

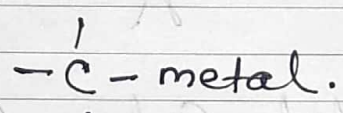
① Organomagnesium compound :- the Grignard reagent formation

Structure and Chemical reaction

② Organo zinc compound :- formation and chemical reaction

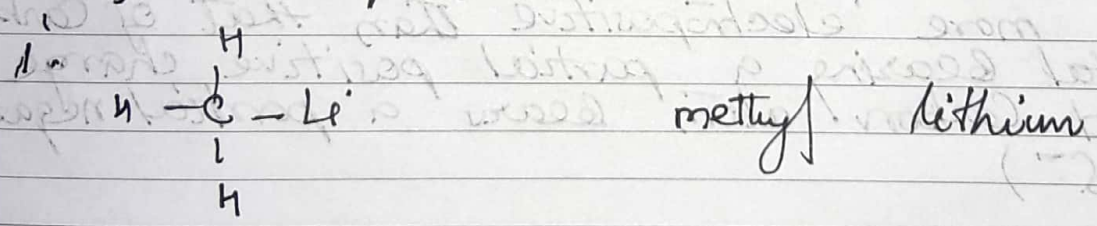
③ Organolithium compound :- formation and chemical reaction.

Organometallic compound are metal bearing organic compd. in which carbon directly bounded to a metal or in which metal is directly bounded with carbon atom.

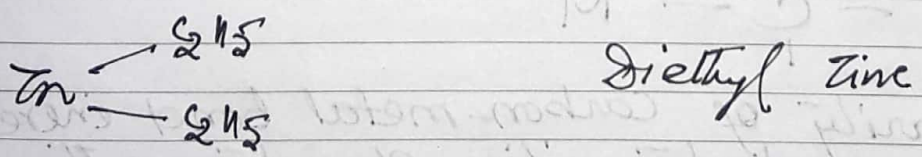


Metal like Li, Na, K, Mg, Ca, Al, Zn, Cd, Hg, Sn, Pb etc are commonly found in the organometallic compound.

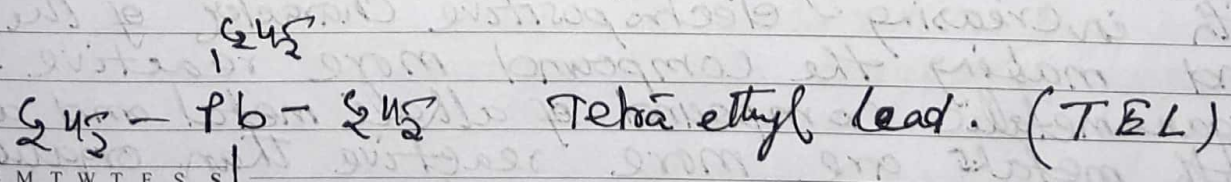
As for Example :-



2.



3.



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27	28	29	30	31									

(iv) $R-Mg-X$ Grignard Reagent

$R = -CH_3, -C_2H_5, -C_3H_7$ etc

$X = -Cl, -Br, -I$ etc.

N.B.

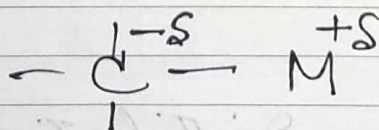
(i) $(CH_3)_3B$ - Trimethyl borane

(ii) $(C_2H_5)_4Sn$ - Tetraethylstannane

(iii) $(C_2H_5)_4Si$ - Tetraethylsilane.

Nature of metal-Carbon bond

In the organometallic compounds, carbon-metal bonds are neither fully ionic nor completely co-valent nature. It is a polar co-valent bond, in which metal are more electropositive than that of carbon. Hence metal bearing a partial positive charge (δ^+) and carbon atom bears a partial negative charge (δ^-).



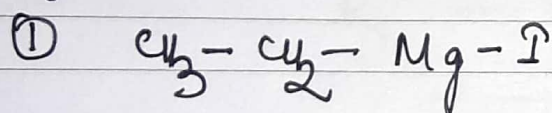
The polarity of carbon-metal bond increases with increasing electropositive character of the metal and making the compound more reactive. Therefore organometallic compound of alkali metal and alkaline earth metals are more reactive than organometallic compound of transition metals.

Grignard - Reagent ($R-Mg-X$)

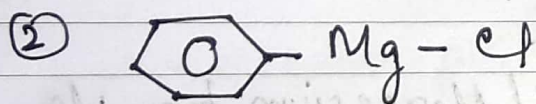
Organo Magnesium halides are called Grignard reagent which was discovered by French chemist VICTOR Grignard. The General formula of Grignard Reagent is $R-Mg-X$

where $R = \text{Alkyl, alkenyl, aryl group}$
 $X = Cl, Br, I \text{ etc.}$

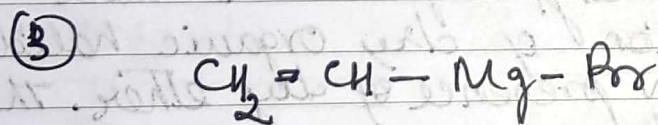
e.g



ethyl Mag. Iodide

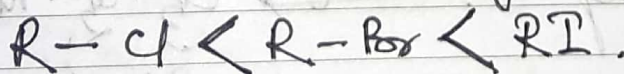


phenyl Mag. chloride



Vinyl Mag. bromide.

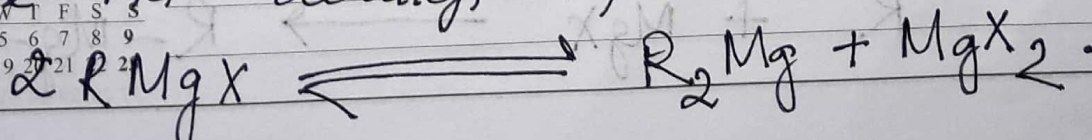
The order of reactivity of halide with Magnesium is



Structure of Grignard Reagent:

The actual structure of Grignard reagent is more complex than its general formula $R-Mg-X$

Experiments done with radioactive Magnesium have established that for most Grignard Reagents there is an equilibrium between alkyl Magnesium halide and dialkyl Magnesium.

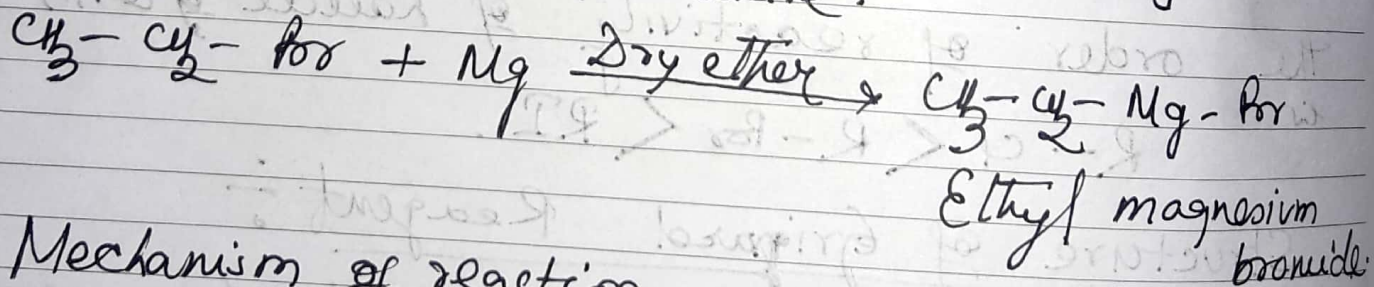


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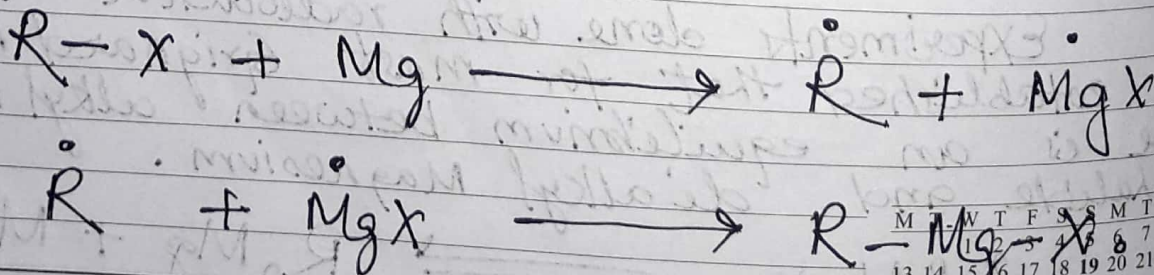
Preparation of Grignard Reagent.

In the laboratory, ethyl Magnesium bromide is prepared by the interaction of dry organic halide and dry magnesium metal in presence of dry ether. The reaction is exothermic in nature.



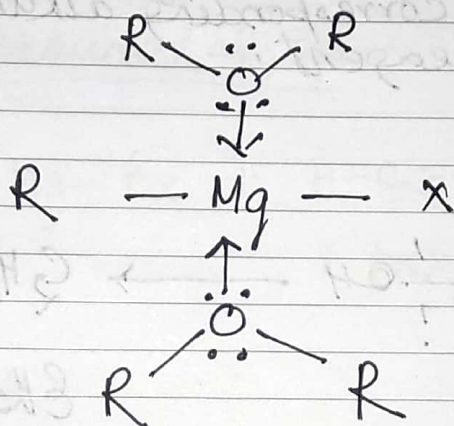
05 Sunday Mechanism of reaction

Reaction proceeds through free radical mechanism in which the following steps are involved.



Role of ether in Grignard Reagent.

Ether provides medium for the reaction and dissolves Grignard reagent through solvolysis. Grignard reagent forms complex with its ether solvent. The structure of the complex can be represented as follows:-



The complex formation of with ether provides stability to the Grignard reagent.

Precaution in the preparation of Grignard reagent

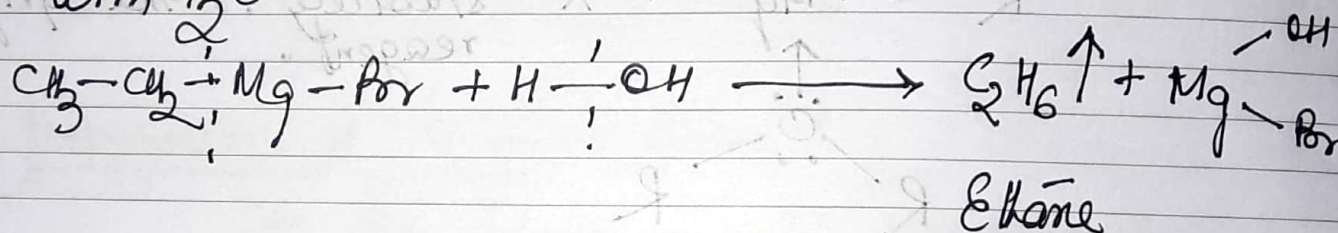
- ① The organic halide, magnesium and ether must be absolutely dry.
- ② ether used as solvent must be completely free from alcohol
- ③ The apparatus must be thoroughly dried before the reaction is started
- ④ An atmosphere of dry Nitrogen should be maintained in the reaction system.
- ⑤

ORGANIC SYNTHESIS FROM Grignard reagent

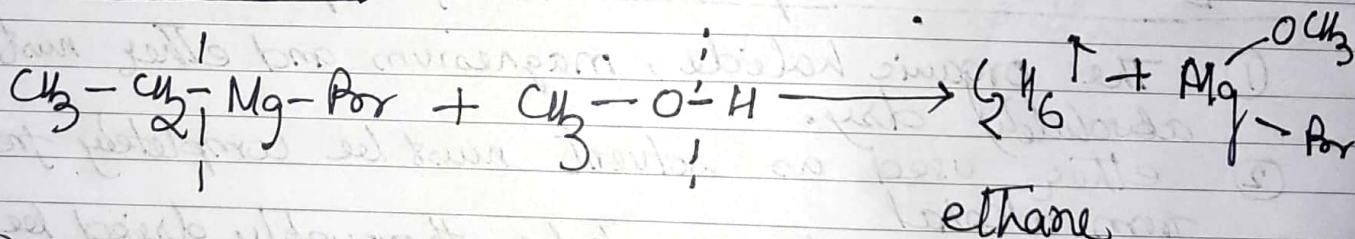
(A) Reaction with compound containing acidic hydrogen.

Compound like water, $R-OH$, $R-COOH$, NH_3 , $R-NH_2$, R_2NH (1° and 2° amine), terminal Alkyne etc contain active hydrogen gives corresponding alkane of alkyl group of Grignard reagent.

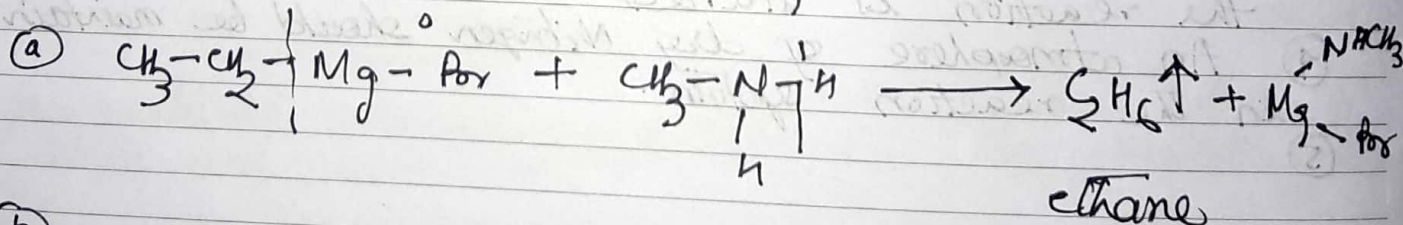
(1) with H_2O



(2) with Alcohol (CH_3-OH)

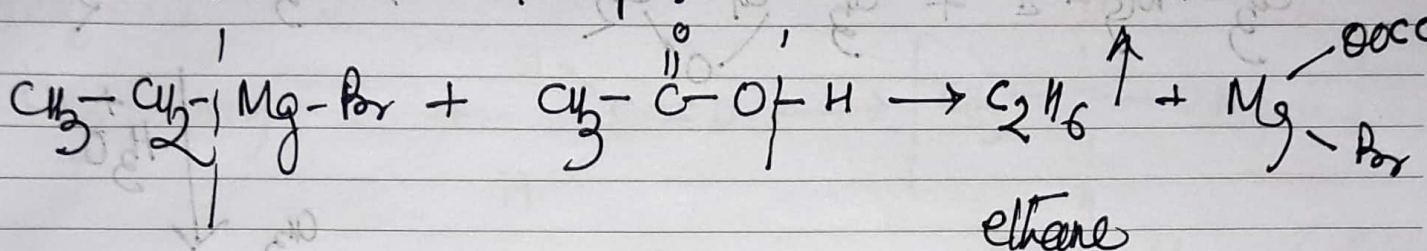


(3) with Amine

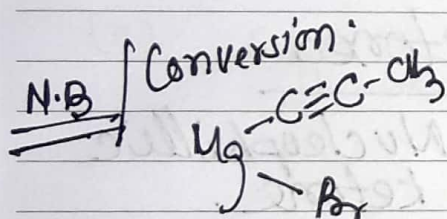
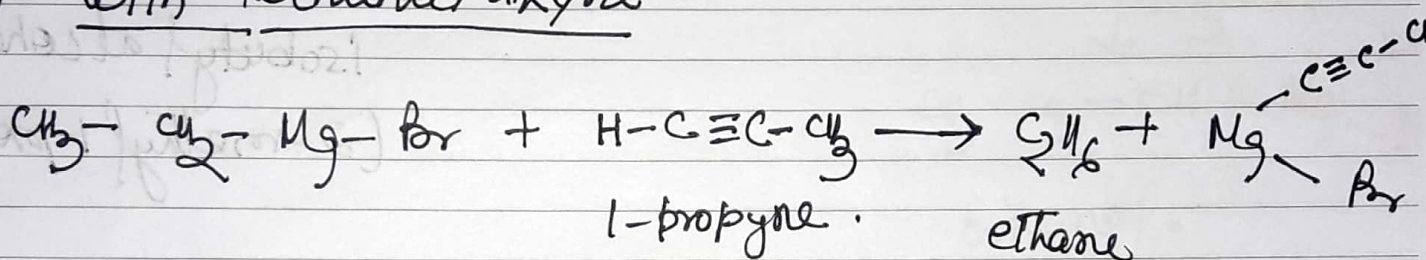


(b)

(4) with Carboxylic acid group :-



(5) with terminal alkyne

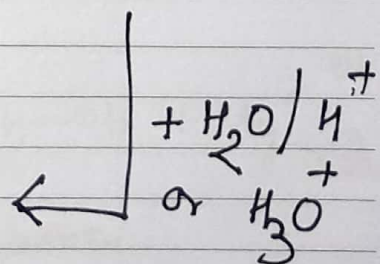
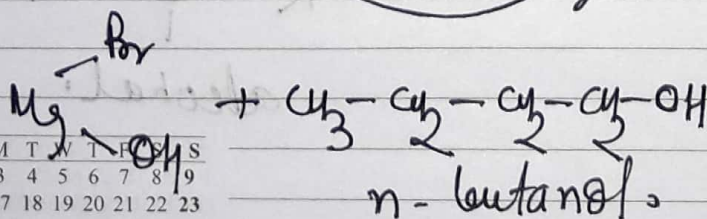
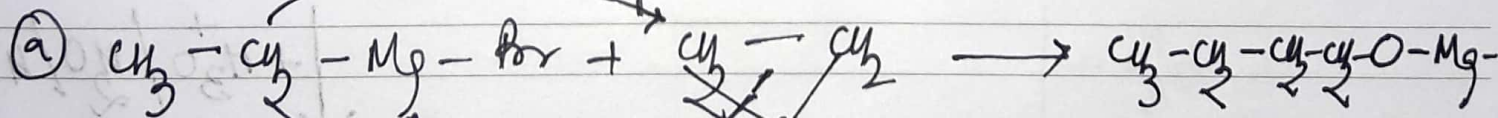


Propyne Magnesium bromide

2-butyne

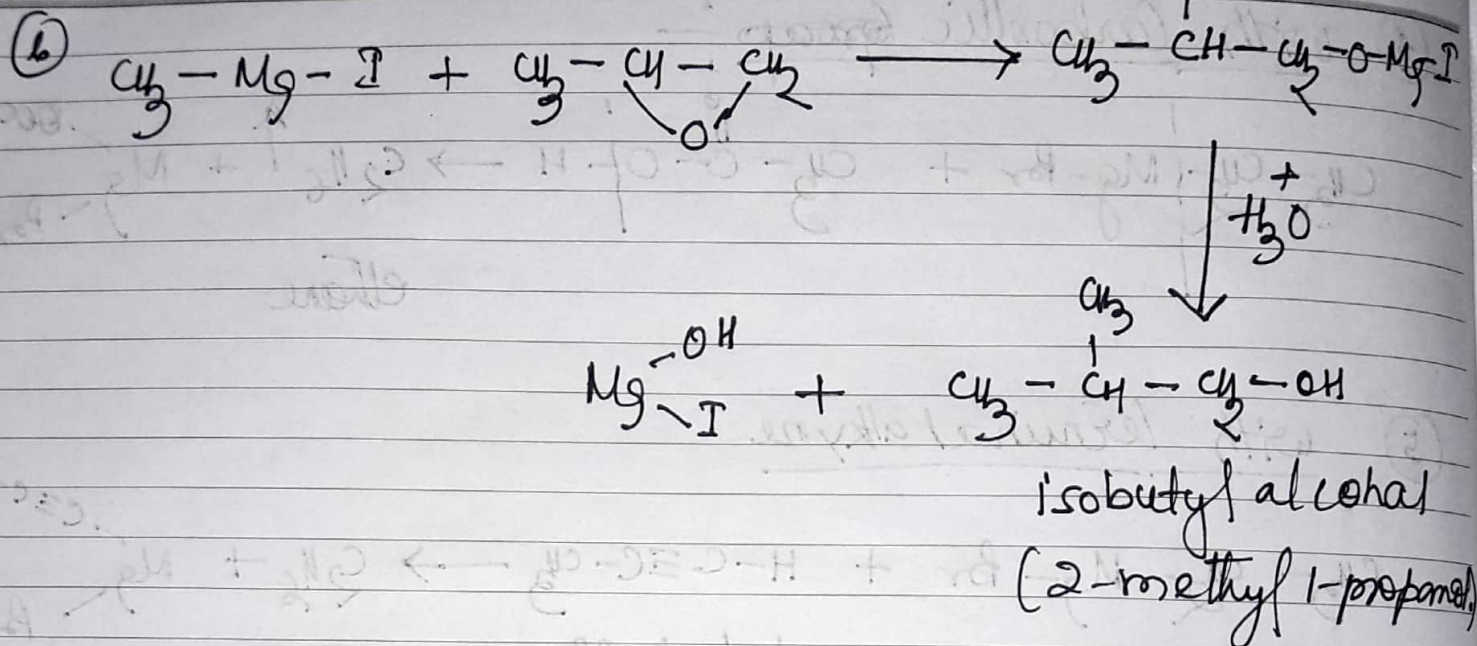
(B) Reaction with epoxide or Oxirane :-

Primary alcohols are obtained



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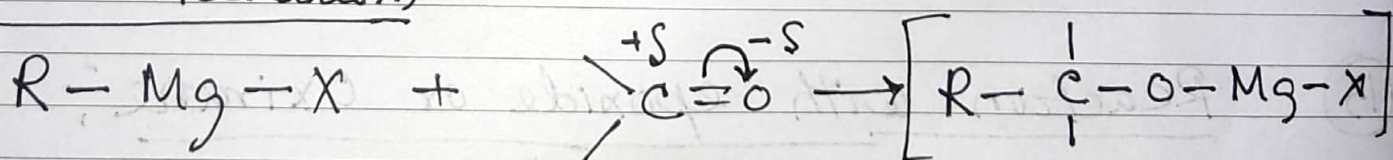
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24	25	26	27	28	29							



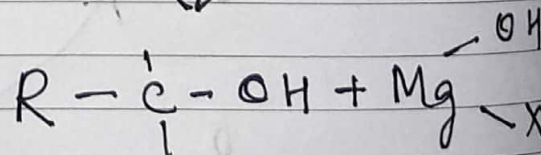
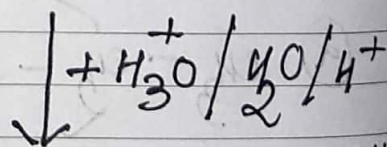
(c) Reaction with Aldehyde and ketones

Grignard reagent undergoes to Nucleophilic addition reaction with aldehyde and ketone.

General mechanism



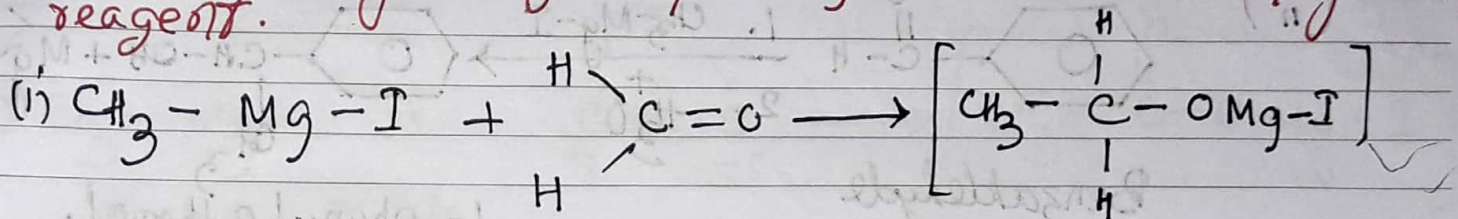
Addition product



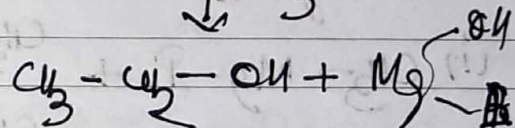
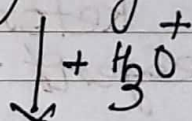
alcohol.

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M	T	W	T	F	S	S	M	T	W	T	F	S	S
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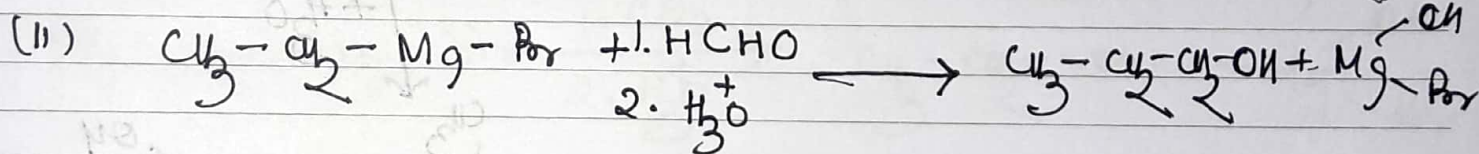
(a) Formaldehyde gives primary alcohol with Grignard reagent.



ethoxy Mag. Iodide

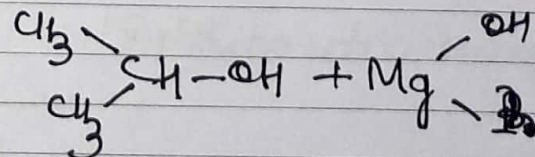
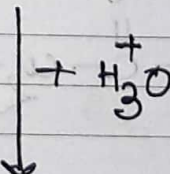
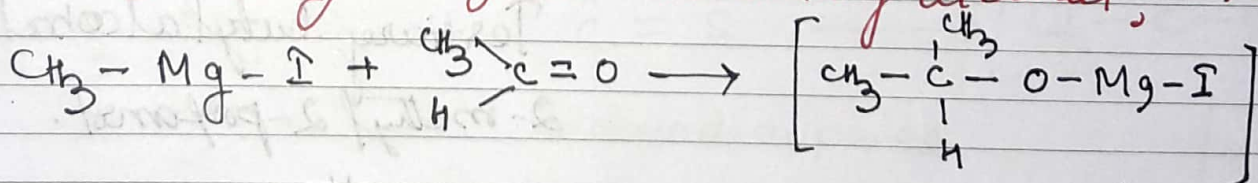


Ethanol.



1-propanol.

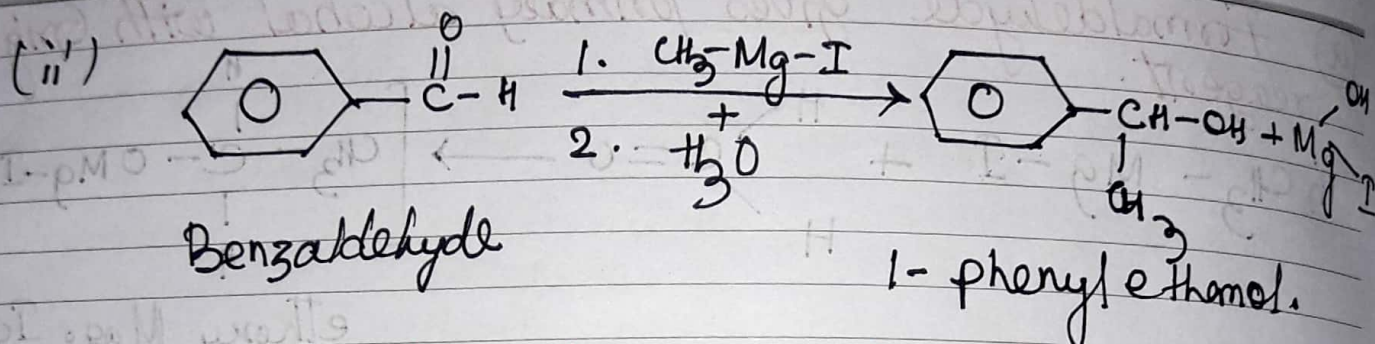
(b) Other aldehyde gives secondary alcohol with Gr. R.



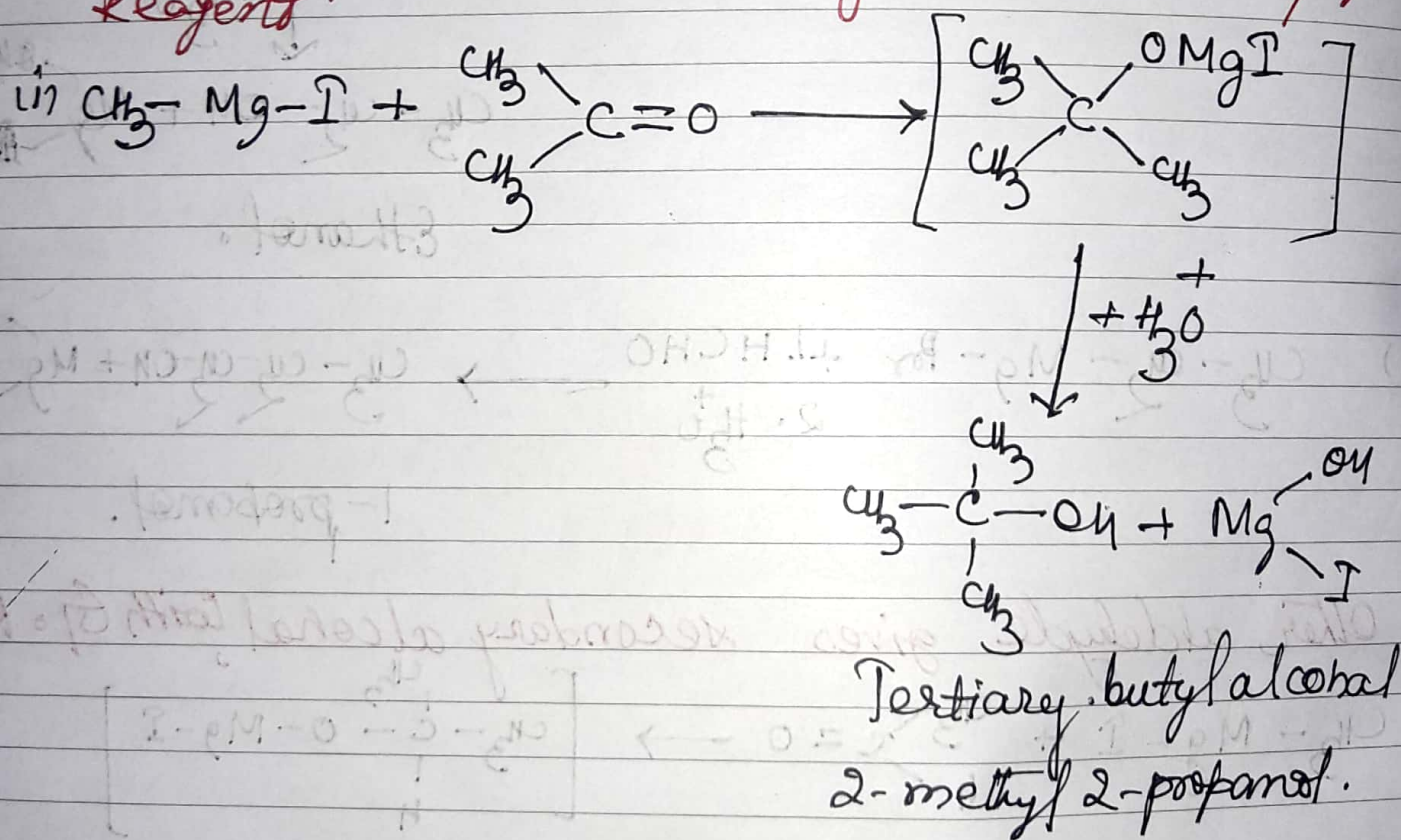
2-propanol.

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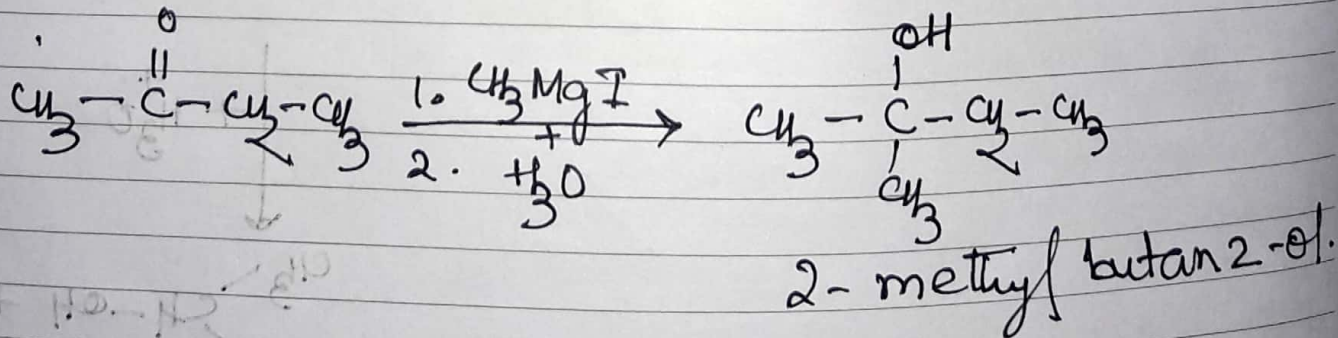
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10	11	12	13	14	15	16	17	18	19	20	21	22	23
24	25	26	27	28	29								



© ketones give tertiary alcohol with Grignard reagent.



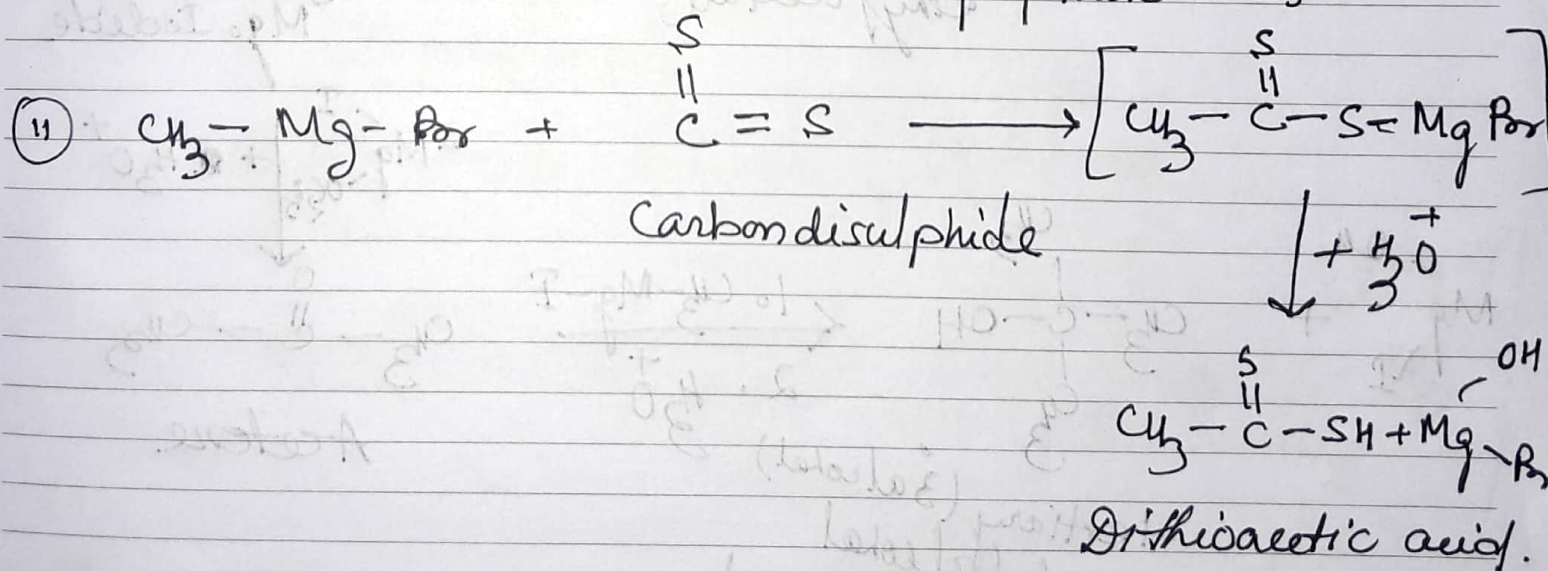
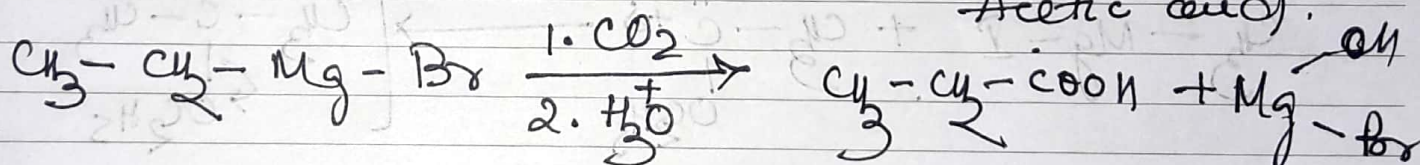
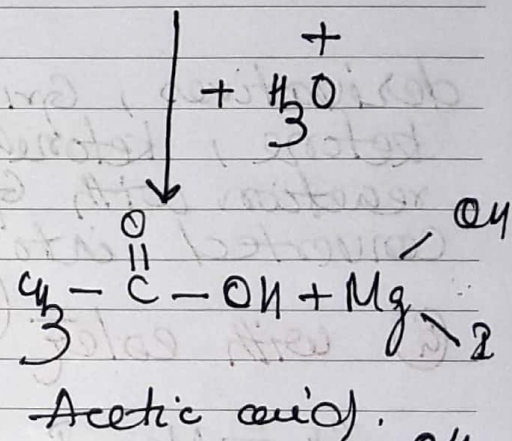
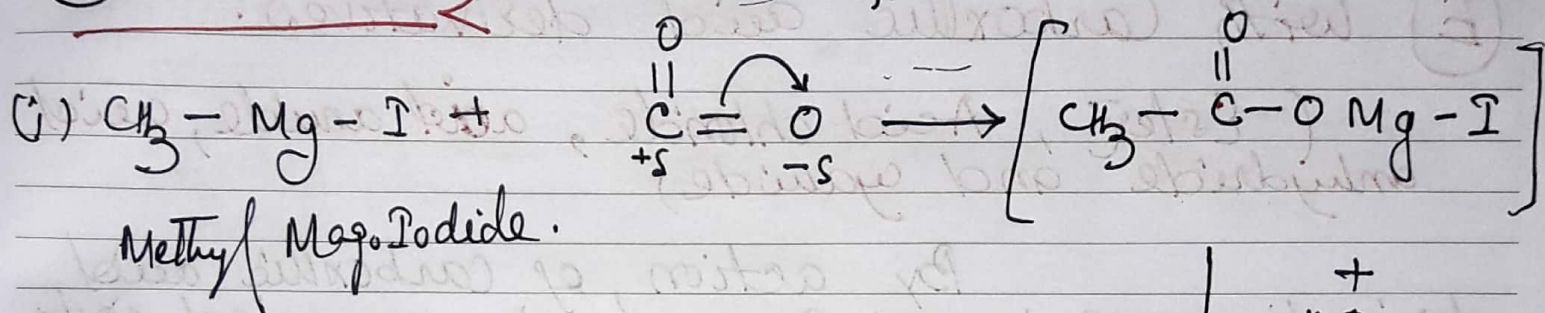
12 Sunday (ii)



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13	14	15	16	17	18	19	20	21	22	23	24	25
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① with CO_2 - 24 forms carboxylic acid.



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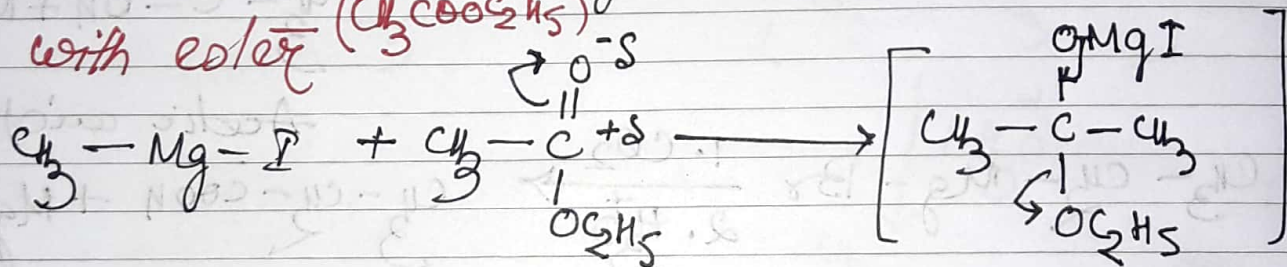
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10	11	12	13	14	15	16	17	18	19	20	21	22	23
24	25	26	27	28	29								

(E) with Carboxylic acid derivatives.

(Ester, Acid chloride, acid anhydride, acid amide and cyanide)

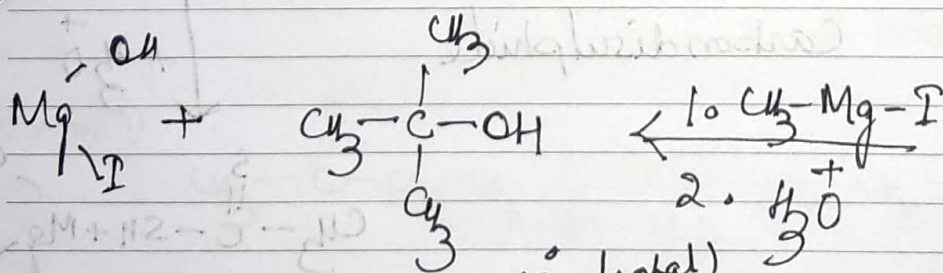
By action of carboxylic acid derivatives, Grignard Reagent is converted into ketone, ketone undergoes to nucleophilic addition reaction with Grignard reagent followed by hydrolysis converted into tertiary alcohol.

(Q) with ester ($\text{CH}_3\text{COOC}_2\text{H}_5$)

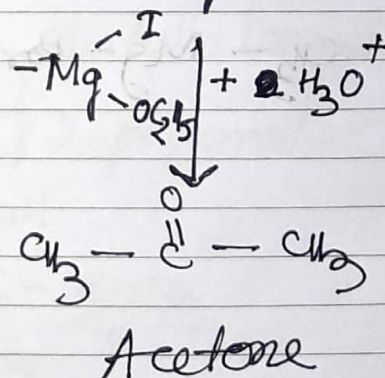


ethyl acetate

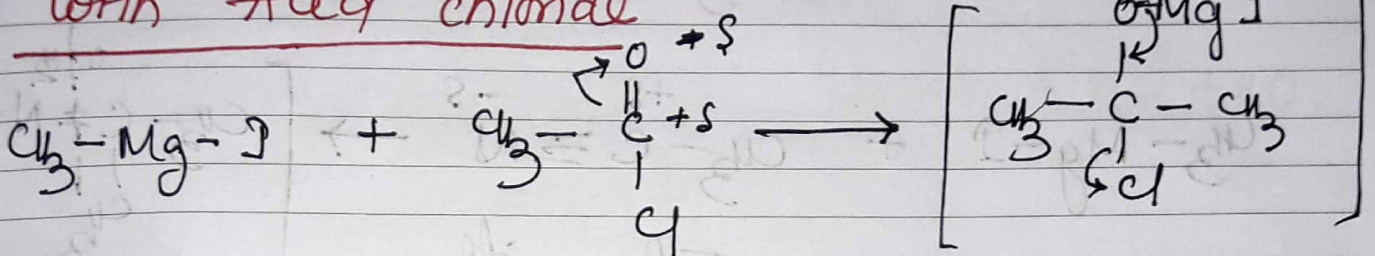
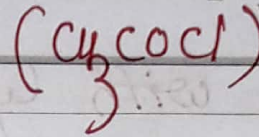
2 (ethoxy 2-proxy) Mg. Iodide



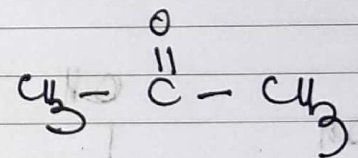
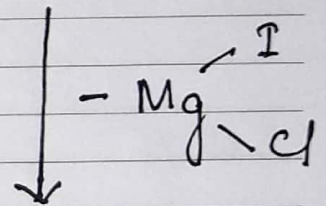
tertiary (3 alcohol)
butyl alcohol
2-methyl 2-propanol



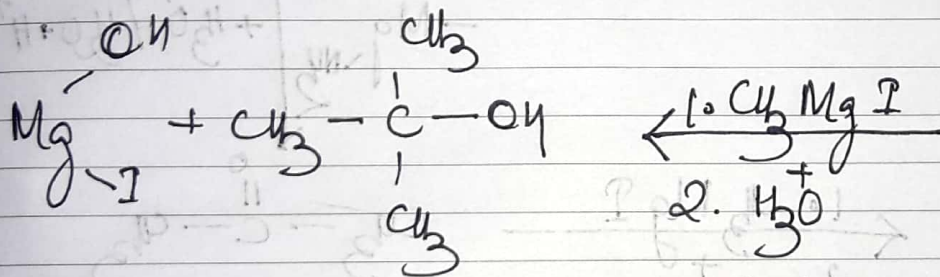
(b) with Acid chloride



Acetyl chloride

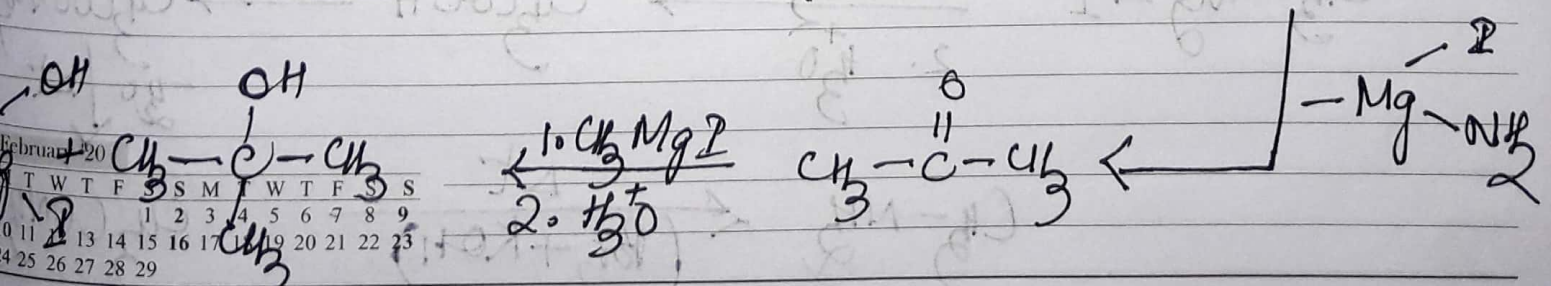
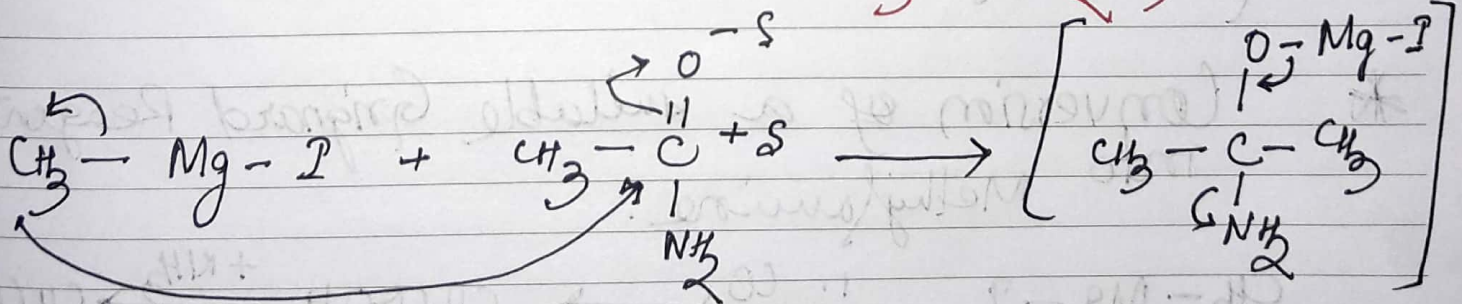


Acetone



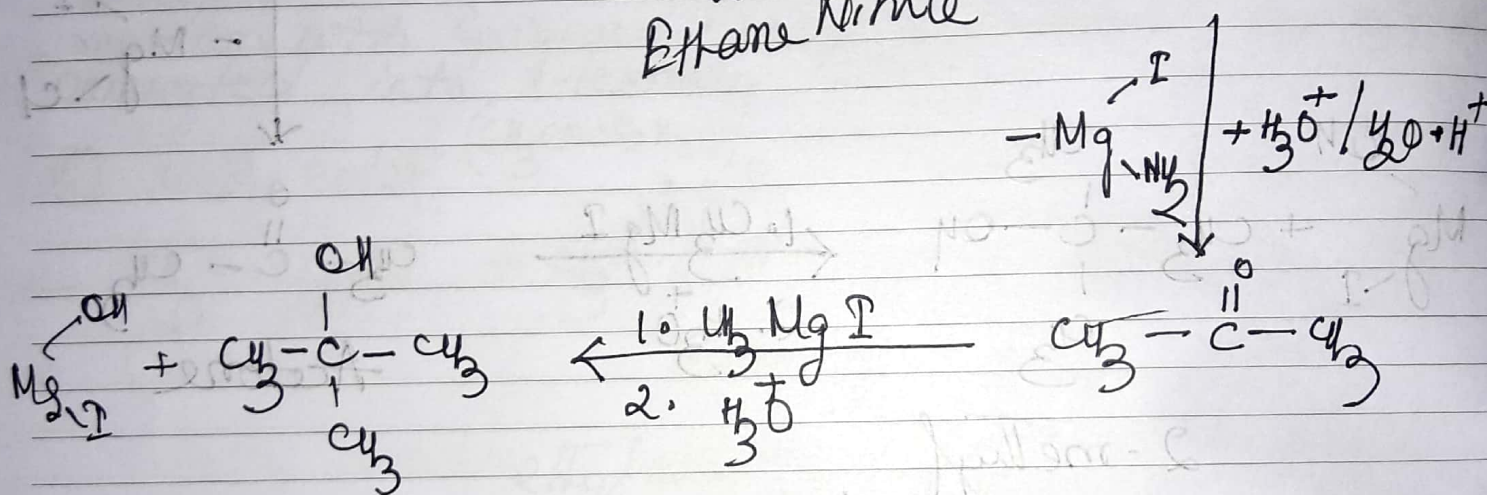
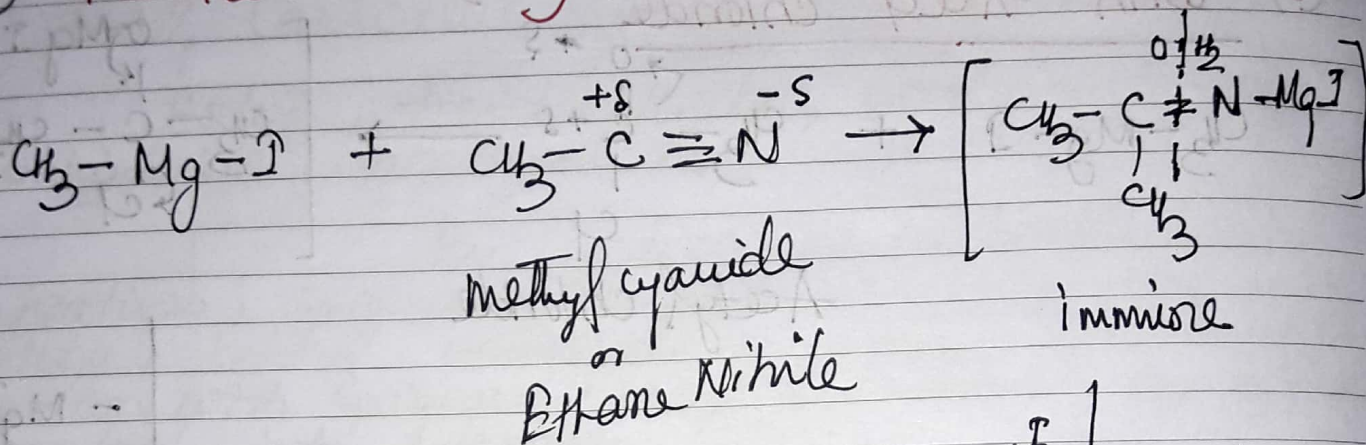
2-methyl
2-propanol.

(c) with Acid Amide $(\text{CH}_3\text{C}(=\text{O})\text{NH}_2)$

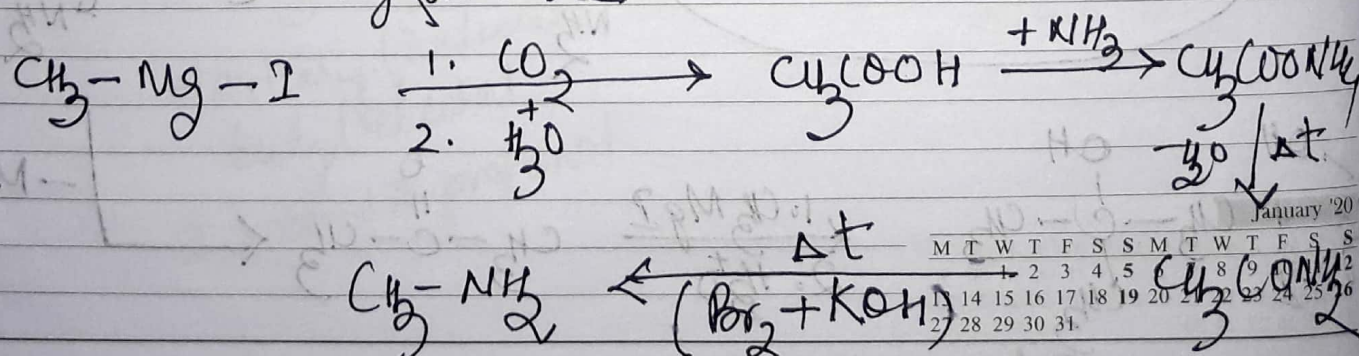


2-methyl 2-propanol.

(a) Reaction with Cyanide or Nitrile (IUPAC)



* Conversion of a suitable Grignard Reagent into Methylamine:



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			2	3	4	5	6	7	8	9	10	11	12
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27	28	29	30	31									