Dr. P. Manikandan
Guest Lecturer.
Dept. of Chemistry
GAC, Ariyalur.

Organolithium Compounds:

→ The Organolithium compounds are characterized by a C–Li bond.

→ The Organolithium Compounds shows similar reactivity as Grignard reagent.

→ These are have more reactive than the Grignard reagents.

→ Lithium is less electronegative than Carbon, and the C–Li bond is polarized ($C^{\delta-}$–$Li^{\delta+}$)

$$(\overset{\delta-}{C} — \overset{\delta+}{Li})$$

→ This C–Li act as both nucleophile and a base.

Preparation:

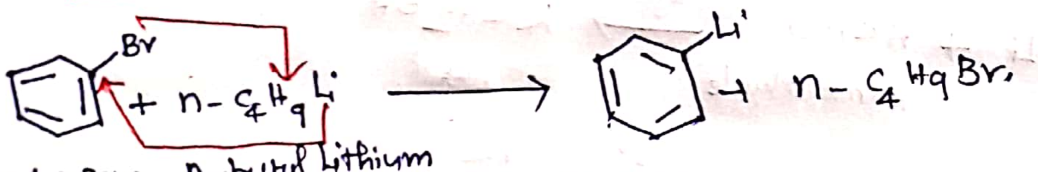
(i) From alkyl (or) aryl halides:

$$R{-}X + 2Li \longrightarrow R{-}Li + LiX$$

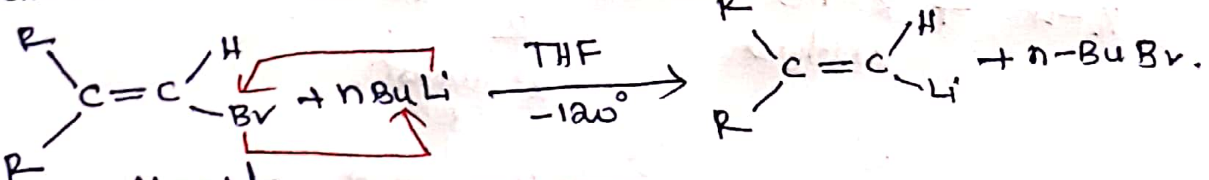
Where R = alkyl or aryl.

(ii) By halogen-metal exchange methods:

$$R{-}X + R'{-}Li \longrightarrow R{-}Li + R'{-}X$$

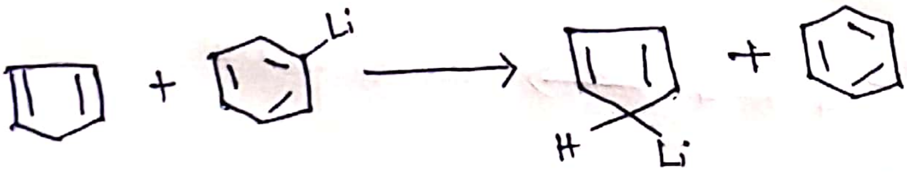


Bromobenzene n-butyl Lithium



vinyl bromide

(iii) By metalation



Chemical Properties of C-Li (Reaction)

(1) Reaction with Compound Containing active hydrogen

(i) with water (H_2O)

$$\overset{\ominus}{R}-\overset{\oplus}{Li} + \overset{\oplus}{H}-\overset{\ominus}{OH} \longrightarrow R-H + LiOH$$

(ii) R-OH

$$\overset{-}{R}-\overset{+}{Li} + \overset{+}{R'}-\overset{-}{OH} \longrightarrow R-R' + LiOH$$

alcohol.

(iii) With amine

$$\overset{\ominus}{R}-\overset{\oplus}{Li} + CH_3\overset{\oplus}{N}\overset{\ominus}{H_2} \longrightarrow R-CH_3 + LiNH_2$$

(IV) With Carboxylic acid $\longrightarrow R-R' + LiCOOH$.

$$R-Li + R'COOH$$

Carboxylic acid

(2) Reaction with Carbonyl compounds: (aldehyde and Ketone)

$$R-Li + HCHO \xrightarrow{H_3O^+} RCH_2OH$$

Formaldehyde — 1° alcohol.

$$R-Li + R'CHO \xrightarrow{H_3O^+} \begin{matrix} R \\ R' \end{matrix}\!\!>CHOH$$

aldehyde — 2° alcohol.

$$R-Li + \begin{matrix} R' \\ R' \end{matrix}\!\!>C=O \xrightarrow{H_3O^+} R-\underset{R}{\overset{R'}{\underset{|}{\overset{|}{C}}}}-OH$$

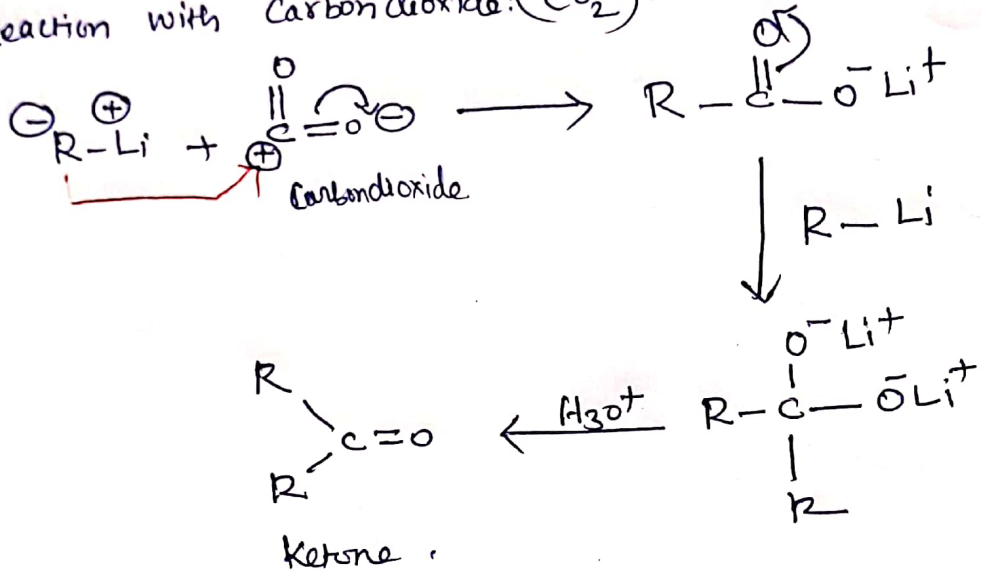
tert-alcohol.

$$\underbrace{CH_2-CH_2}_{\diagdown O \diagup} + R-Li \xrightarrow{H_3O^+} R-CH_2-CH_2OH$$

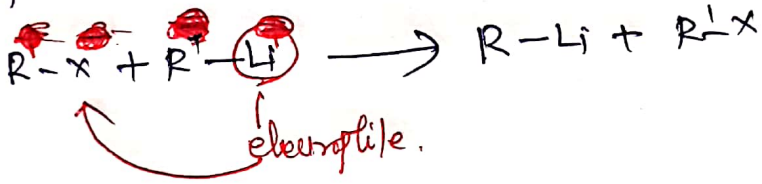
epoxide

Scanned by CamScanner

(B) Reaction with Carbon dioxide (CO_2).



(4) Electrophilic displacement.



(5) Nucleophilic displacement.