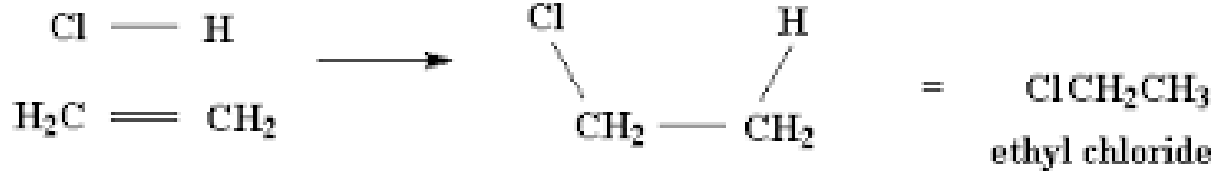
$HCl \dashrightarrow H^+ + Cl^-$





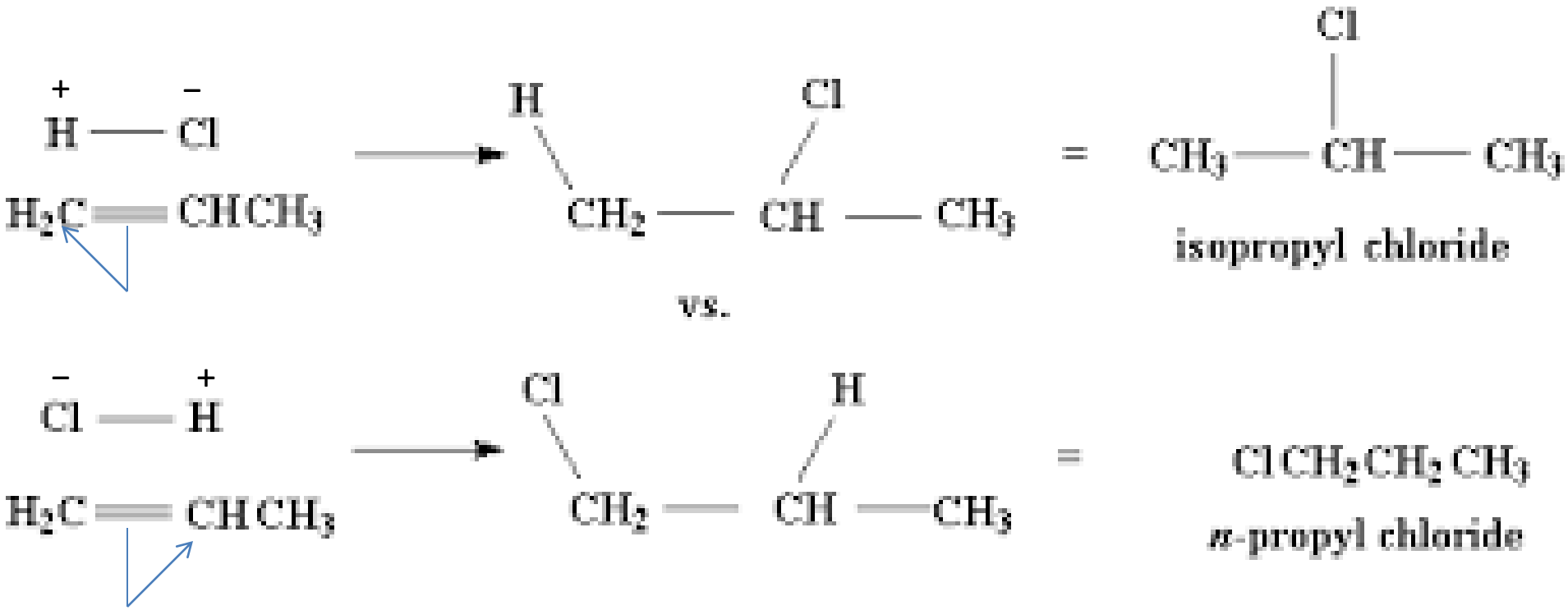


vs.

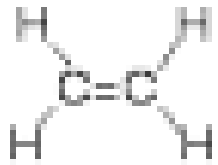


Halogenation of Alkenes

Hydro chlorination of Propane

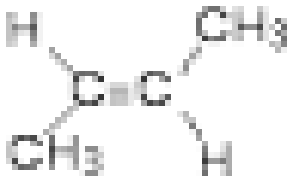


Halogenation of Alkenes



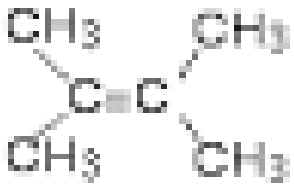
CH_3-CH_2 +

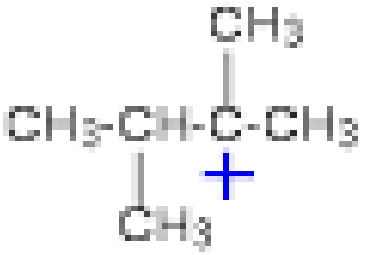
a primary carbocation



CH_3-CH_2-CH-CH_3 +

a secondary carbocation





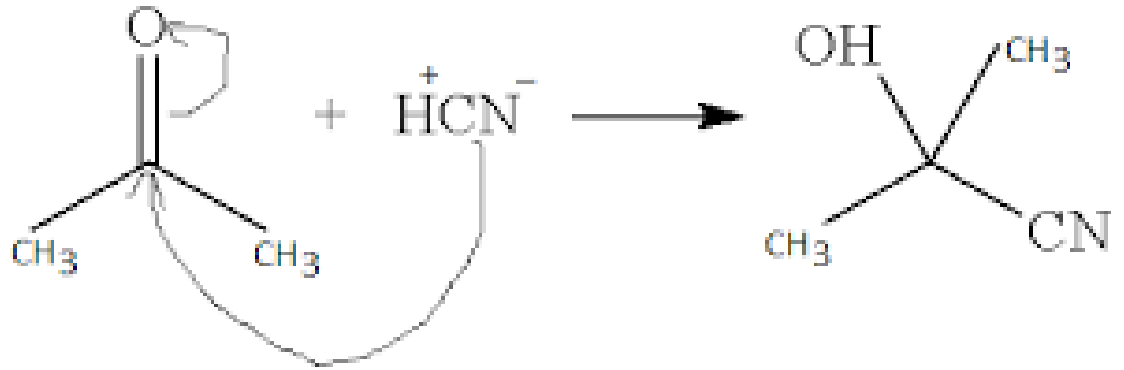
a tertiary carbocation

IONS ARE GETTING MORE ENERGETICALLY STABLE AND SO ARE EASIER TO FORM

3° >2° >1°

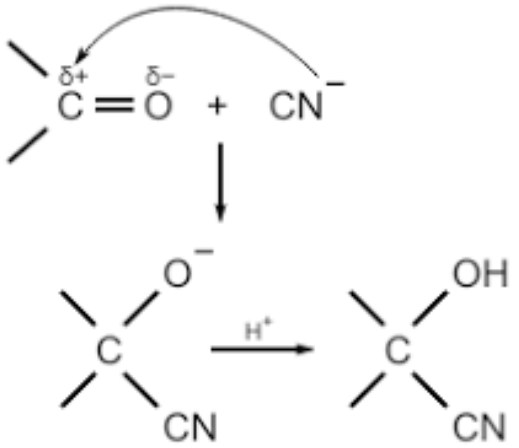
NUCLEOPHILIC ADDITION
Reactions of hydrogen cyanide with acetone or aldehyde

Addition bought about by a nucleophile. The reaction between Hydrogen cyanide and Acetone.



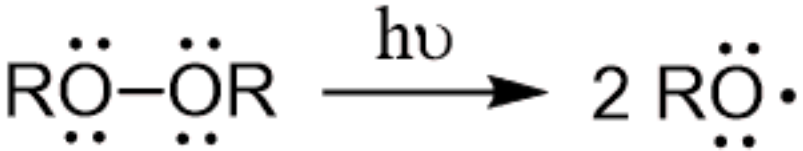
Acetone

Acetone cyanohydrin



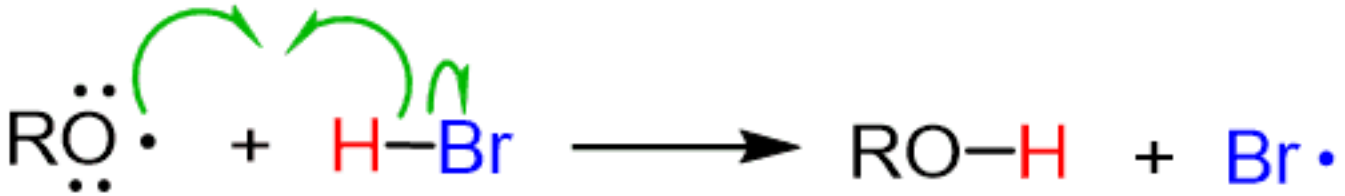
FREE RADICAL ADDITION
Hydrogen Bromide to ethylene (Anti Markownikoff/Peroxide Effect)

The reaction goes by formation of free radical mechanism when a peroxide is present. The first step is homolytic cleavage of the RO-OR bond.



The resulting radical reacts with HBr by abstracting the H and a new radical Br• is formed.

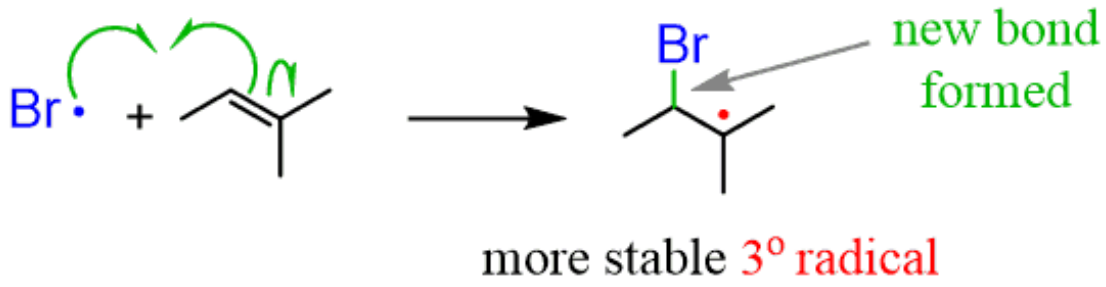
single-headed or fish-hook arrows



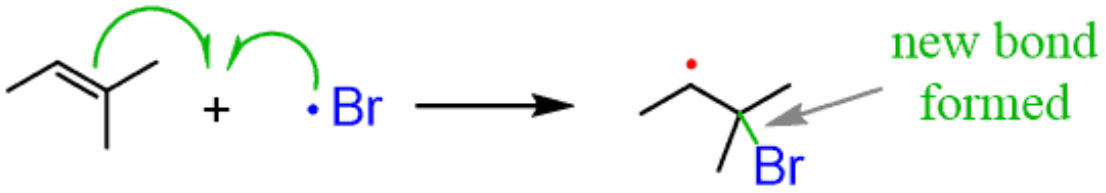
FREE RADICAL ADDITION
Hydrogen Bromide to ethylene (Anti Markownikoff/Peroxide Effect)

After this, a regioselective addition of the Br to the alkene happens.
It is regioselective because the more substituted one forms as the major intermediate.

The more stable 3° radical dictates the regioselectivity



more stable 3° radical

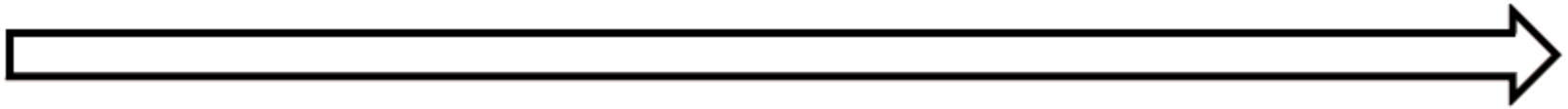


less stable 2° radical

FREE RADICAL ADDITION
Hydrogen Bromide to ethylene (Anti Markownikoff/Peroxide Effect)

Free radical stability increases with the degree of substitution.

1^{o} radical < 2^{o} radical < 3^{o} radical



Increasing Stability