B.Sc. Part-III (Hons), Paper-VI (Inorganic Chemistry)

Group-C, Unit-1 Organometallic Chemistry: Metal alkyls of Gp 1, 2 & 13.

[By Dr. Birendra Kumar, Maharaja College, Ara]

## Organo Lithium Compounds: Alkyl Lithium

Those compounds in which Lithium metal atom is directly linked with C-atom of alkyl group, i.e; Li-C bond exists are called alkyl lithium/organo lithium compds. For example: $CH_3-Li$ (Methyl lithium), $CH_3-CH_2-Li$ (Ethyl Lithium), $CH_3-CH_2-CH_2-Li$ (n-propyl Lithium)

* **General methods of preparation:** 1. **From alkyl halide:** When alkyl halide is treated with Lithium metal in ether medium, alkyl Lithium is formed.

e.g., $CH_3I + 2Li \xrightarrow[(-10°C)]{Ether} H_3C-Li + LiI$
(Methyl iodide) (Methyl Lithium)

$n\text{-}C_4H_9-Br + 2Li \longrightarrow n\text{-}C_4H_9Li$
(n-butyl bromide) (n-butyl Lithium)

2. **By metallation reaction:** When alkane is treated with n-butyl lithium, alkyl lithium is formed. $R-H + n\text{-}C_4H_9Li \longrightarrow R-Li + C_4H_{10}$ (R = Alkyl gr.)
(Alkane) (Alkyl Lithium) (n-butane)

3. **By metal displacement reaction:** When diallyl mercury is treated with lithium, alkyl lithium is formed. e.g. $(C_2H_5)_2Hg + 2Li \longrightarrow 2C_2H_5-Li + Hg$
(Di ethyl mercury) (Ethyl Lithium)

* **Properties:** Alkyl Lithium compds. are highly reactive due to more polar C-Li bond. They are particularly sensitive towards air and moisture. They react with active H-containing compounds e.g. $H_2O$, aldehydes, ketones, $CO_2$, $CH_3OCH_3$ etc.

1. **Reaction with $H_2O$:** Alkyl lithium compds. reacts with water to form alkanes.

e.g. $H_3C^{\delta-}-Li^{\delta+} + H^{\delta+}-OH^{\delta-} \longrightarrow CH_4 + LiOH$
(Methyl Lithium) (Methane)

2. **Reaction with aldehydes:** (a) formaldehyde reacts with alkyl lithium to give an addition compound, which hydrolysed into primary alcohol.

e.g. $H-C(=O)-H + CH_3-Li \longrightarrow [H-C(H)(CH_3)-O^-Li^+] \xrightarrow{H_2O/H^+} H_3C-CH_2-OH + LiOH$
(formaldehyde) (Methyl Lithium) (Ethyl alcohol)

(b) Other aldehydes react with alkyl lithium compds. to give addition compds; which on hydrolysis yield secondary alcohol

e.g. $H_5C_2-C(=O)-H + H_3C-Li \longrightarrow [H_5C_2-C(H)(CH_3)-O^-Li^+] \xrightarrow{H_2O/H^+} H_5C_2-C(H)(CH_3)-OH + LiOH$
(Propanaldehyde) Addition product (Unstable) (Butan-2-ol)

3. **Reaction with ethylene oxide:** They react with ethylene oxide to give an addition product which on hydrolysis yields primary alcohol.

e.g. $H_3C-Li + H_2C(-O-)CH_2 \longrightarrow [H_3C-CH_2-CH_2-O^-Li^+] \xrightarrow{H_2O/H^+} H_3C-CH_2-CH_2-OH + LiOH$
(Ethylene oxide) (1-Propanol)

4. **Reaction with ketones:** They react with ketones to form addition compds, which on hydrolysis give tertiary alcohol.

e.g. $H_3C-Li + H_3C-C(=O)-CH_3 \longrightarrow [H_3C-C(CH_3)(CH_3)-O^-Li^+] \xrightarrow{H_2O/H^+} H_3C-C(CH_3)(CH_3)-OH + Li(OH)$
(Methyl Lithium) (Acetone) or, Propanone (2-Methyl propan-2-ol)

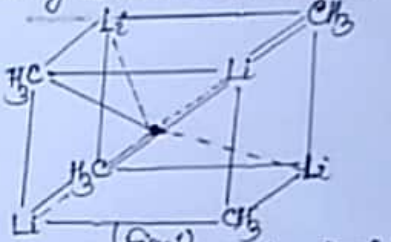
5. Reaction with $CO_2$: They react with $CO_2$ to give addition compounds, which on hydrolysis give carboxylic acid.

e.g. $H_3C^{\delta-}-Li^{\delta+} + O=C=O \longrightarrow [O=C(CH_3)-O^-Li^+] \xrightarrow{H_2O} H_3C-C(=O)-OH + LiOH$

(Methyllithium) (Addition compd.) (Ethanoic acid)

*Uses/Applications: Alkyl lithium compds. are used (i) as stereospecific catalysts (ii) in synthesis of a number of organic compounds.

*Structure & Bonding: Alkyl lithium compounds are polymeric having considerable covalent character in their Li-C bonds. $Li-CH_3$ (Methyllithium) is an electron deficient molecule. It exists as tetrameric molecule, $(LiCH_3)_4$. The bonding in this tetrameric molecule cannot be explained either by ionic or covalent bonding. The structure can be considered as derived from a cube in which two tetrahedra, one of $(CH_3)_4$ and the other of $Li_4$, are linked together. These tetrahedra have a common centre. Each Li-atom is linked with 3 $CH_3$ groups and each $CH_3$ group is associated with 3 Li-atoms (fig. 1)



(Fig. 1)

⟹ Organoberyllium Compounds / Dialkylberyllium

Beryllium (Be) forms a variety of organometallic compounds, of which dialkyl beryllium ($BeR_2$) compounds are more common.

*Preparation: 1. The dialkyl beryllium compds can be conveniently prepared by treating alkyl lithium with beryllium chloride in ether medium.

e.g. $2H_3C-Li + BeCl_2 \xrightarrow{Ether} Be(CH_3)_2 + 2LiCl$

(Methyllithium) (Dimethylberyllium)

2. They can also be prepared by treating Grignard reagent with beryllium chloride.

e.g. $2C_2H_5-Mg-Cl + BeCl_2 \xrightarrow{Ether} Be(C_2H_5)_2 + MgCl_2$

(Ethylmagnesium chloride) (Diethylberyllium)

3. By metal-metal displacement reaction: when dialkyl mercury is treated with beryllium metal, dialkyl beryllium is obtained.

$R_2Hg + Be \xrightarrow{\Delta} BeR_2 + Hg$

(Dialkyl beryllium)

*Properties: 1. They are colourless solids or viscous liquids. Dimethyl beryllium is a white sublime solid. In vapour state, it consists of monomer, dimer & trimer.

2. Dimethyl beryllium is spontaneously inflammable in air.

3. It reacts with water vigorously to form alkane. $R_2Be + 2H-OH \longrightarrow 2R-H + Be(OH)_2$

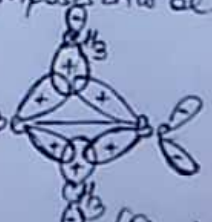
4. It is an electron deficient compound and forms addition compds. with ethers, amines etc. $R_2Be + RNH_2 \longrightarrow [R_2Be \leftarrow :NH_2-R]$

(Amine) (Adduct)

5. It is stable upto more than 200°C but at higher temperatures, it decomposes into Be.

$R_2Be \xrightarrow[(high\ temp.)]{\Delta} R-R + Be.$

*Structure & bonding: Dimethyl beryllium is polymeric $[Be(CH_3)_2]_n$ & contains Be-$CH_3$-Be bridges in its structure. The extent of polymerisation of other dialkyl beryllium decrease with the increase of size of alkyl group. Each Be & C atoms of the bridge are $sp^3$ hybridised. The bridge bond has two electrons & three nuclei (3 Be & 1 C atoms). Thus, this bond is called three centre-two electron bond & represented as (3c-2e) bond (shown in figure-2).



(Fig. 2)