

EC-204

Lecture-1

ADDITION REACTIONS

Electrophilic Addition to C=C

Some Important reactions are given below.

- **Addition of halogens**

Bromine gives dibromoalkane via bromium ion intermediate.

- **Addition of hydrogen halides**

Rule of addition of hydrogen halides is given by markovnikov (also known as markinikov's rule) which states that "The negative part is added to the highly substituted carbon atoms".



There is another rule name as antimarkonikov's rule also known as peroxide effect given by Kharasch rule in 1933. Mechanism of this rule is free radical chain reaction. Peroxide generates free radical. Thus The oxidation of HCL to $\text{CH}_3\text{CH}=\text{CH}_2$ gives $\text{CH}_3\text{CH}_2\text{CH}_2\text{CL}$.

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Lecture-2

Regioselectivity and Chemoselectivity

- Substrates which are capable of reacting at more than one centre (polydent molecules) but react at one centre with higher rate than at the other. This is known as regioselectivity. Regioselectivity can be understood by following examples.
 - a) During acylation of aminophenols it is aminogroup which is acylated at faster rate than OH group.
 - b) Reaction of ethyl acetoactate with methyl iodide in basic medium methylene carbon is selectively methylated.
- When a functional group is selectively attacked in the presence Of a different functional group, the reaction is said to be chemoselective. Chemoselectivity can be understood further by the fact that a number of reagents have been found to reduce aldehydes much faster than ketone.

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Lecture-3
Free Radicals

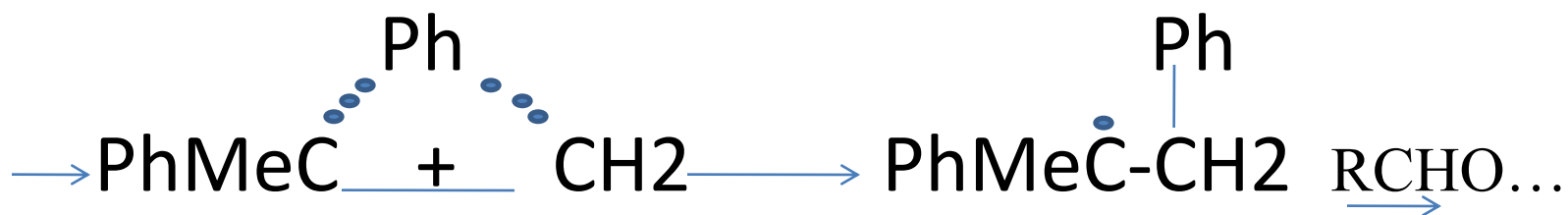
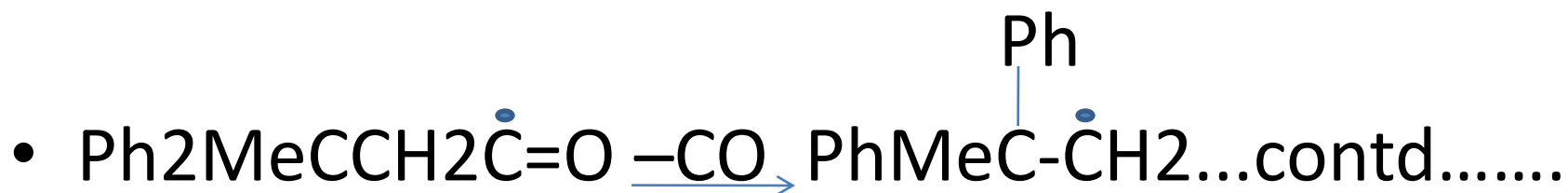
■ **Hunsdickers Reaction**

Hunsdicker found that silver salts of the carboxylic acids in carbon tetra chloride solution are decomposed by chlorine or bromine to form alkyl halides e.g,



■ **Free Radical Rearrangement Reaction**

A good example is with the aldehyde which undergoes H-abstraction from the CHO group by Me_3CO (e.g. $\text{Me}_3\text{COOCMe}_3$) to yield the acyl radical (1) which readily loses CO to form (2). This can undergo rearrangement according to the reaction shown below.



PhMeCH-CH₂Ph

Hydrocarbon