ALKANE
(Part-III)

By

Dr. JYOTI CHANDRA

Assistant Professor

Department of Chemistry

Email ID- jyotic09@gmail.com

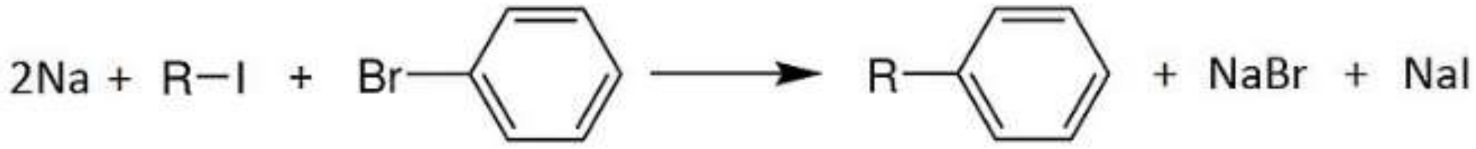
B.Sc-Ist Year (SEM-II)

Patna Women's College

Patna University

Wurtz-Fittig Reaction

- The chemical reaction of aryl halides with alkyl halides and sodium metal with dry ether present to yield substituted aromatic compounds is called the Wurtz-Fittig reaction.



- This reaction is modification of the Wurtz reaction.
- The reaction works best for forming asymmetrical products.
- This reaction is used for the alkylation of aryl halides; however, with the use of ultrasound the reaction can also be made useful for the production of biphenyl compounds.

Mechanism of Wurtz-Fittig reaction

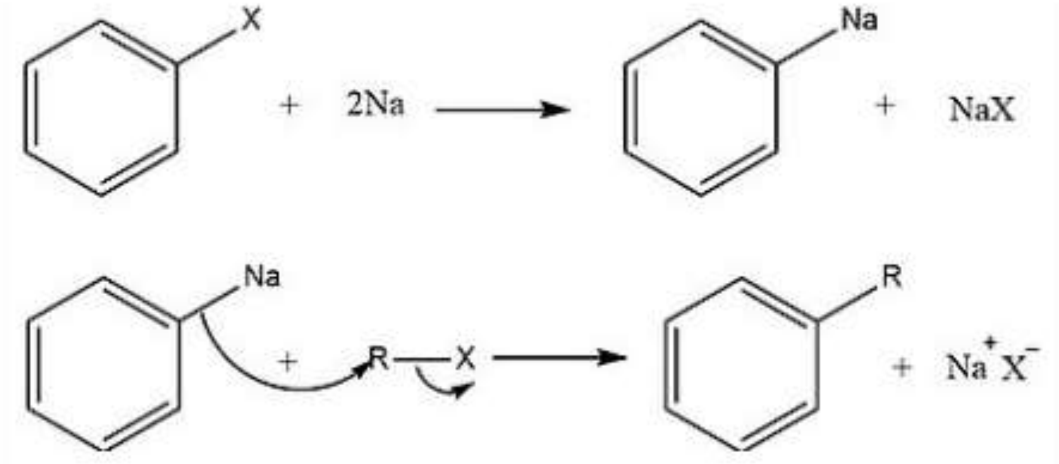
☐ There are two approaches to describe the mechanism of the Wurtz–Fittig reaction:

1) The Organo-Alkali Mechanism

2) The Radical Mechanism

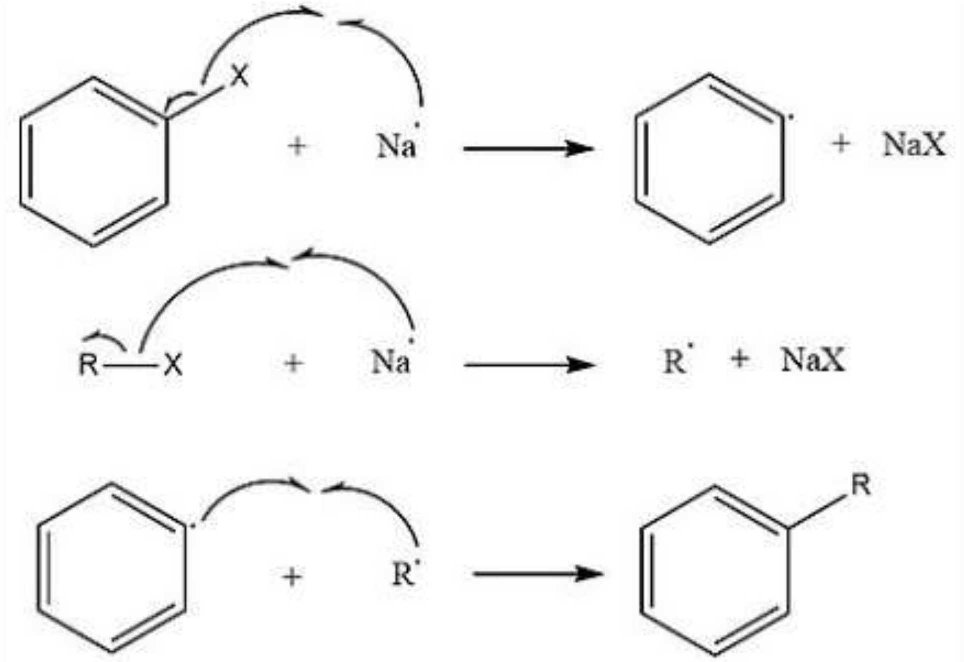
1) The Organo-Alkali Mechanism

When the aryl halide is reacted with sodium metal, an intermediate organo-alkali compound is formed, which is followed by a nucleophilic attack of the alkyl halide. Thus, the required alkyl-aryl is formed.



2) The Radical Mechanism

The sodium atom acts as a moderator for the formation of alkyl radicals and aryl radicals. These alkyl and aryl radicals now combine to form a substituted aromatic compound.



In conclusion, the reaction can also be conducted using metals other than sodium (such as potassium, iron, copper, and lithium). The reaction can also be called a coupling reaction. It requires an aprotic solvent as the reaction medium for which dry ether is quite suitable as it is a good non-polar aprotic solvent.

Free radical substitution reaction

- In free radical substitution reactions, radical substitution takes place in 3 steps with halogen reagents and alkanes substrates in the presence of ultraviolet light.
- Consider chlorination of methane in the presence of ultraviolet light

$$CH_4 + Cl_2 \xrightarrow{\text{UV light}} CH_2Cl_2$$

Mechanism

- **Step 1 – Initiation:** The first step of free radical substitution is initiation step, where the chlorine to chlorine bond undergoes homolytic fission to form 2 chlorine atoms or radicals.

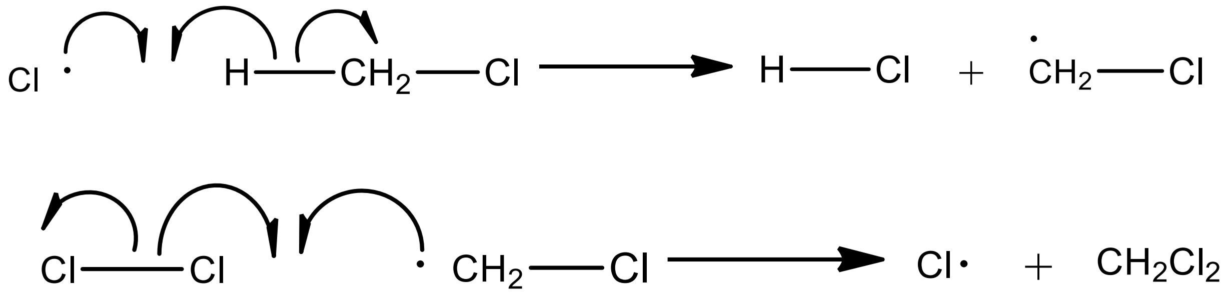
$$Cl{-}Cl \xrightarrow{\text{UV}} 2Cl\cdot$$

- **Step 2 – Propagation:** Second step is propagation step, where the radical attacks a stable molecule and generates a stable molecule and another radical.

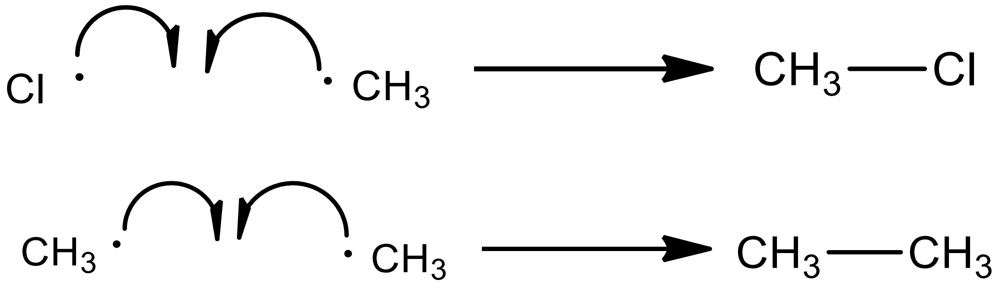
- First propagation step is where the chlorine radical attacks methane, breaks the C-H bond homolytically and forms HCl to generate a methyl radical.

- Second propagation step is where the methyl radical attacks Cl_2 molecule, breaks the Cl-Cl bond homolytically and forms CH_3Cl or chloromethane and generate a chlorine radical.

- Since we are doing a disubstitution, we need 2 more propagation steps for the second substitution to form dichloromethane, CH_2Cl_2



- **Step 3 – Termination:** Last step will be termination step where any two radicals will undergo homolytic fusion and form a stable product.

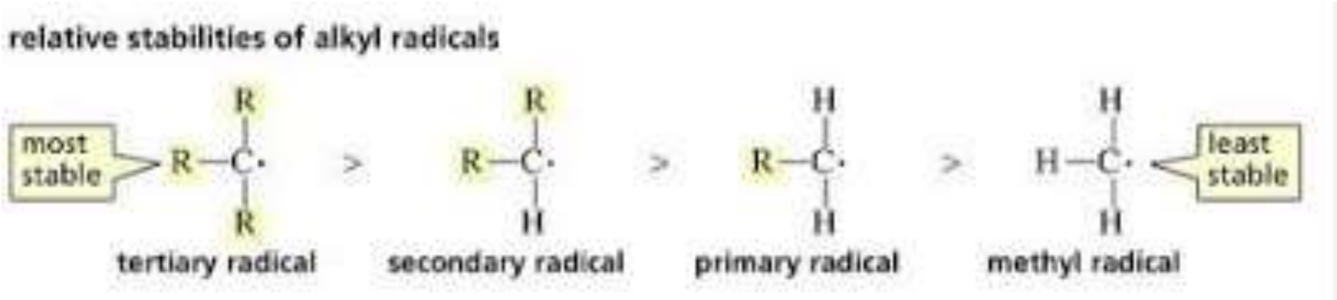


The over-all process is known as **free radical substitution,** or as a **free radical chain reaction.**

The Relative Reactivity-Selectivity Principle in Halogenation of Alkanes

1) Reactivity of R-H system

- The differences in reactivity of alkanes are attributed to the differences in C-H bond dissociation energies (energy required to break a bond homolytically).
- The differences in bond dissociation energies can be attributed to the differences in the stability of alkyl radicals. This leads to the relative stabilities of alkyl radicals:



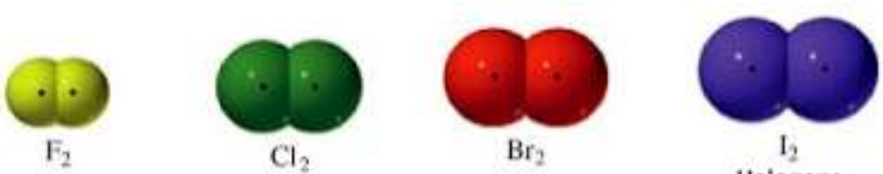
relative stabilities of alkyl radicals

- The weaker bonds more easier to be broken than stronger bonds. Thus, the relative order of reactivity for alkanes: **methyl < primary < secondary < tertiary**

- The more stable the reactant, the less reactive it will be. This means that the more stable the reactant, the slower it will react.

2) Reactivity of halogen radical

- The order of reactivity of halogens: **$F_2 > Cl_2 > Br_2 > I_2$**



Halogens

- The fluorine radical is the most reactive of the halogen radicals, and it reacts violently with alkanes. In contrast, the iodine radical is the least reactive of the halogen radicals. in fact, it is so unreactive that it is unable to abstract a hydrogen atom from an alkane.

- The bromination is a much a *slower* reaction than chlorination. It has been found experimentally that the activation energy for abstraction of a hydrogen atom by a bromine radical to be about *4.5 times greater* than that for abstraction of a hydrogen atom by a chlorine radical.

- Bromine radical is less reactive and more selective. In contrast, chlorine radical is more reactive and less selective in its reaction.

Reactive ∞ 1/ selective

- The relative rates of radical formation when a bromine radical abstracts a hydrogen atom are different from the relative rates of radical formation when a chlorine radical abstracts a hydrogen atom.
- The relative rates of radical formation by a bromine radical shows that a bromine radical is 1600 times faster to abstract a hydrogen atom from a tertiary carbon than abstract a hydrogen atom from a primary carbon. Consequently, a bromine radical is 82 times faster to abstract a hydrogen atom from a secondary carbon than abstract a hydrogen atom from a primary carbon.

  For example, the bromination of butane gives 98% of 2-bromobutane, compared with the 71% of 2-chlorobutane for chlorination of butane. Thus, **bromination is more highly regioselective than chlorination**.