CONCEPT BOOSTER

Dear Students! Thanks a lot for your response to the last article. This article is in continuation with the last article, some problems are given at the end of this article which will help you to better understand the topic. Do read carefully and smartly. Stay healthy, all the best.

*Arunava Sarkar

A BRIEF OVERVIEW OF ORGANOMETALLIC REAGENTS AND ORGANOMETALLIC CHEMISTRY

ORGANOCOPPER COMPOUNDS

- Organocopper compounds are very important reagents in many synthesis reactions. The most widely used organocopper reagents are given by a general formula R_2CuLi and are called lithium organocuprates or lithium dialkylcuprates. The general preparation strategy is :

$$R - X \xrightarrow{2\text{Li}} R - \text{Li} + \text{Li}X$$

$$2R - \text{Li} + \text{CuI} \longrightarrow \underset{\substack{\text{Lithium}\\ \text{dialkyl}\\ \text{cuprate}}}{R_2\text{CuLi}} + \text{LiI}$$

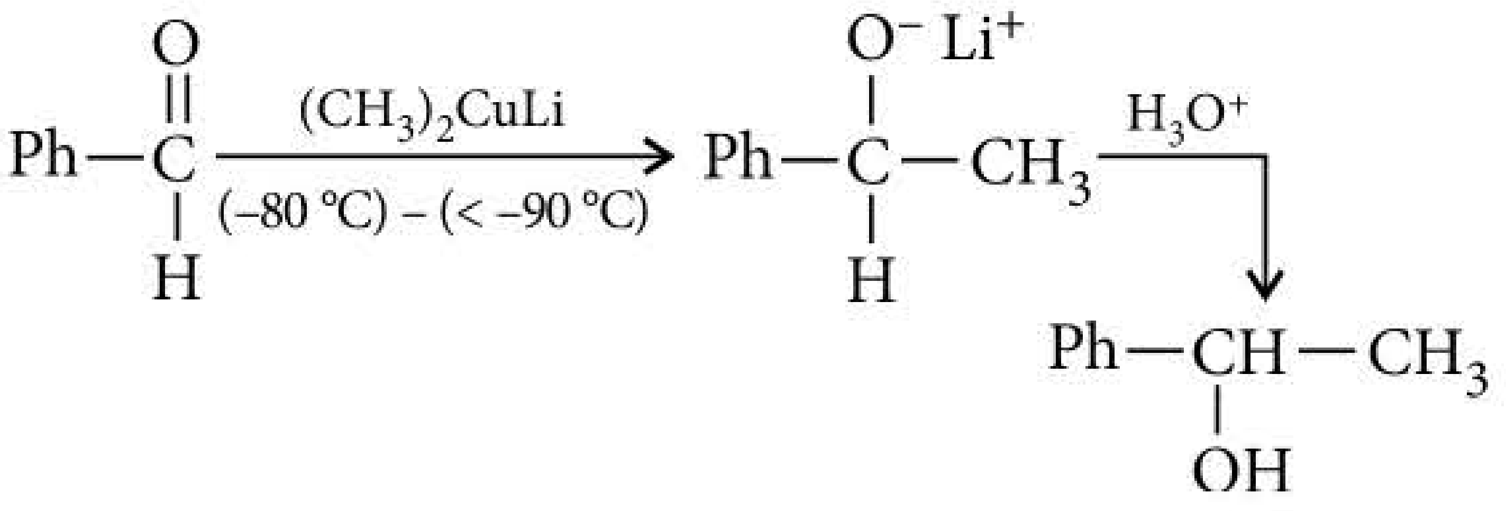
Organocopper reagents are usually referred to as Gilman reagents. Organocopper reagents are comparatively less stable and therefore, they are prepared in situ. These reagents are chemoselective in nature. Organocopper reagents are particularly useful in transmetallating Grignard reagents.

$$\text{CH}_3\text{MgBr} \xrightarrow[\text{Transmetallation}]{\text{CuCl}} \text{CH}_3\text{Cu} + \text{MgBrCl}$$

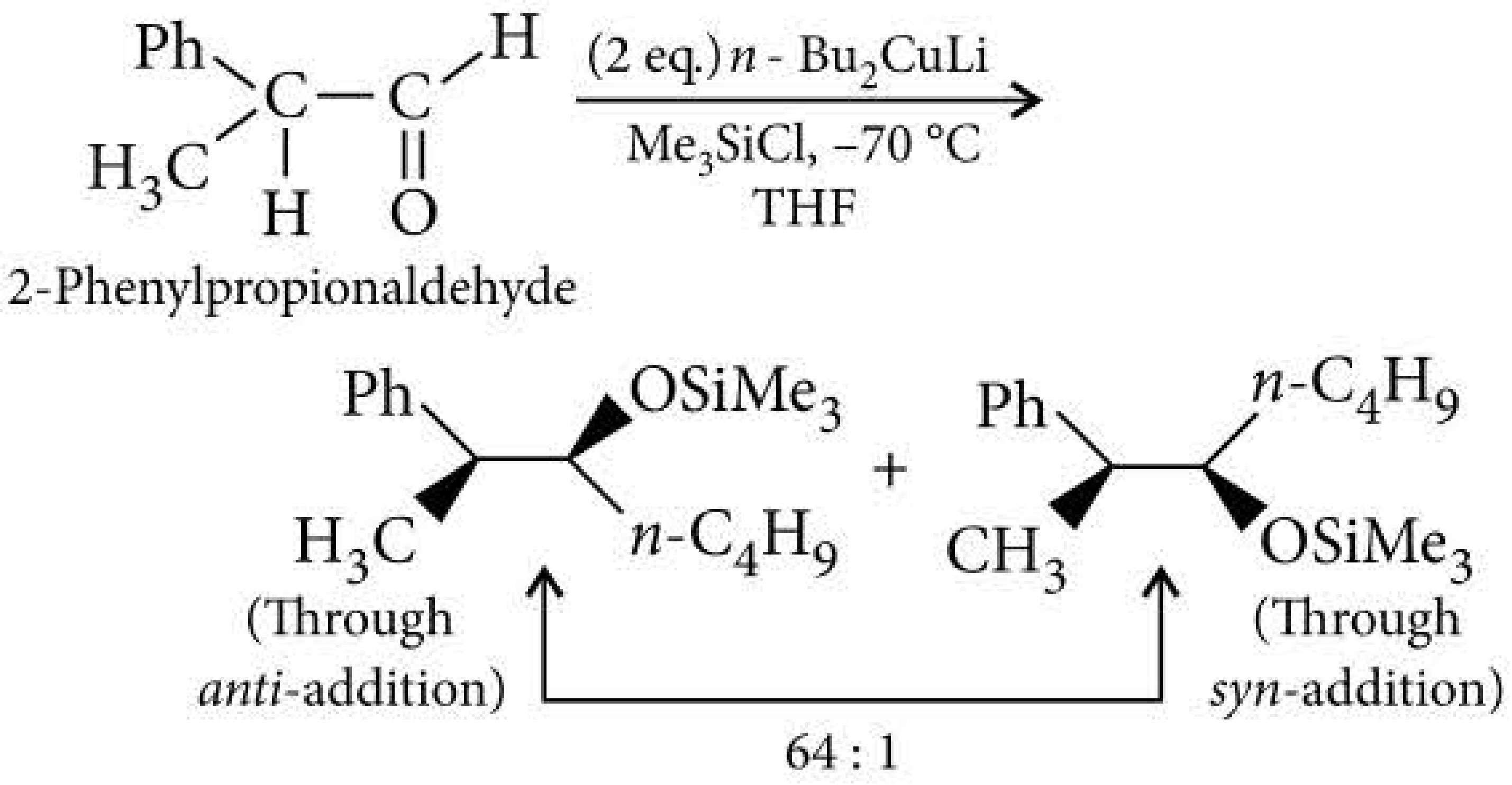
Now, Let us take an overlook on the major reactions exhibited by organocopper compounds :

- **Reactions with aldehydes and ketones**

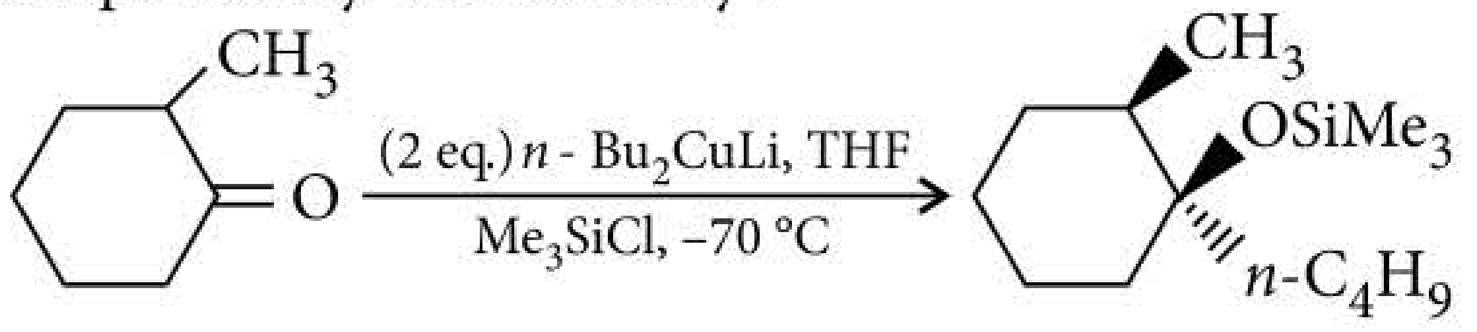
At the beginning be informed that organocuprate reacts conveniently with aldehydes but quite sluggishly with ketones. On an average, it is found that organocuprates react at around – 70 °C with aldehydes to give products via *anti*-and *syn*-addition where the *anti*-addition product is found to be the major one. Take a few examples :



Sometimes, chlorotrimethyl silane is used along with lithium dialkylcuprates.



The following reaction with ketone is found to occur comparatively conveniently :



- **Reactions with α, β-unsaturated carbonyl compounds**

Exclusively 1,4-addition product (conjugate addition) is obtained. Let us take the example of the reaction between lithium dialkyl cuprate with cyclohexen-2-one.

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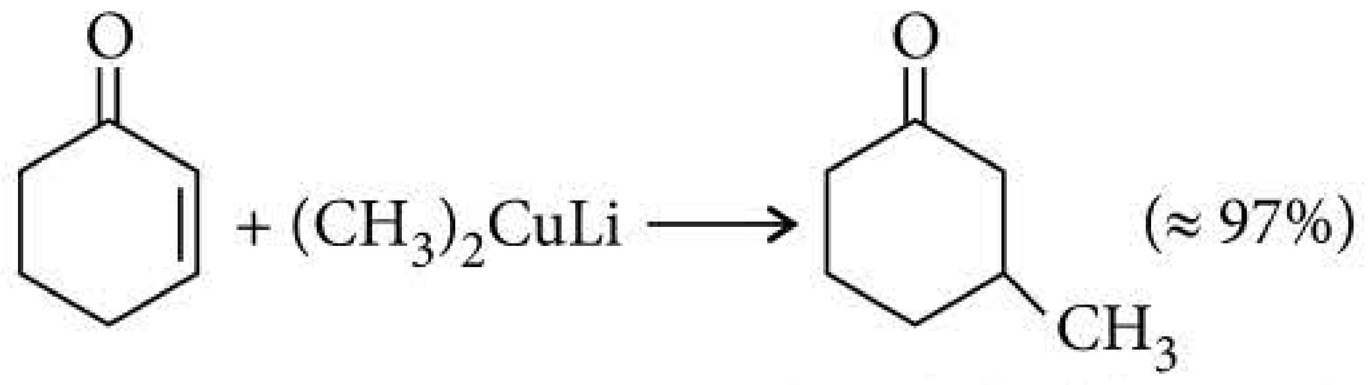
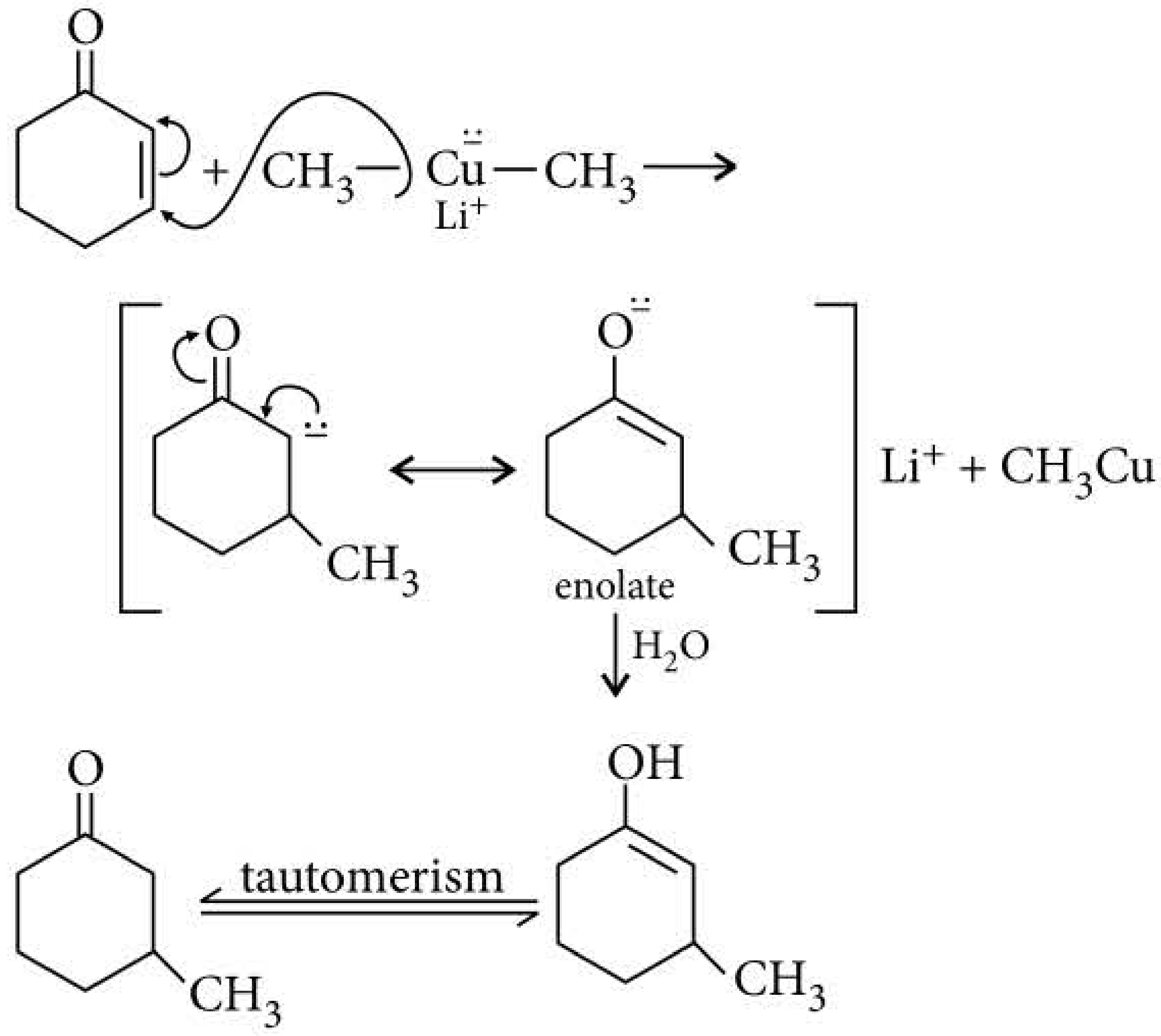
*Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna



(3-Methylcyclohexanone)

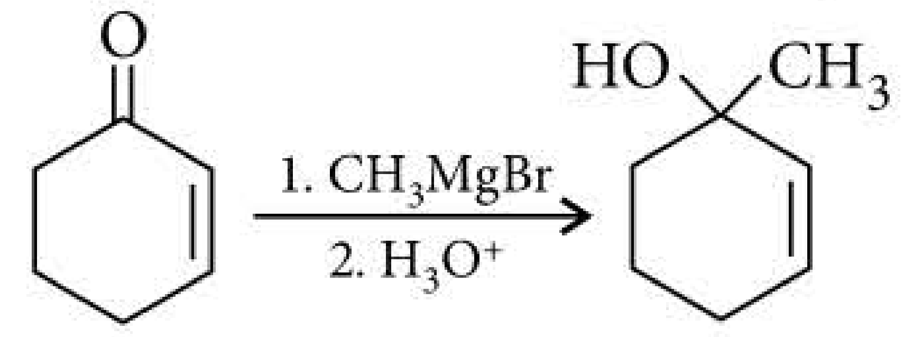
Mechanism :



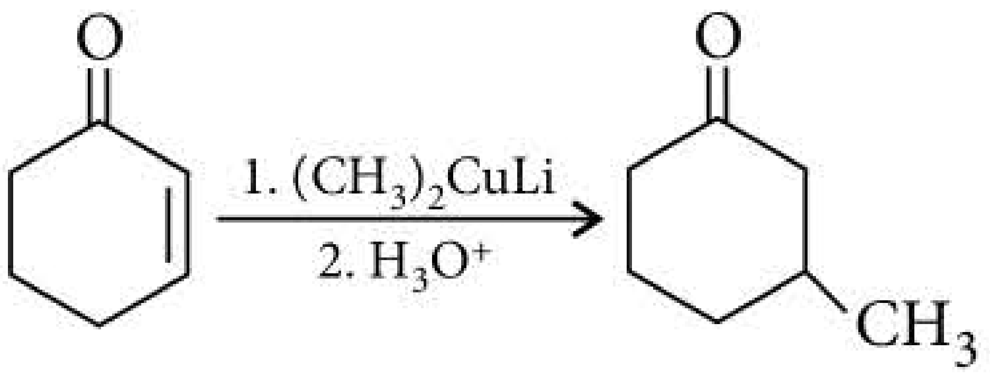
Now, a question comes that, why organocopper reagents undergo addition in conjugate fashion?

Actually, copper is less electropositive than magnesium and it attacks softer $\rangle C=C \langle$ bond which is considered to be an 'inferior' bond or unstable bond in comparison to $\rangle C=O$ bond, whereas Grignard reagent attack a 'better' bond or stable bond *i.e.*, $\rangle C=O$.

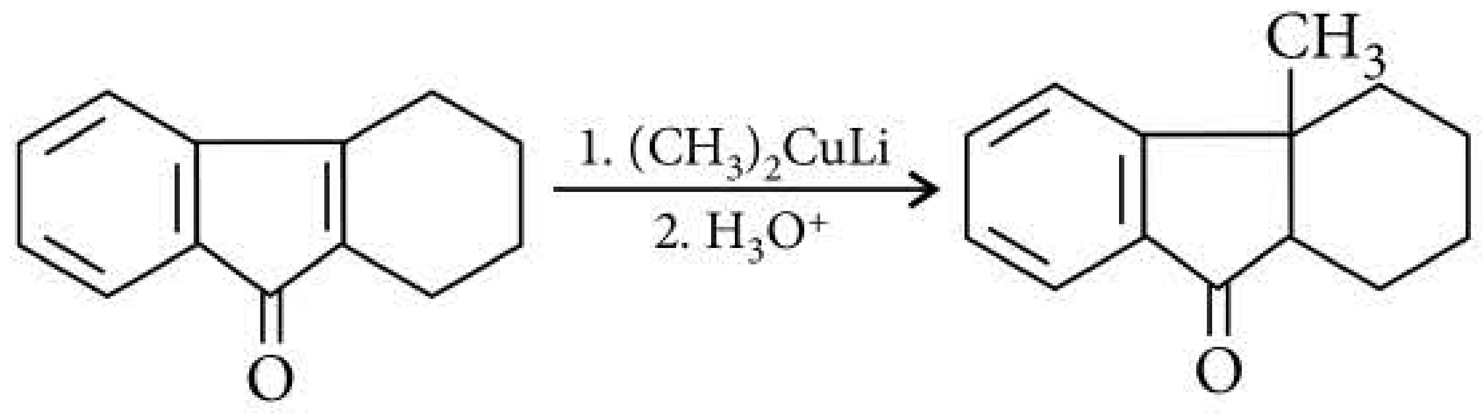
So,



But,

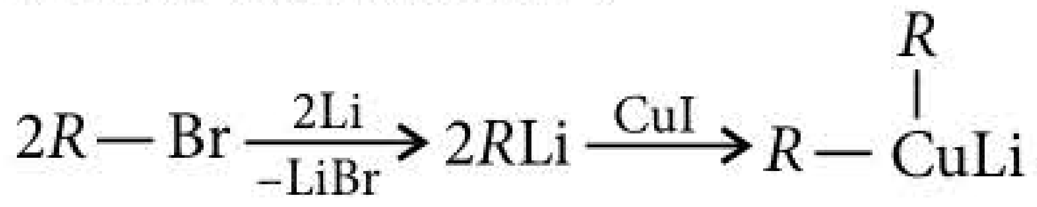


Take another example where you will understand the synthetic application of using organocopper compounds.

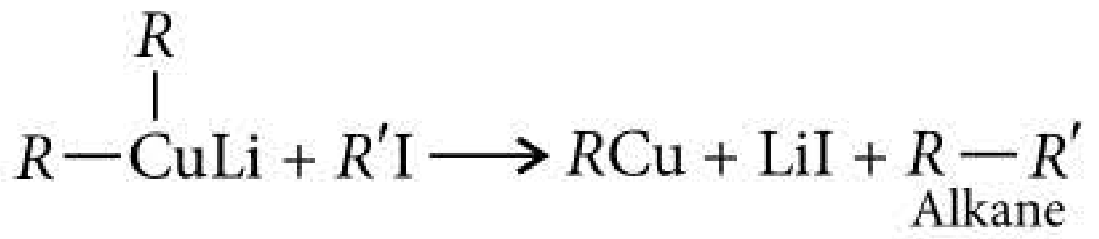


❍ Reaction with alkyl and aryl halide

These reactions are well known as the coupling reactions. Preparation of alkane through this reagent is better known as Corey-House synthesis and is usually carried out as below :

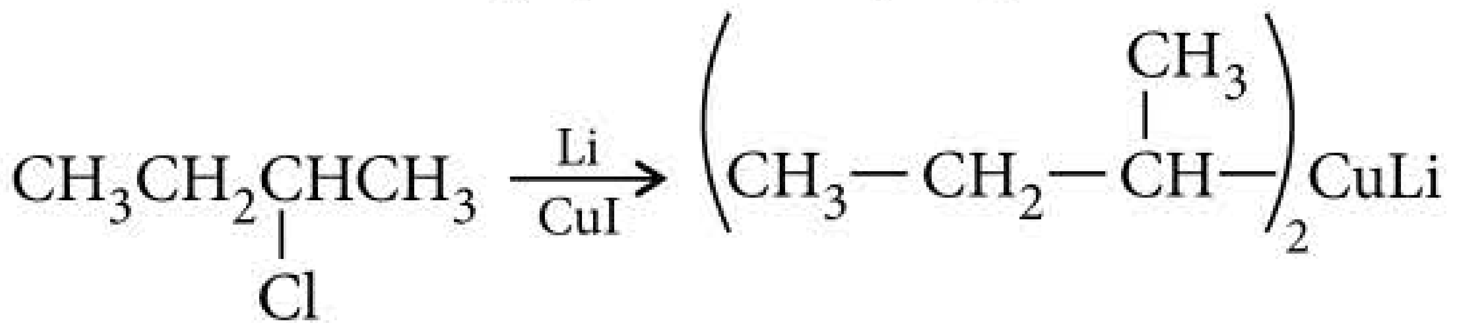


$$2R-Br \xrightarrow[-LiBr]{2Li} 2RLi \xrightarrow{CuI} R-\overset{\displaystyle R}{\overset{|}{\text{CuLi}}}$$

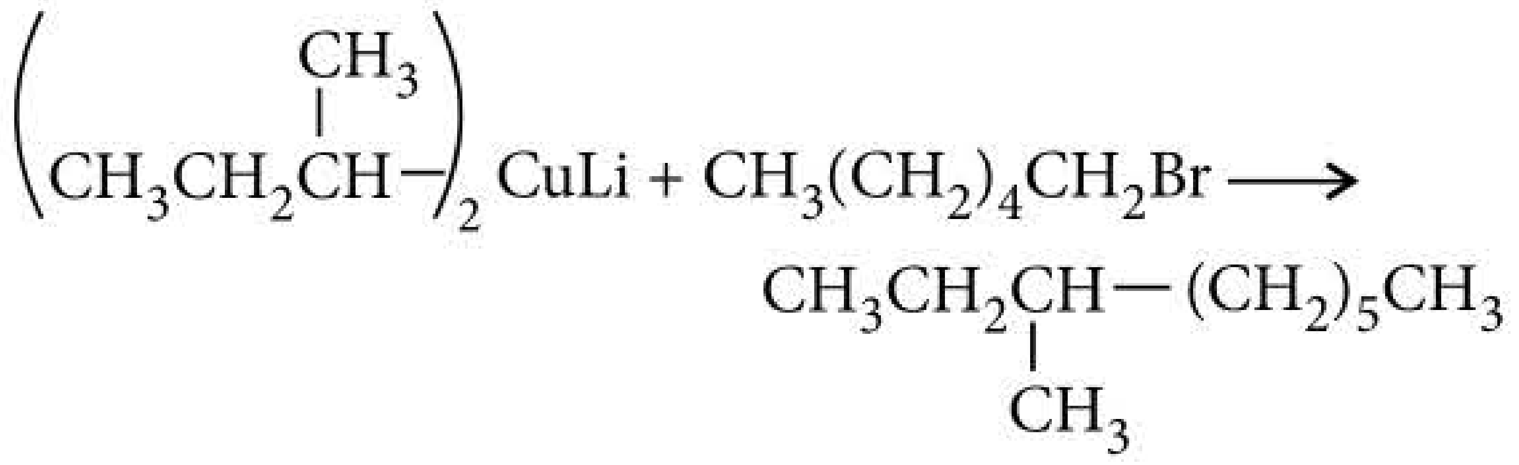


$$R-\overset{\displaystyle R}{\overset{|}{\text{CuLi}}} + R'I \longrightarrow RCu + LiI + \underset{\text{Alkane}}{R-R'}$$

Take the following synthetically important reaction :

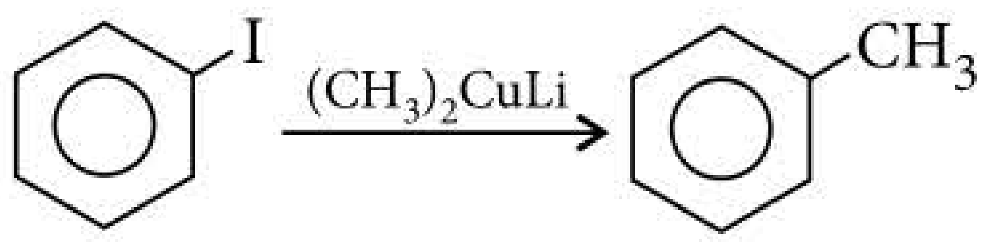


$$CH_3CH_2\underset{\underset{\displaystyle Cl}{|}}{C}HCH_3 \xrightarrow[CuI]{Li} \left(CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\right)_2CuLi$$

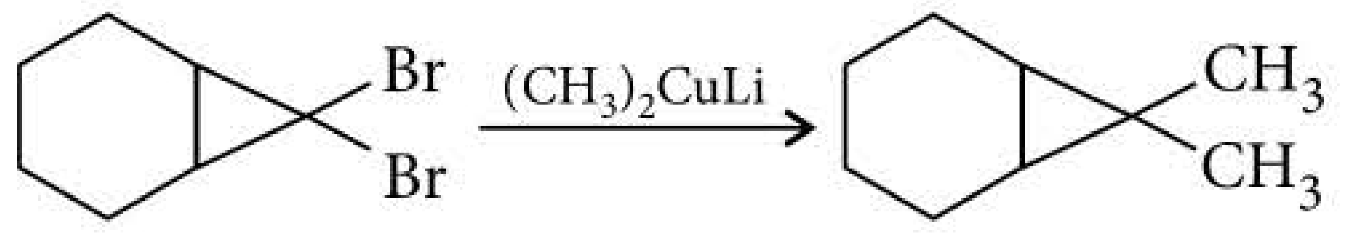


$$\left(CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{CH}-\right)_2CuLi + CH_3(CH_2)_4CH_2Br \longrightarrow CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{CH}-(CH_2)_5CH_3$$

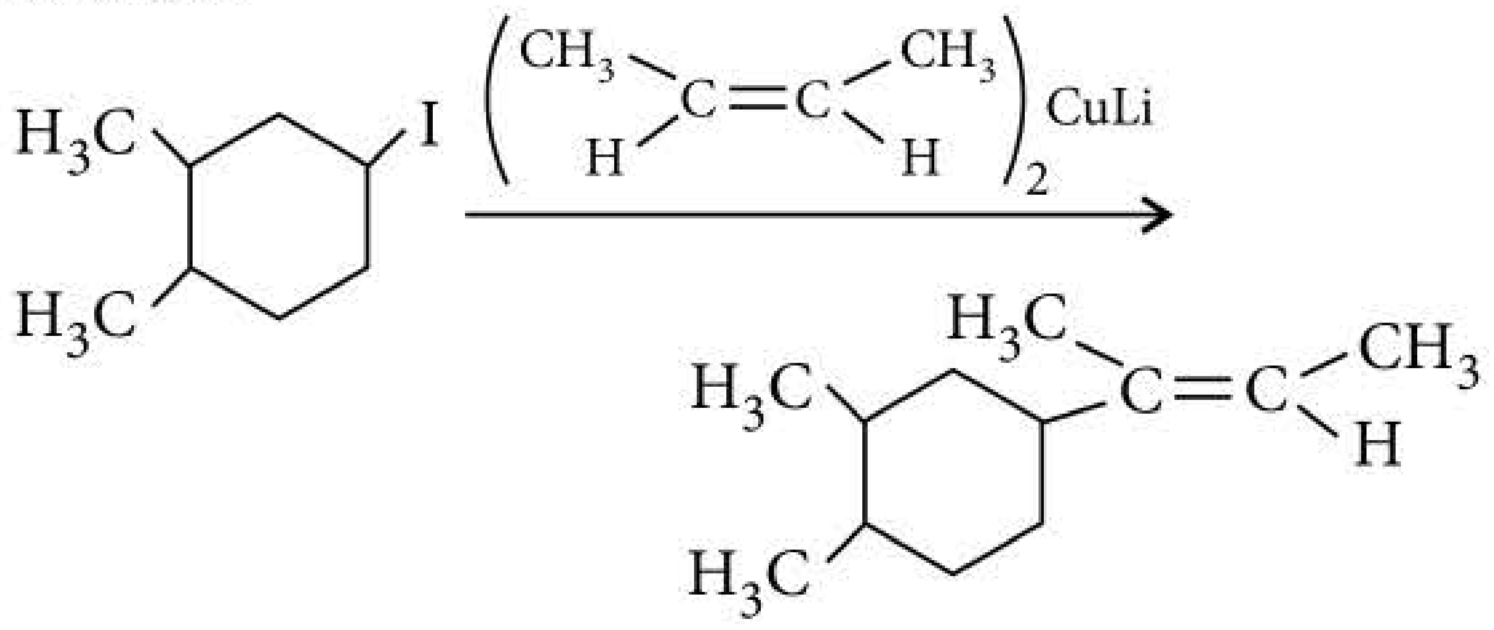
with aryl halides, replacement of halogen takes place *via* the alkyl group of lithium dialkyl cuprate.



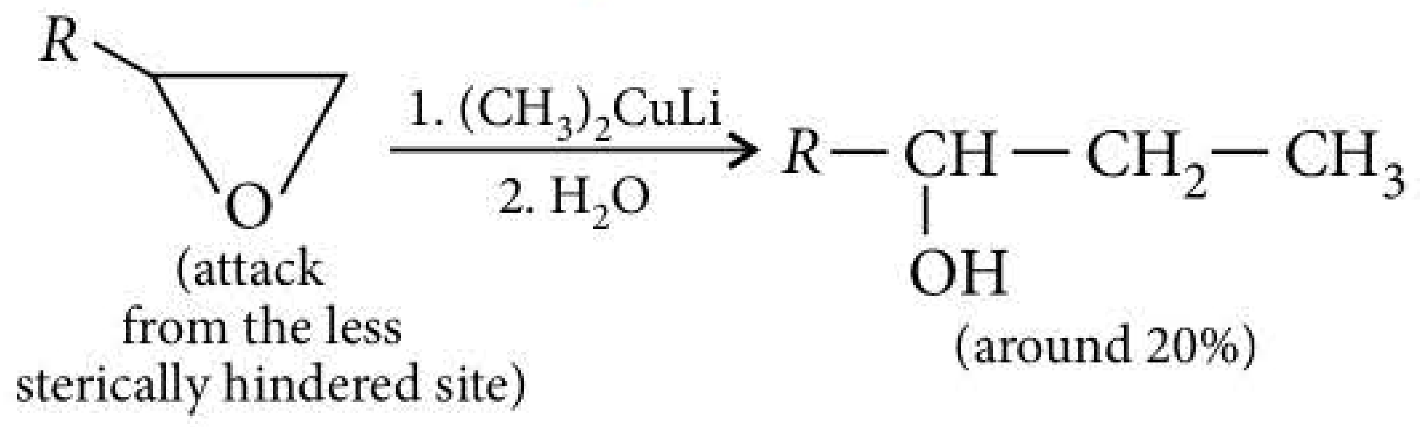
Double halogen substitution is also visible with alicyclic ring :



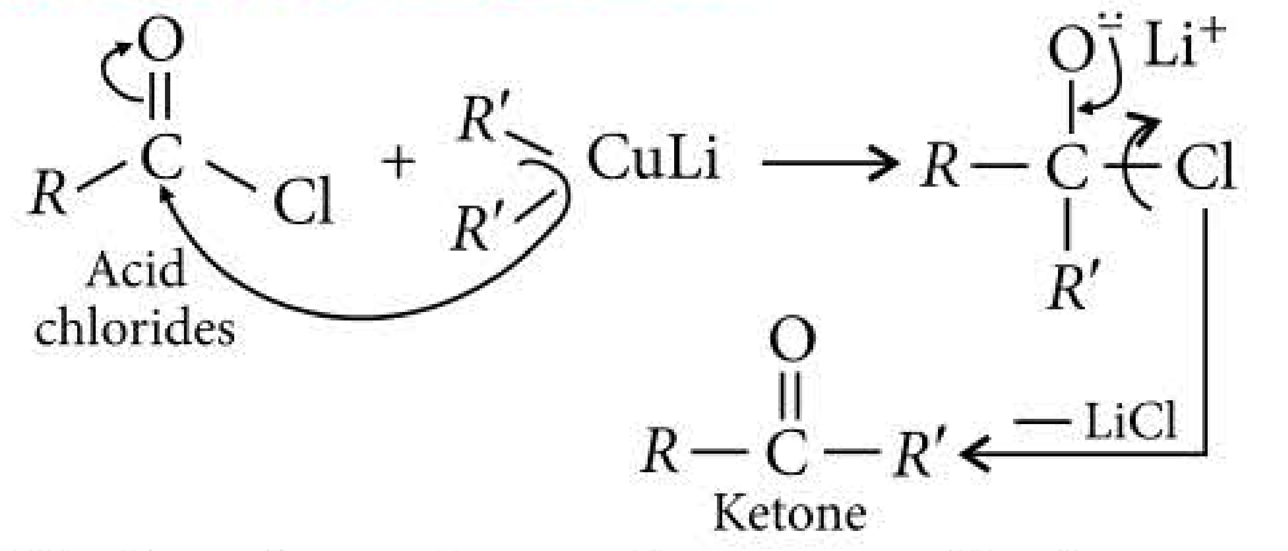
You can also replace a halogen atom with an alkene skeleton.



❍ Reaction with Epoxide



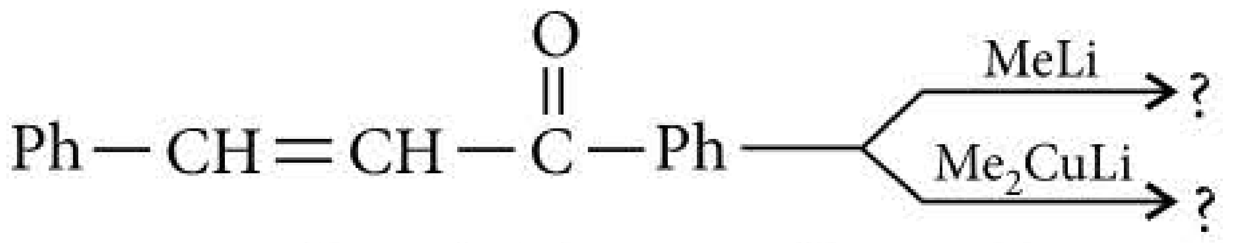
❍ Reaction with acid chlorides and chemoselectivity of organocopper compounds.



Would it have been Grignard reagent, a further reaction with ketone takes place to give 3° alcohol. But, here the case is NOT similar. Due to lower reactivity, organocopper reagents do not react further. Remember that in many cases organocopper reagents show chemoselectivity with $-NO_2$, $-CN$, $-COOR$, $-CO-$ etc., Grignard reagents and organolithium reagents react with these functional groups but organocopper compounds DO NOT.

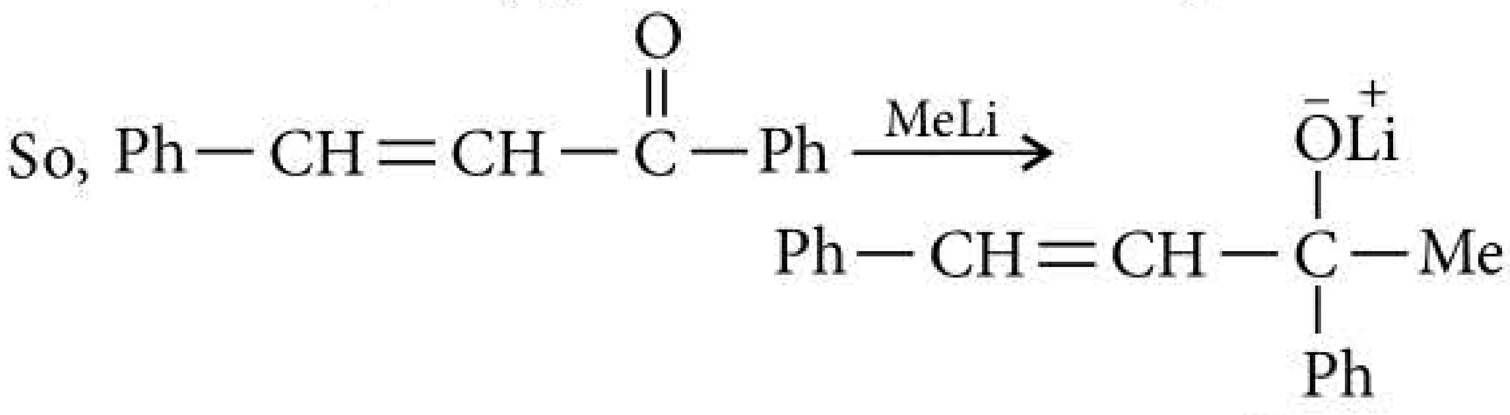
PRACTICE PROBLEMS

1. Identify the products :

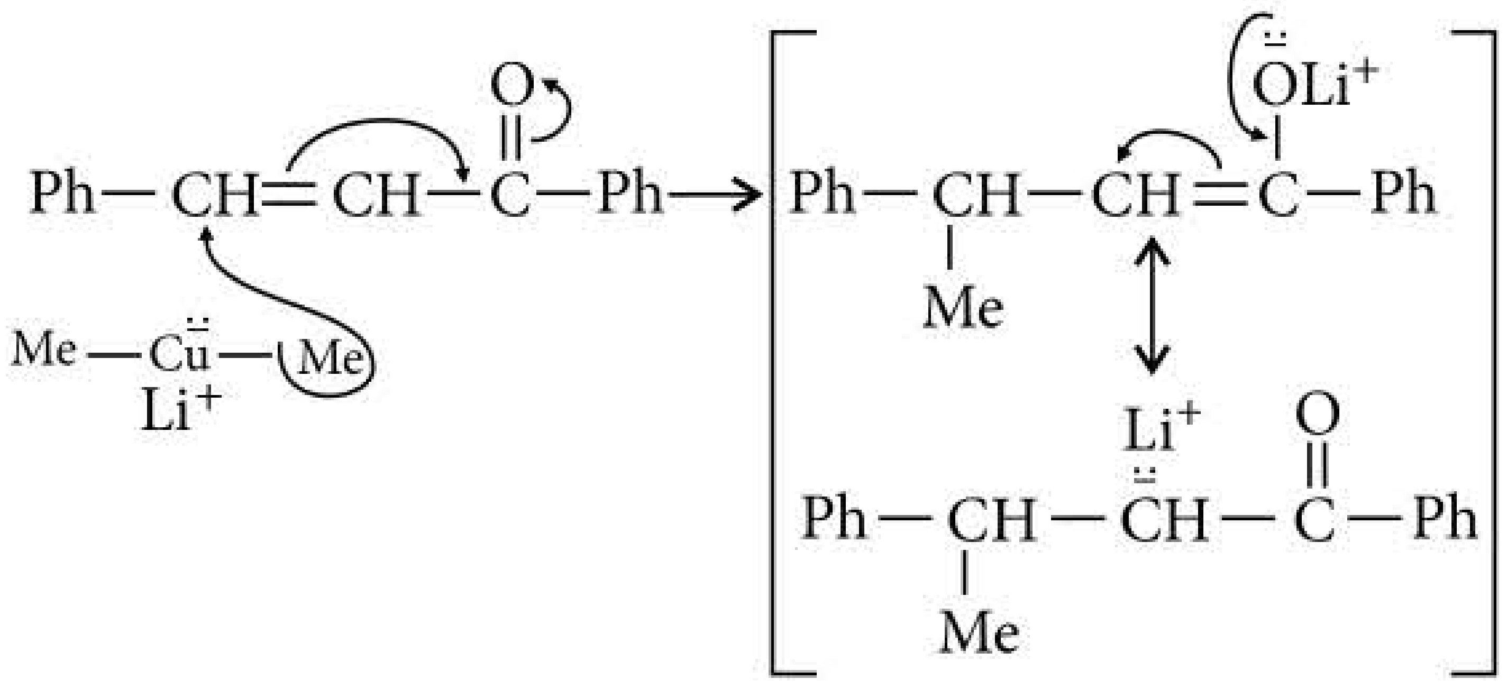


$$Ph-CH=CH-\overset{O}{\overset{\|}{C}}-Ph \begin{cases}\xrightarrow{MeLi} ? \\ \xrightarrow{Me_2CuLi} ?\end{cases}$$

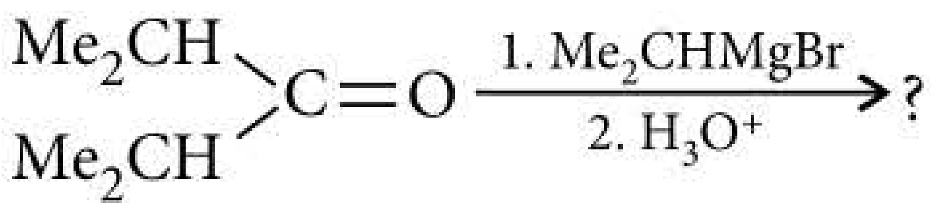
Soln : Here, carbonyl addition will take place with MeLi and conjugate addition will take place with Me_2CuLi. Organolithium reagents are very powerful nucleophiles and therefore, they give irreversible carbonyl addition.



$$\text{So, } Ph-CH=CH-\overset{O}{\overset{\|}{C}}-Ph \xrightarrow{MeLi} Ph-CH=CH-\underset{Ph}{\overset{\bar{O}\overset{+}{Li}}{C}}-Me$$

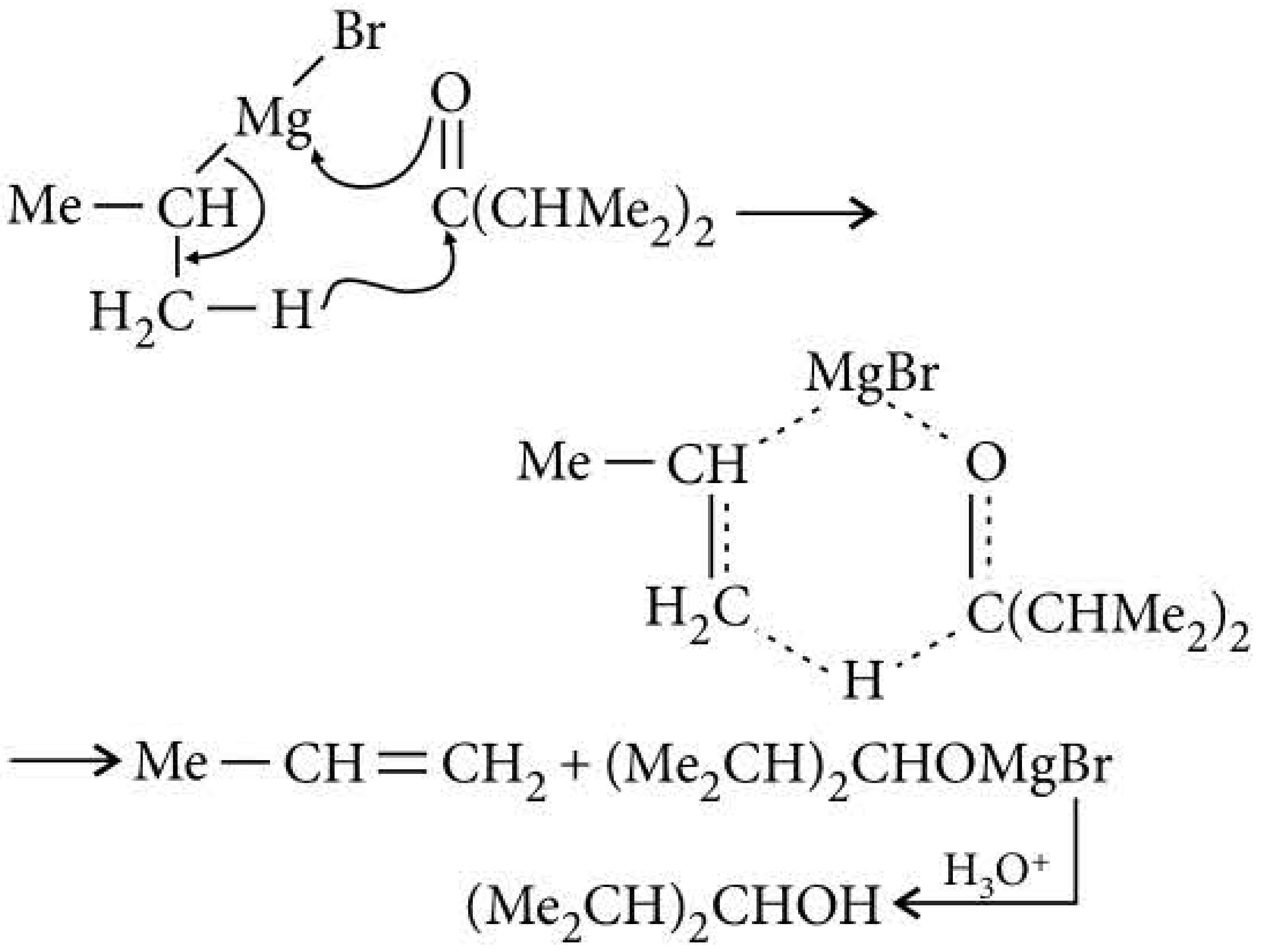


2. **Identify the product :**

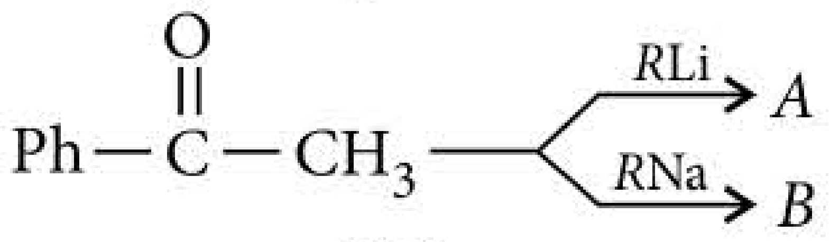


$$\begin{matrix}Me_2CH \\ Me_2CH\end{matrix}\!\!>C=O \xrightarrow[2.\ H_3O^+]{1.\ Me_2CHMgBr} ?$$

Soln : When the alkyl group of Grignard reagent is very large and the groups attached with the carbonyl carbon of ketone are also very large rather branched then in that case normal addition reaction doesn't take place. In that case, if the Grignard reagent contains β-hydrogen then reduction takes place. The reaction scenario is as below :

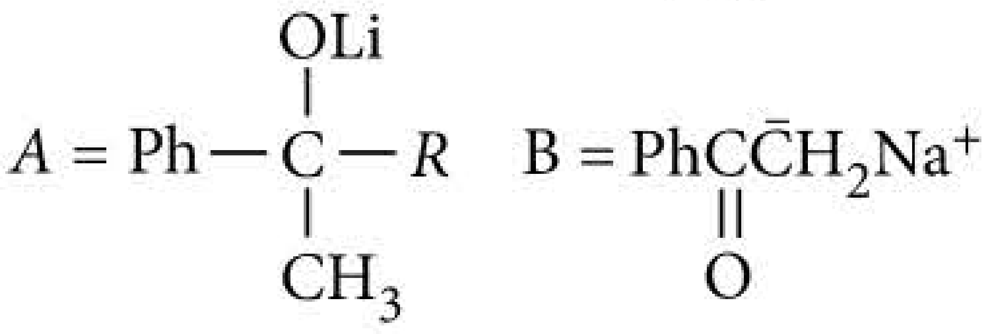


3. **Identify the products :**



$$Ph-\overset{O}{\overset{\|}{C}}-CH_3 \begin{cases}\xrightarrow{RLi} A \\ \xrightarrow{RNa} B\end{cases}$$

Soln.:



$$A = Ph-\underset{CH_3}{\overset{OLi}{C}}-R \qquad B = Ph\underset{O}{\underset{\|}{C}}\bar{C}H_2Na^+$$

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EXAM CORNER 2018

Exam	Date
VITEEE	4th to 15th April
JEE Main	8th April (Offline), 15th & 16th April (Online)
SRMJEEE	16th to 30th April
Karnataka CET	18th & 19th April
WBJEE	22nd April
Kerala PET	23rd & 24th April
NEET	6th May
MHT CET	10th May
COMEDK (Engg.)	13th May
AMU (Engg.)	13th May (Revised)
BITSAT	16th to 31st May
JEE Advanced	20th May
AIIMS	27th May
JIPMER	3rd June