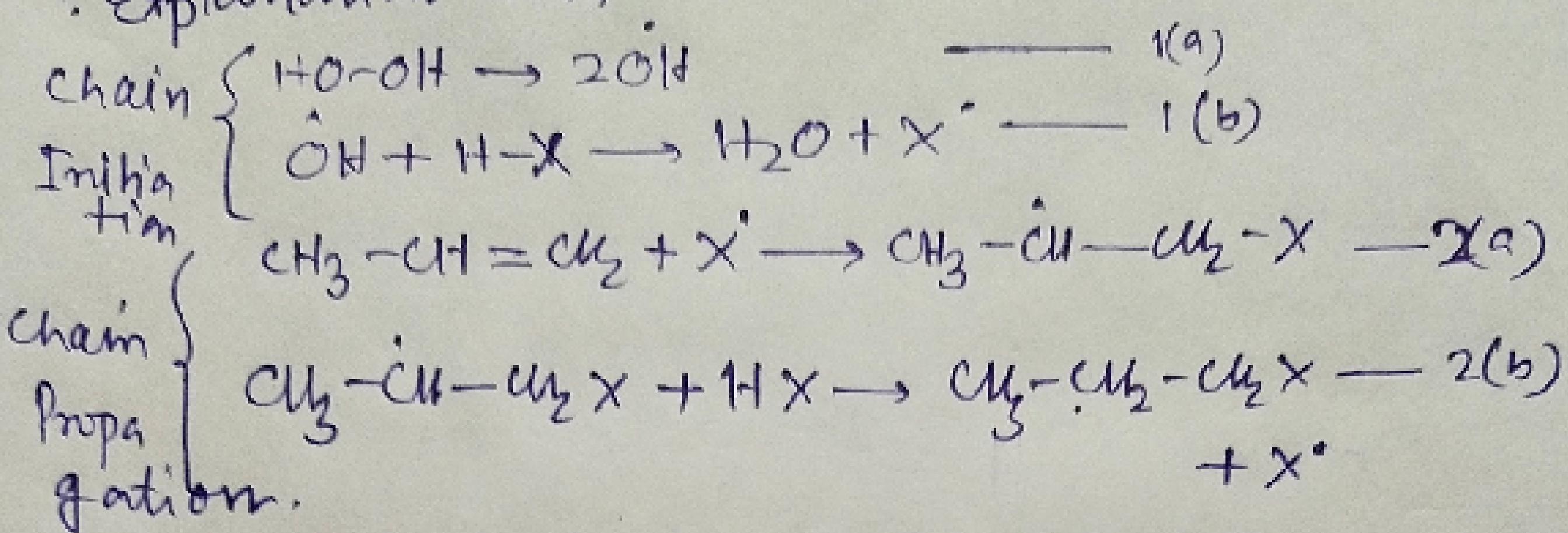


28'

: Explanation with mechanism:



for reaction to occur both 2a & 2b

must be spontaneous.

(ΔH) for (2a) & (2b) must be $-ve$.

for HF, HCl, HBr, HI, ($\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$) stability

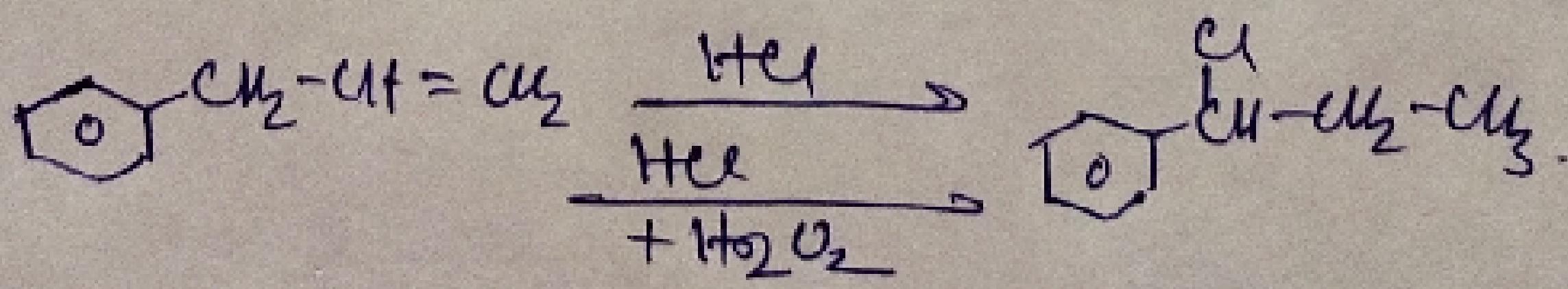
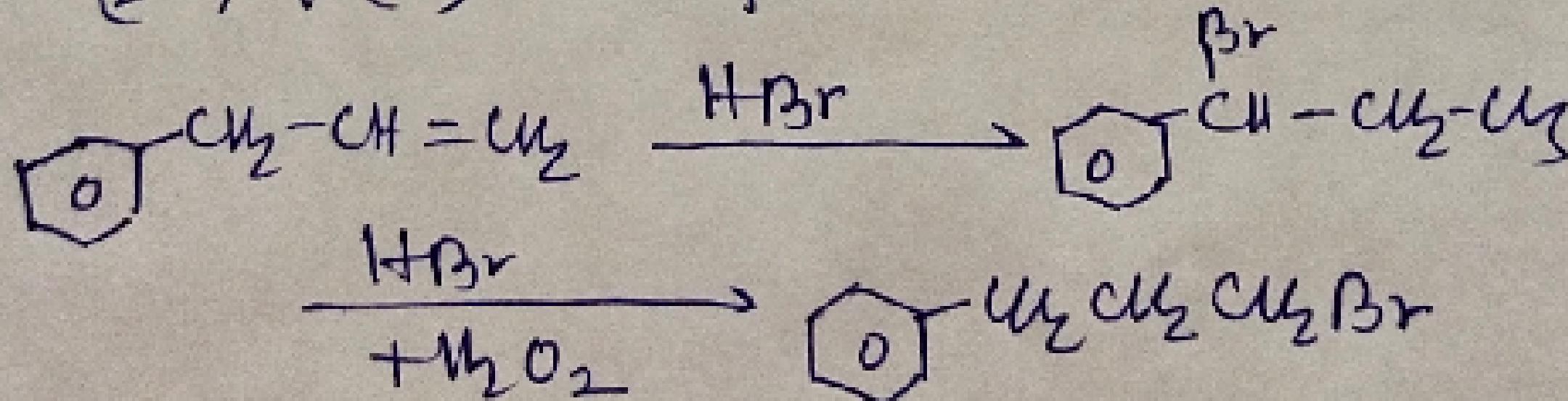
for I⁻, reaction (2a) is nonspontaneous,

because I⁻ is least reactive

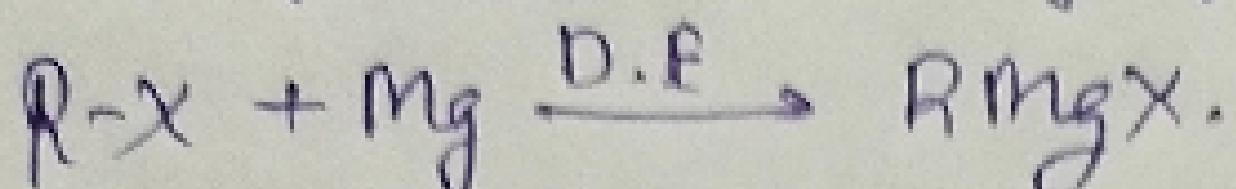
for HF, HCl, HBr, HI. [b. d. e. HF > HCl > HBr > HI].

HF & HCl reaction (2b) is nonspontaneous. So it is HBr for which both

(2a) & (2b) are spontaneous.

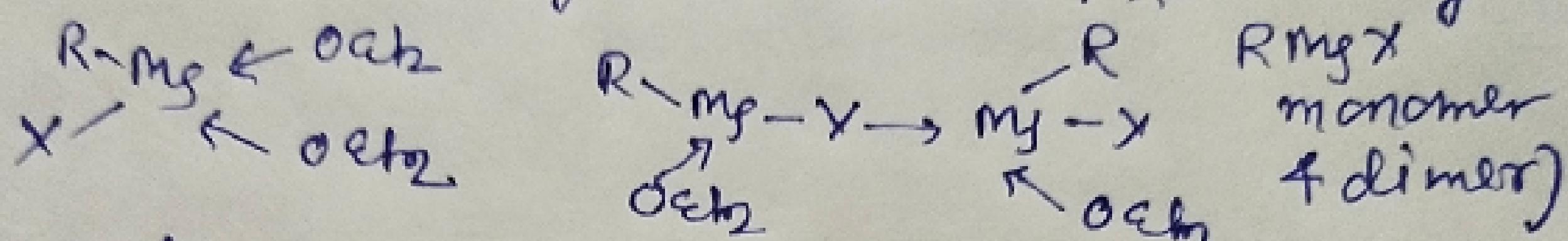


When alkyl halide is allowed to react with Mg in dry ether, then Grignard reagent is formed.



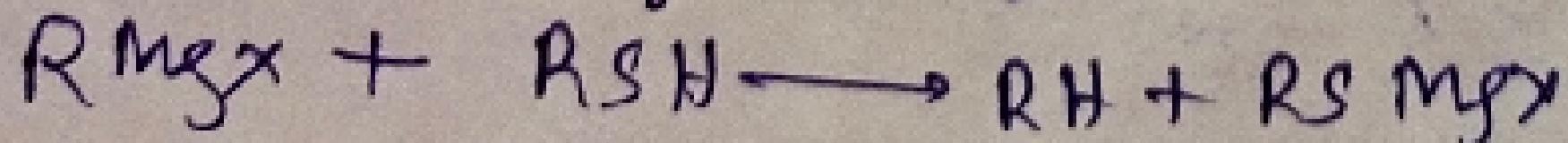
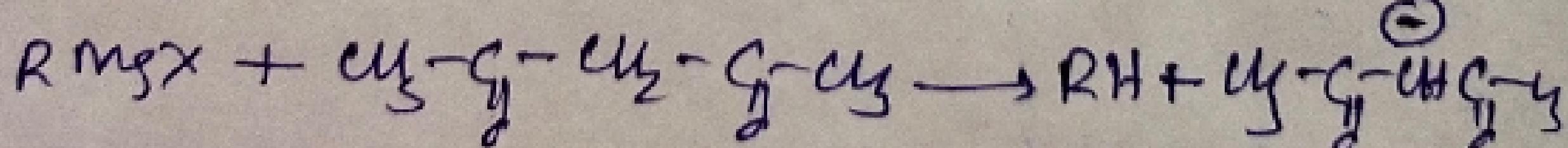
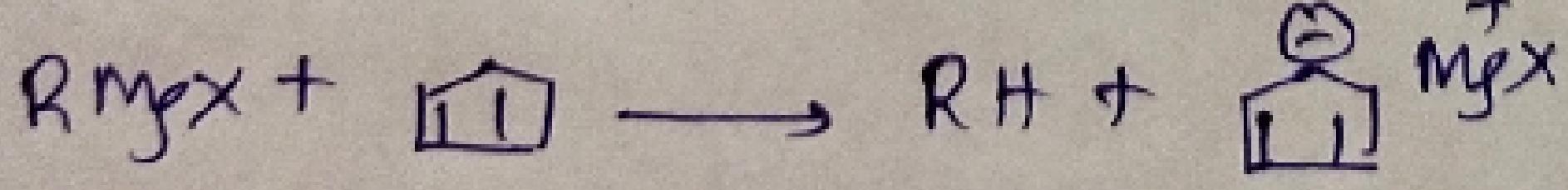
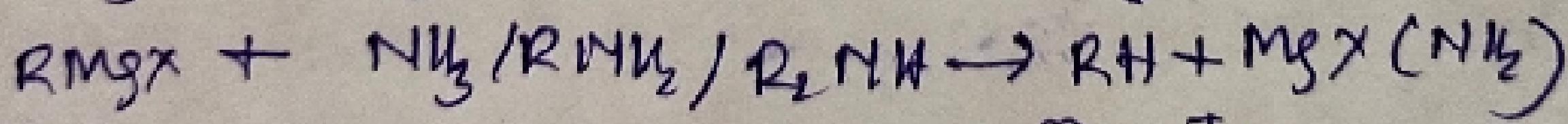
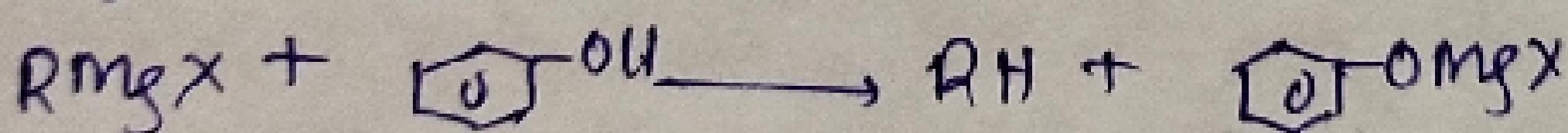
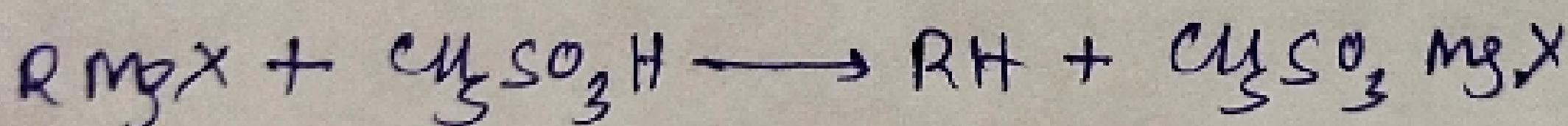
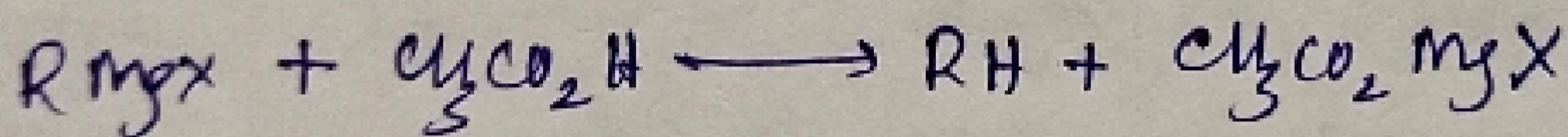
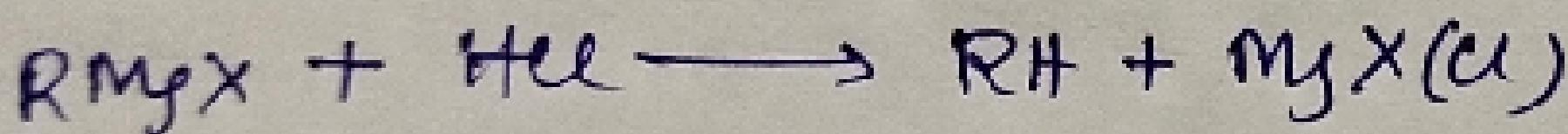
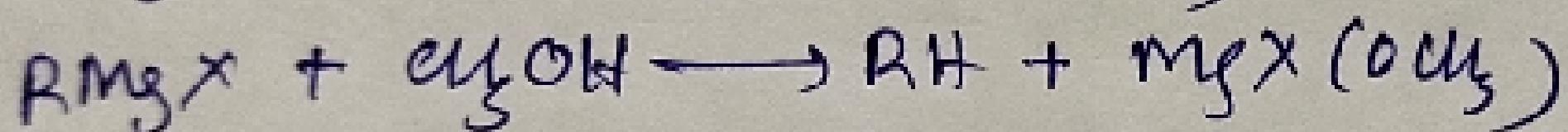
Reactivity of R-X: $R-I > R-Br > R-Cl > R-F$.

$RMgX$ is solvated by ether solvent. (solvation)



$RMgX$ is the source of anion (carbanion).

So it can act as very strong base as well as very strong nucleophile.



In reactions, $RMgX$ acts as base.

Other examples:

$$R\text{MgX} + \text{CH}_3-\text{C}(=\text{O})-\text{NH}_2 \rightarrow \text{RH} + \text{MgX}(\text{H}-\text{C}_2\text{H}_5)$$

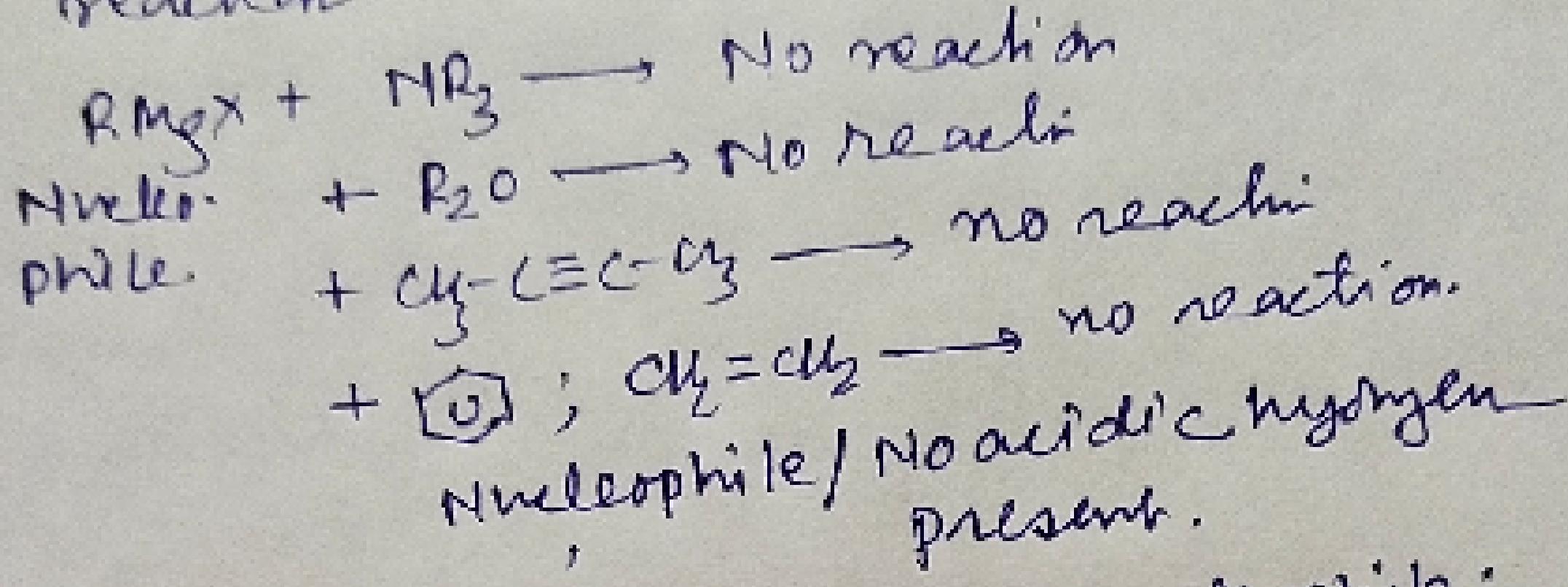
$$R\text{MgX} + \text{CH}_3-\text{C}(=\text{O})-\text{SH} \rightarrow \text{RH} + \text{MgX}$$

$$R\text{MgX} + \text{D}_2\text{O} \rightarrow \text{RH} + \text{MgX(D)}$$

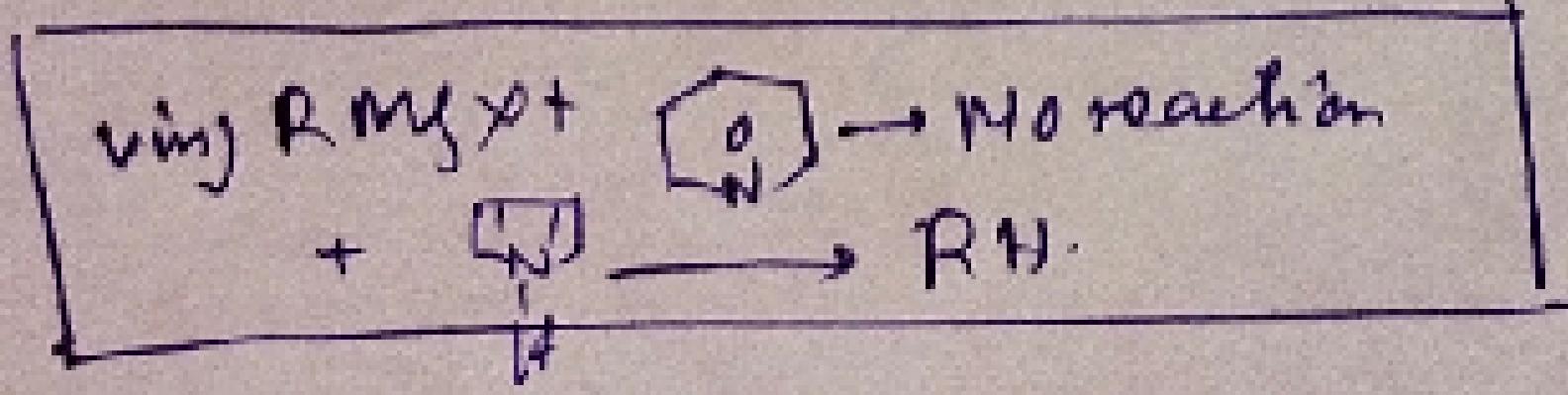
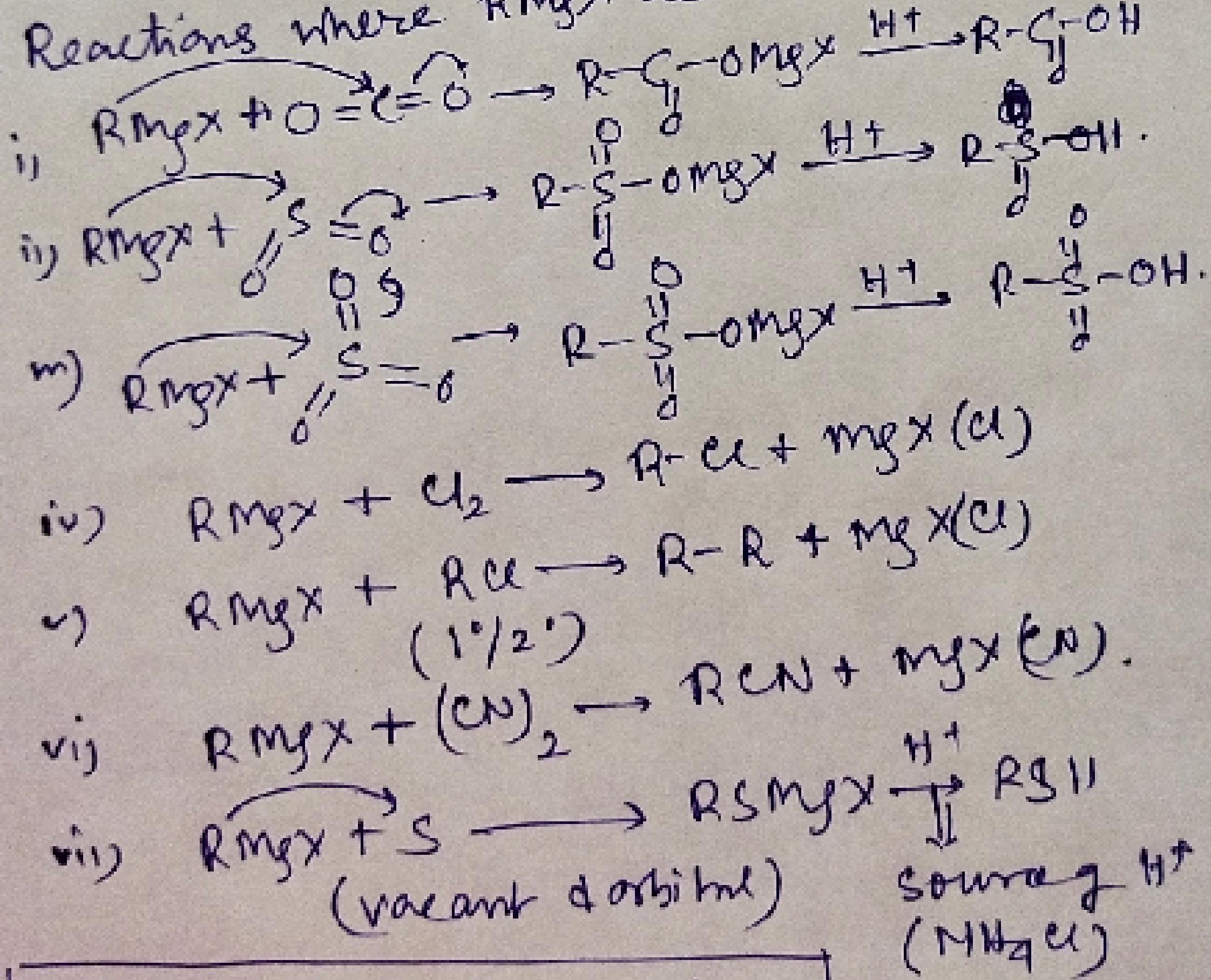
$$R\text{MgX} + \text{HC}(=\text{O})-\text{Cl} \rightarrow \text{RH} + \text{C}_2\text{H}_5\text{C}(=\text{O})\text{MgX}$$

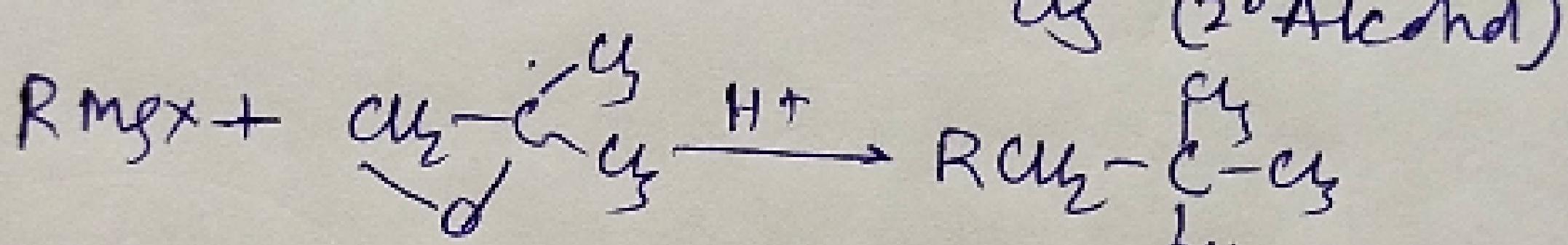
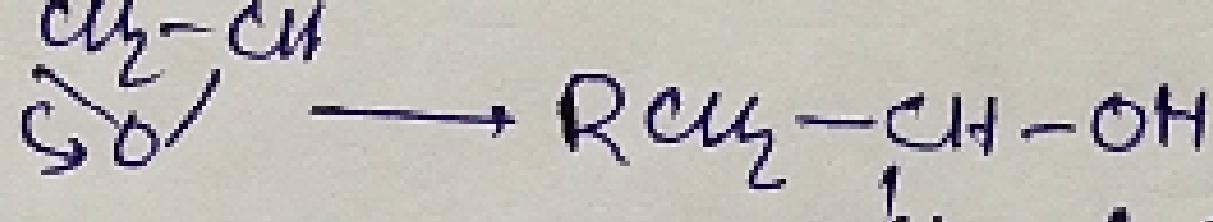
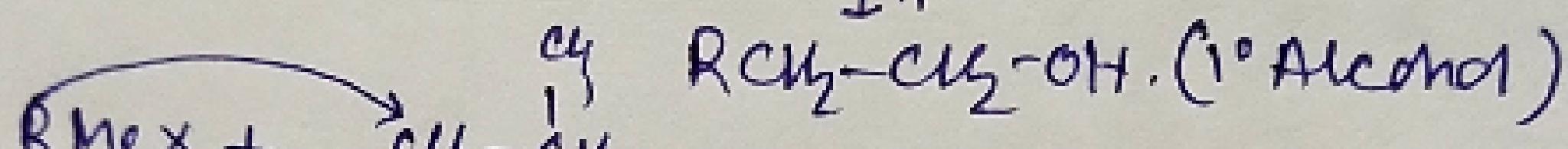
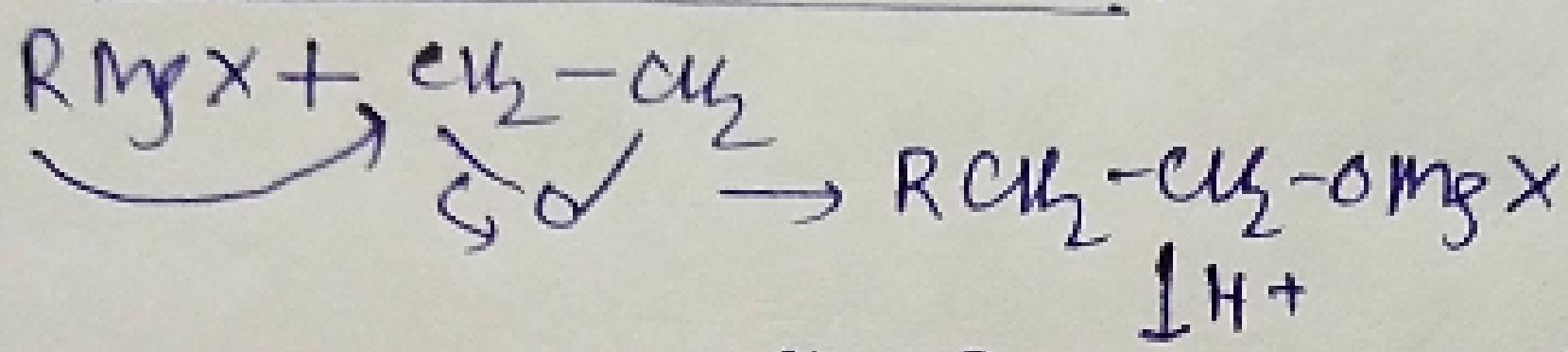
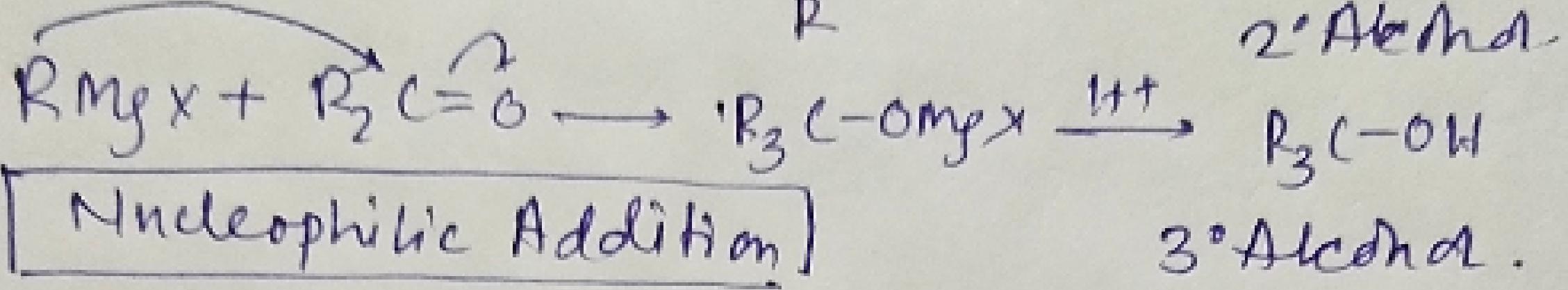
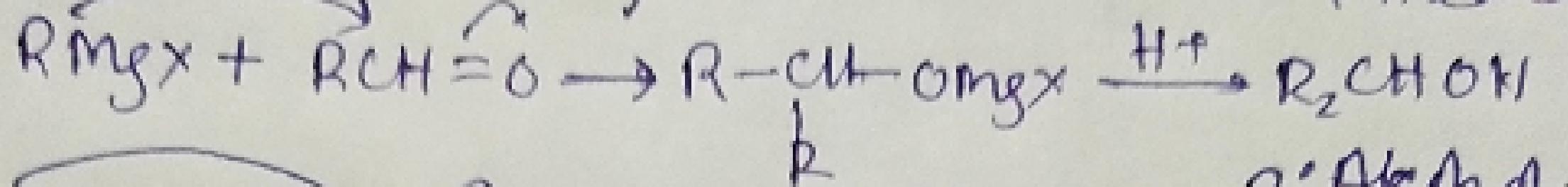
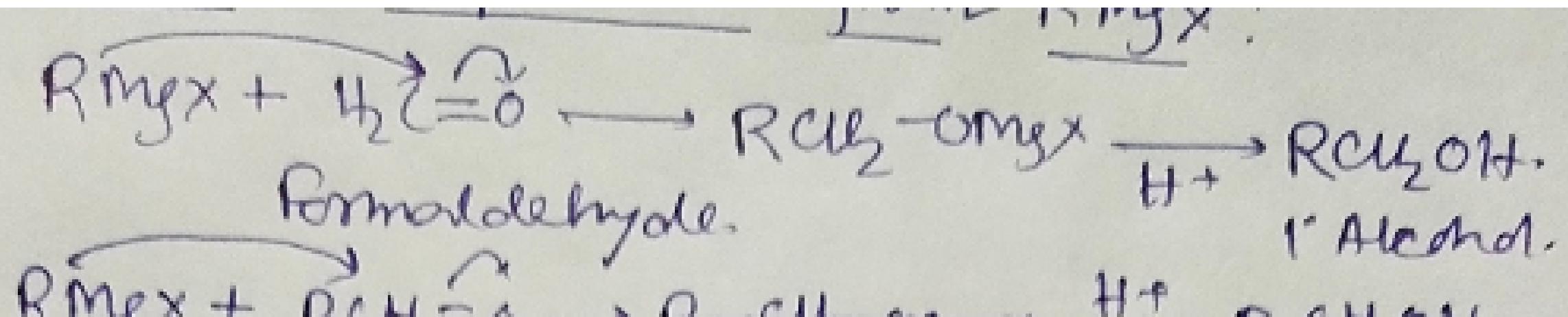
+ base & in every

In all cases Rmex acts as base & in every reaction RH is formed as product.

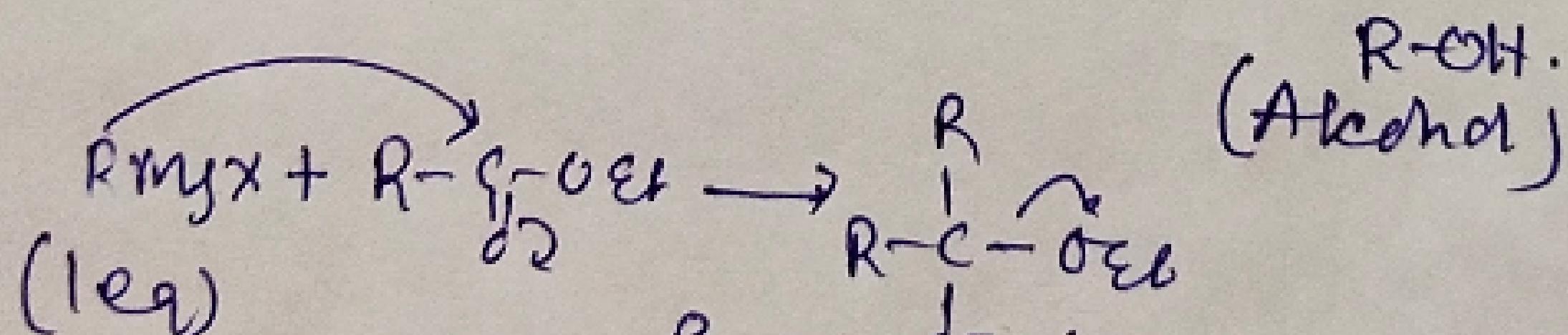
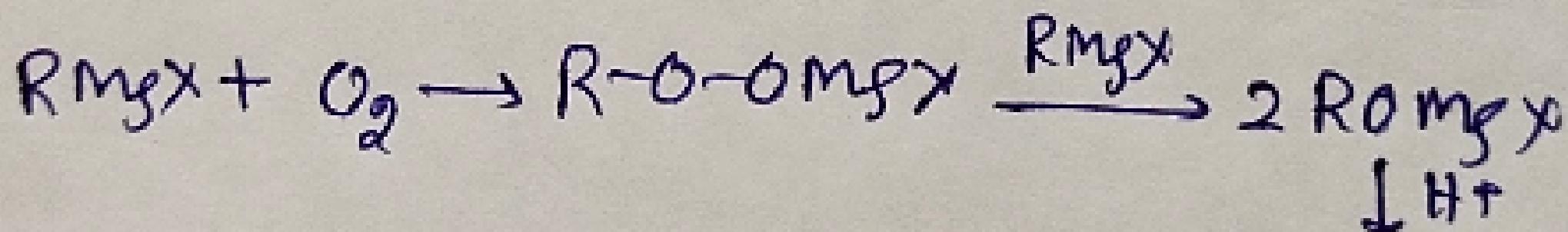


Reactions where RMgX act as nucleophile:

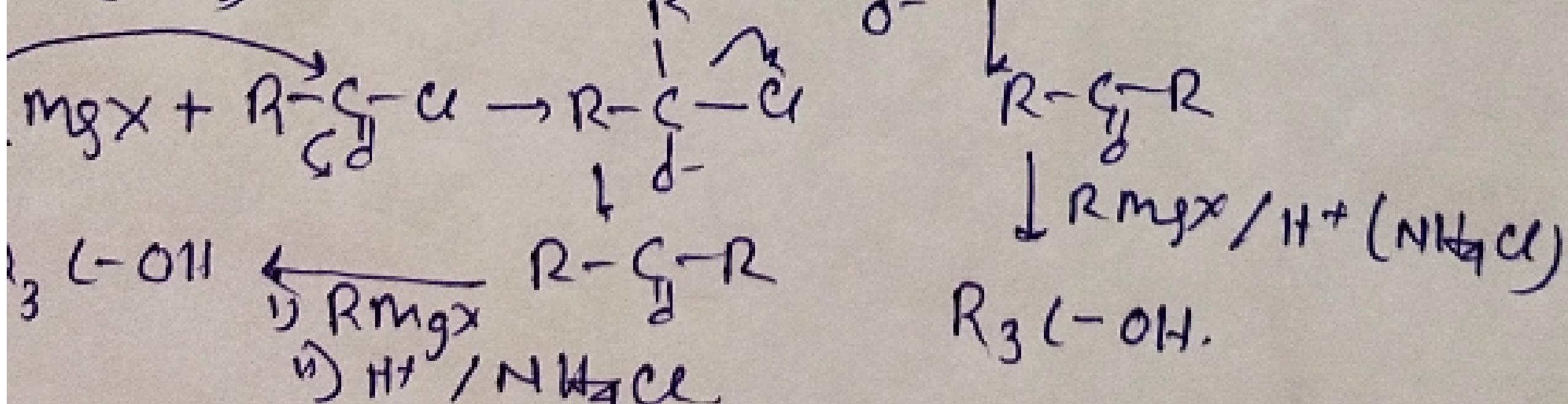




Substitution Reaction



$R-OH.$
(Alcohol)



$R-\overset{O^-}{C}-R$
 $\downarrow RMgX/H^+ (NH_4Cl)$

$R_3C-OH.$

ii) H^+/NH_4Cl

Reactivity order: $R-\text{C}_\delta-\text{H} > R-\text{C}_\delta-\text{O}-\text{C}_\delta-\text{R} > R-\text{C}_\delta-\text{OR}$.

More is the δ^+ charge on carbonyl carbon 32
more will be the reactivity.

In all cases, using 1 eq. RMgX ; $R-\text{C}_\delta-\text{R}$ is favored.

using 2 eq. RMgX , $\text{R}_3\text{C}-\text{OH}$ (3° alcohol) is favored.

$\text{R}-\text{C}_\delta-\text{MIBr} > \text{R}-\text{C}_\delta-\text{H} > \text{R}-\text{C}_\delta-\text{O}-\text{C}_\delta-\text{R} > \text{R}-\text{C}_\delta-\text{OR} > \text{R}-\text{C}_\delta-\text{NR}_2$

Reactivity order towards RMgX .

a) $\text{H}-\text{CH}=\text{O} > \text{CH}_3-\text{C}_\delta-\text{H} > \text{CH}_3-\text{C}_\delta-\text{CH}_3$.

b) $\text{CH}_3-\text{C}_\delta-\text{CH}_3 > \text{CH}_3-\text{C}_\delta-\text{Ph} > \text{Ph}-\text{C}_\delta-\text{Ph}$.

c)

$\text{C}_\delta=\text{O}$	$\text{C}_\delta=\text{O}$	$\text{C}_\delta=\text{O}$	$\text{C}_\delta=\text{O}$	$\text{C}_\delta=\text{O}$

$>$ $>$ $>$ $>$

a) Total no. g equivalent g
 RMgX consumed -

b) c)

d)

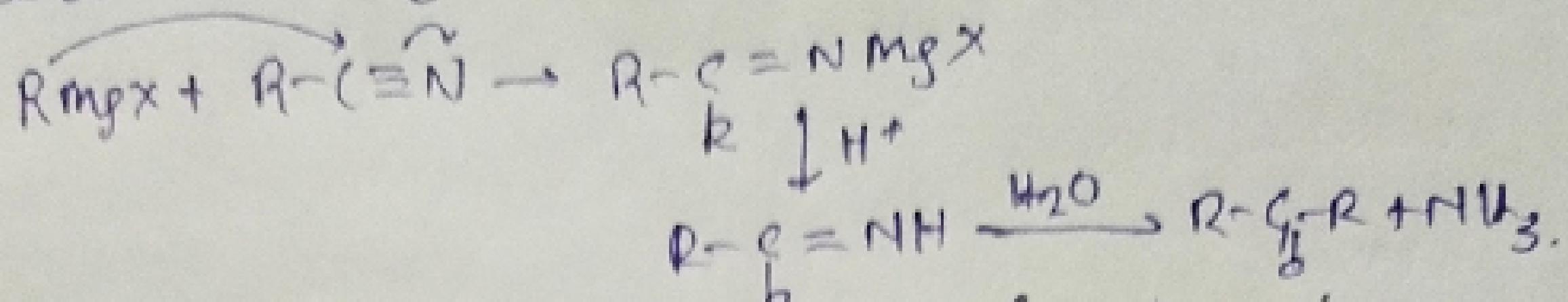
e)

f)

g)

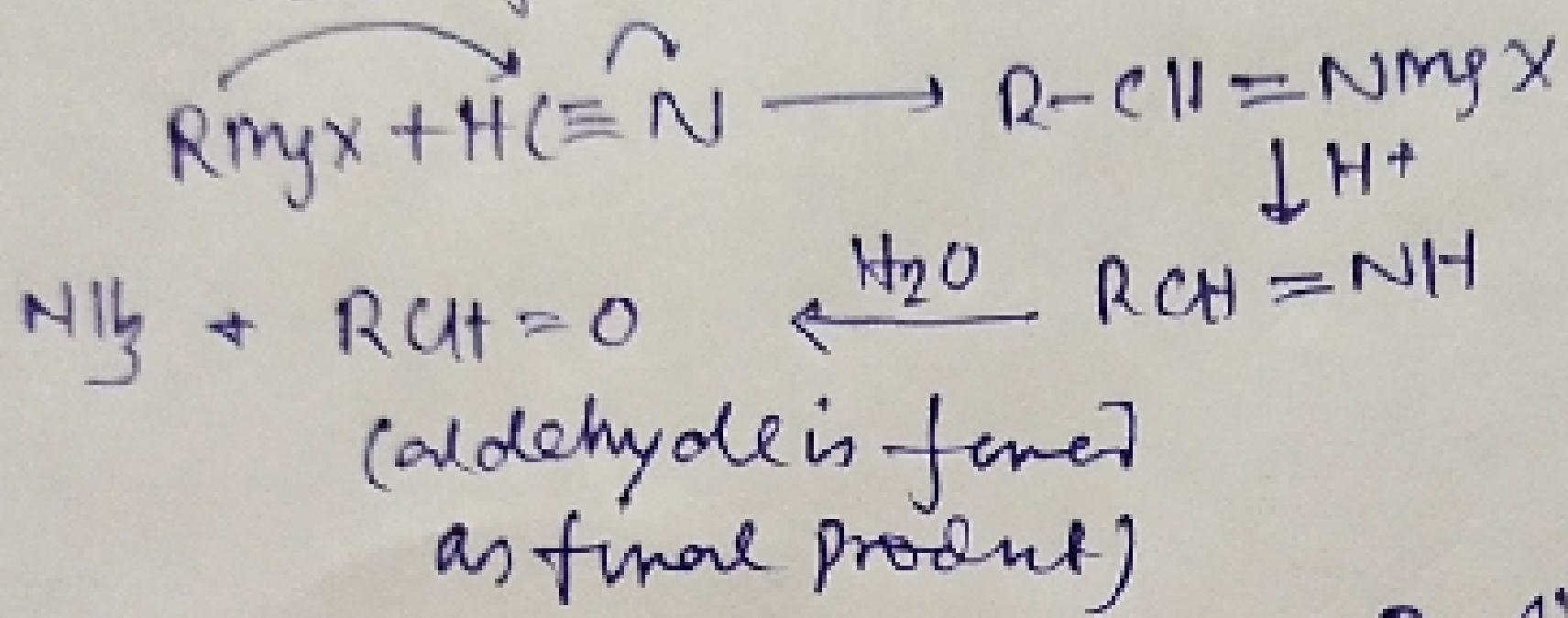
33

: Reaction with nitrile $R-C\equiv N^+$:

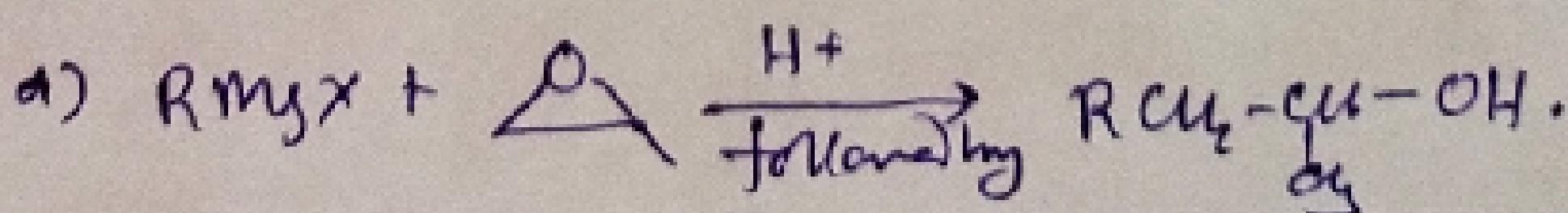
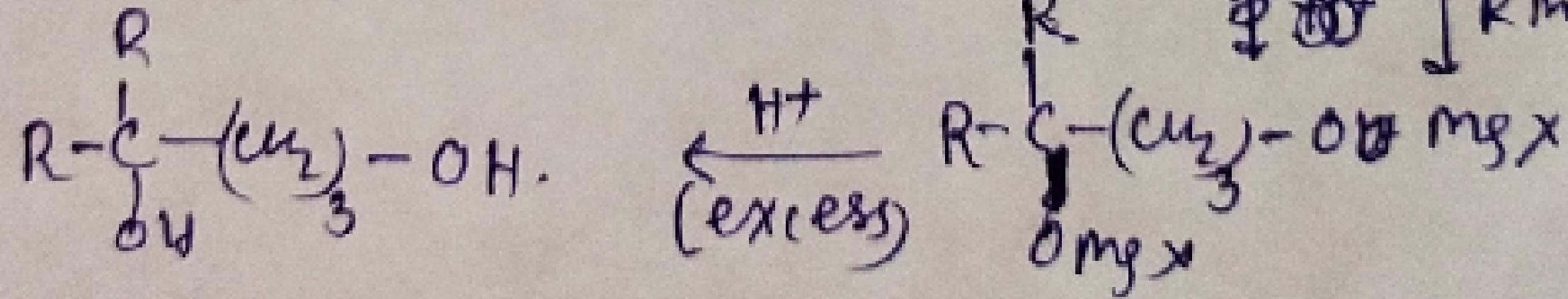
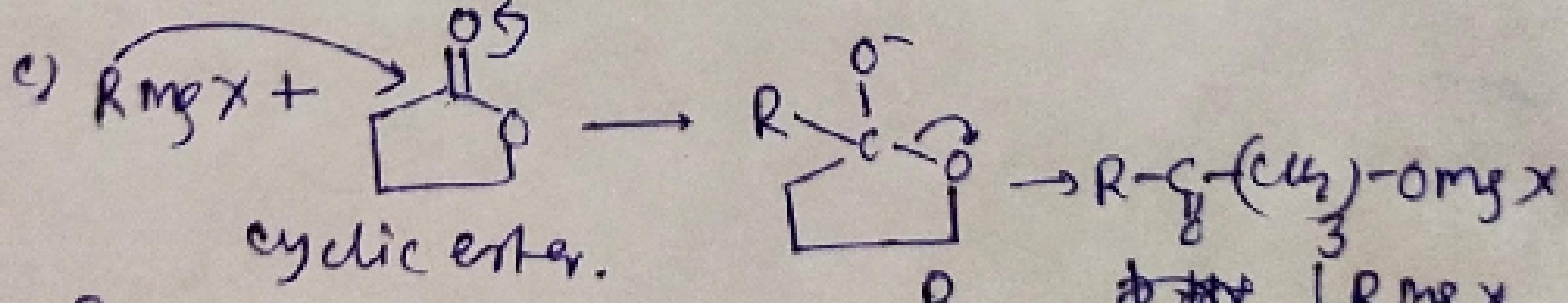
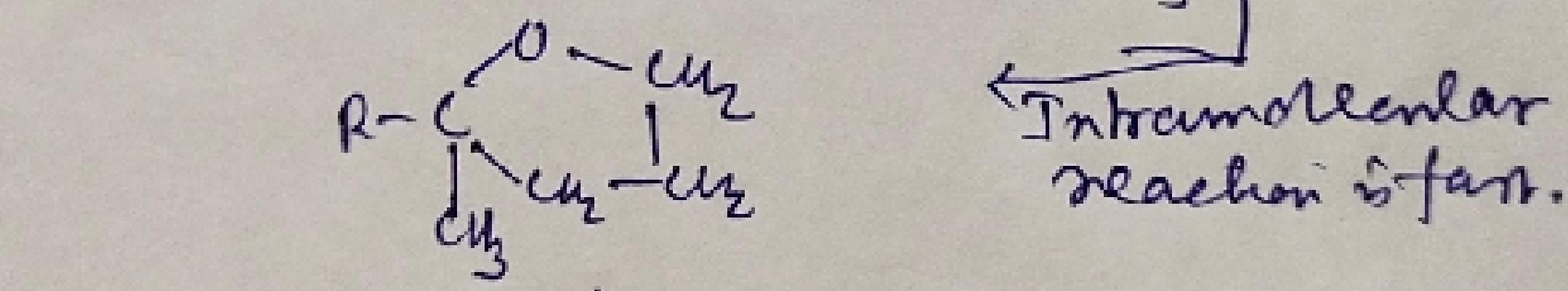
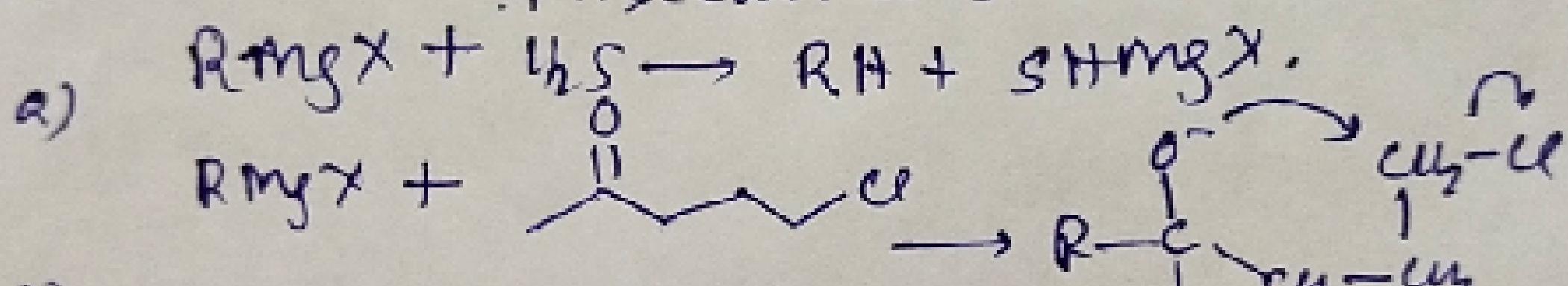


Once H_2O /protic solvent
is used, Rm^{x} can not be
used further.

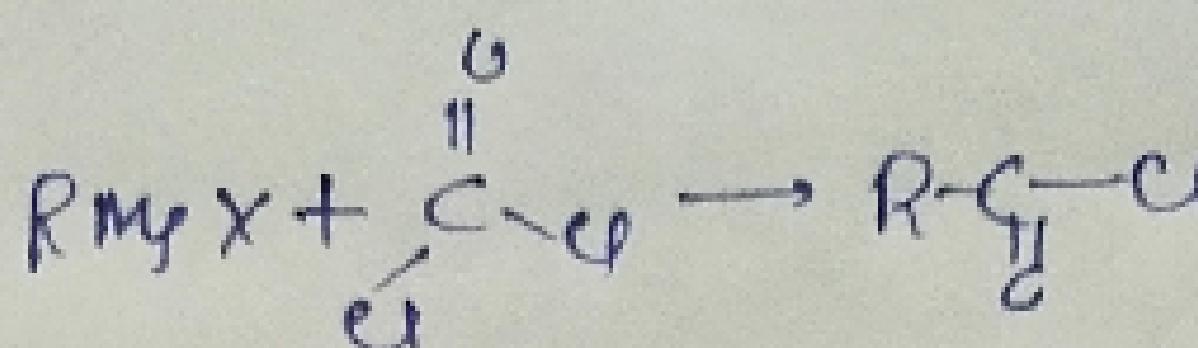
(Ketene is
the final
product)



Miscellaneous Questions:



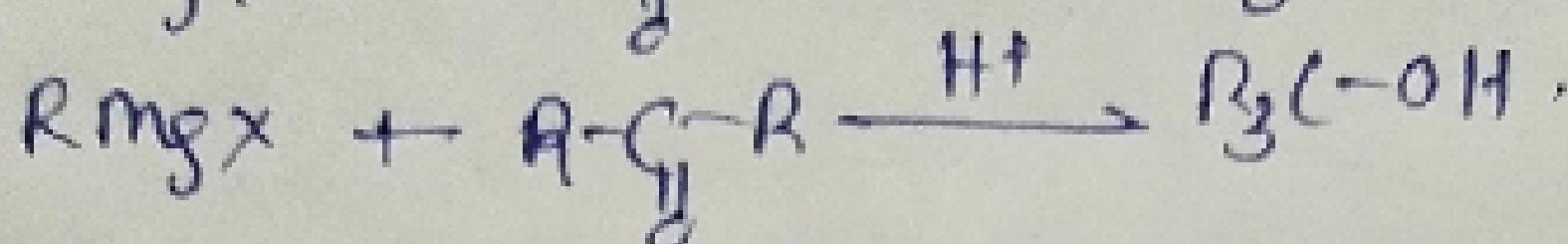
34



[3 eq. of $RMgX$ is consumed]



[for complete reaction].



Similarly for following compound 3 eq. of $RMgX$ is consumed.

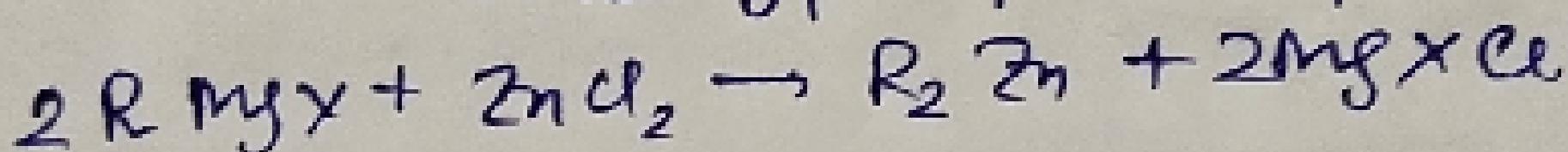
$Cl-C(=O)OC_2H_5$ (chloro ester); $EtO-C(=O)OC_2H_5$ (Diethyl carbonate).



organo
metallic
Compound.

Another organo
metallic compound

Same type of example.



Other than $RMgX$, organometallic compound known are as follows: i) R_2Cd (Diethyl Cadmium)

ii) R_2Zn (Diethyl zinc).

iii) RLi (alkyl Lithium)

iv) R_2CuLi (Gilman's Reagent).

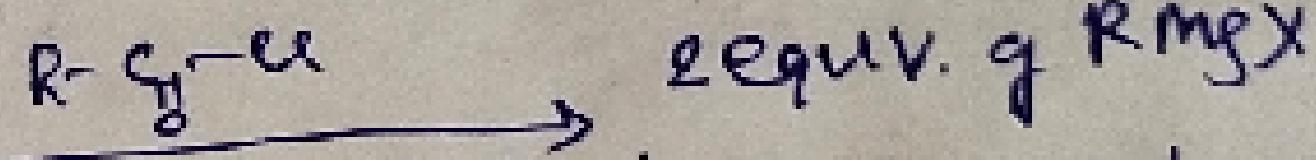
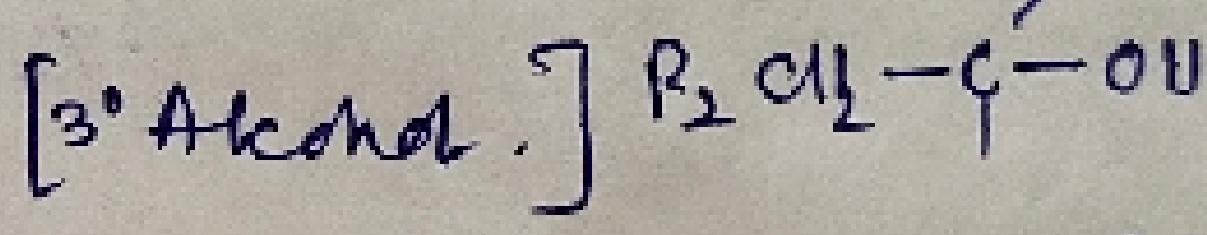
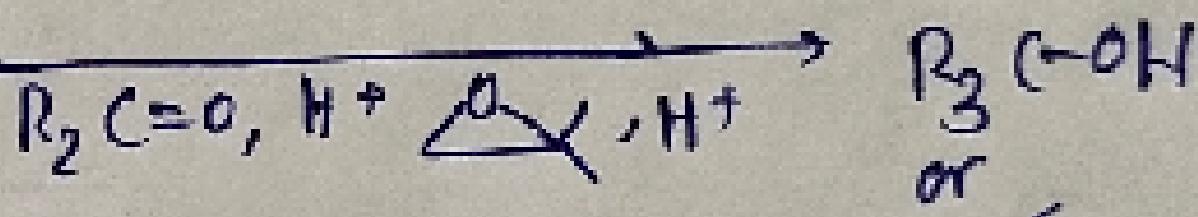
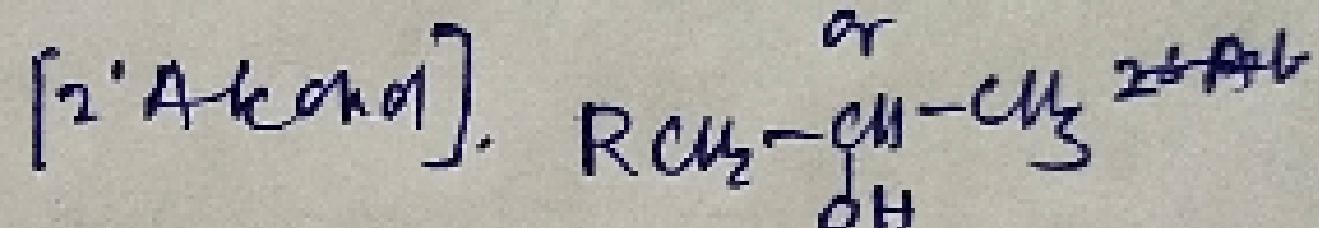
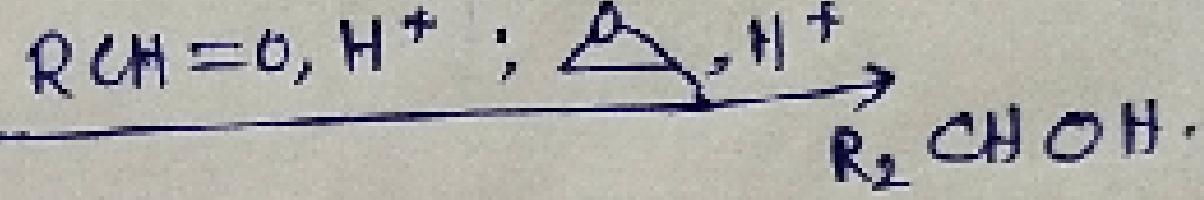
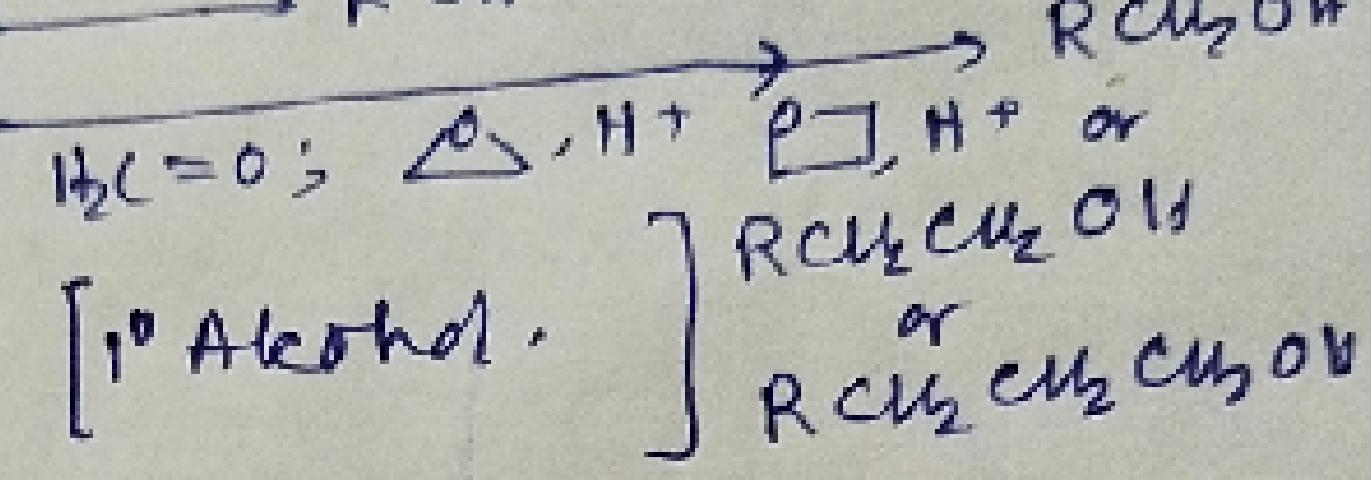
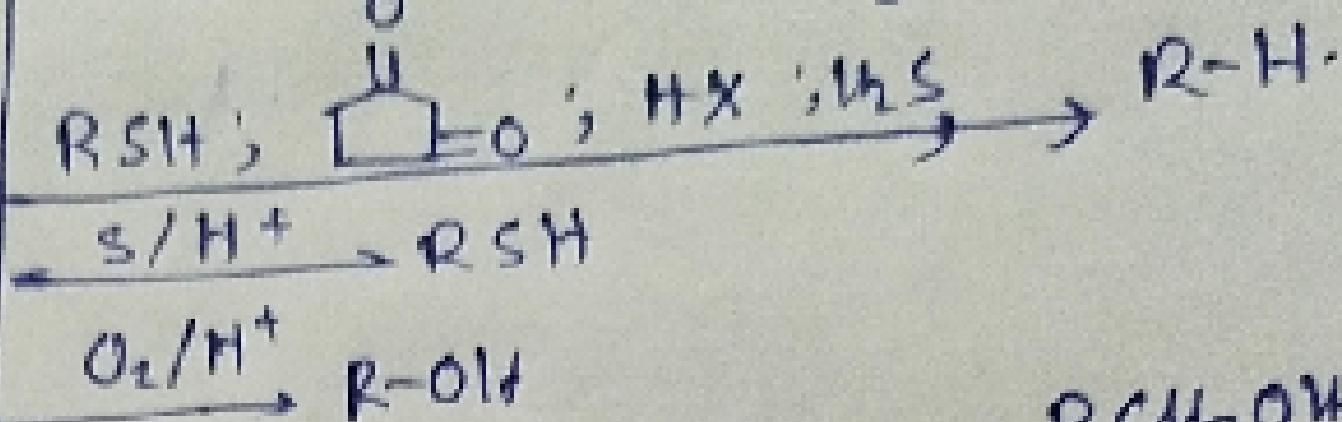
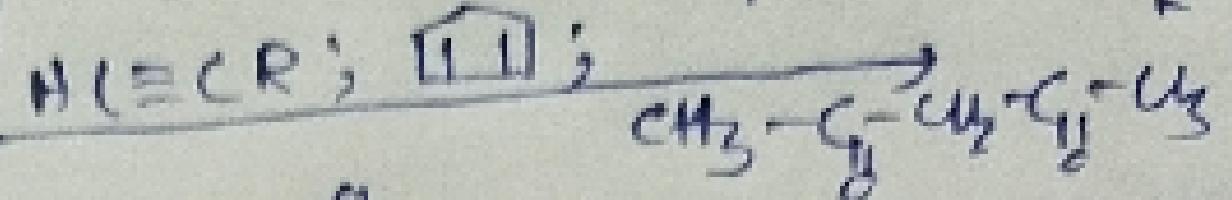
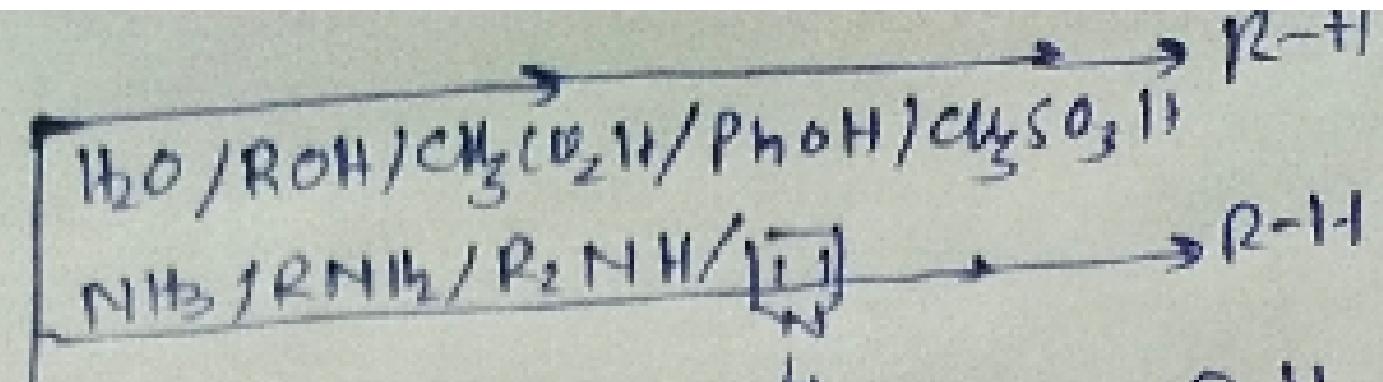
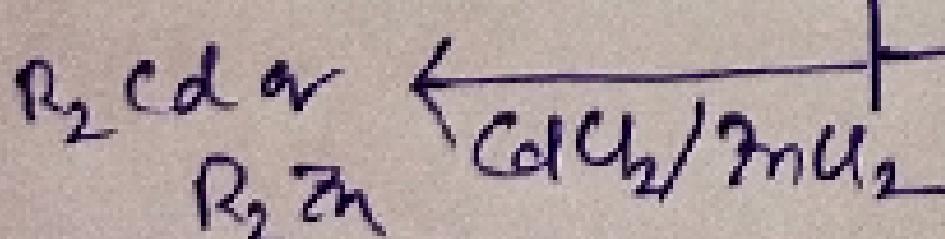
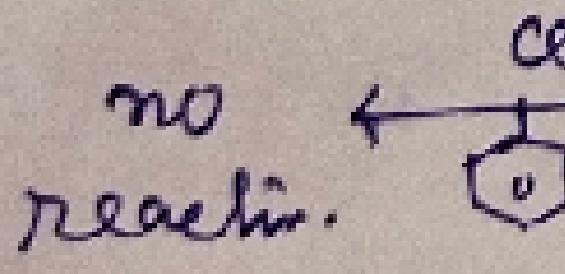
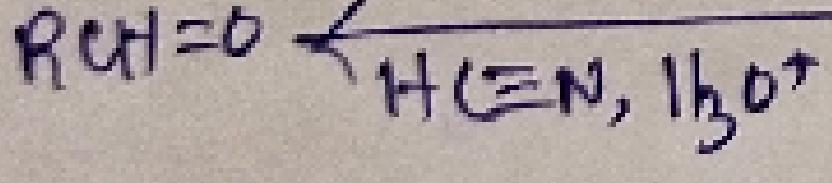
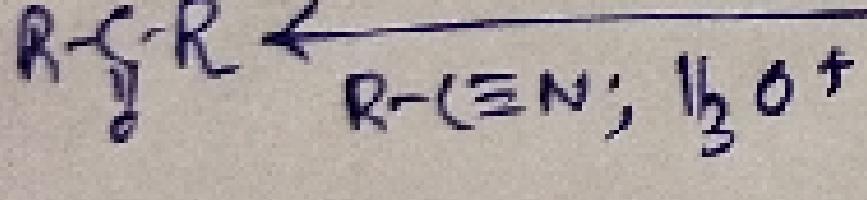
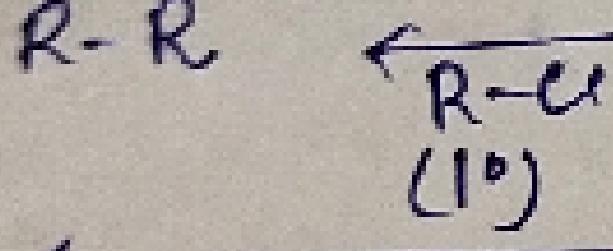
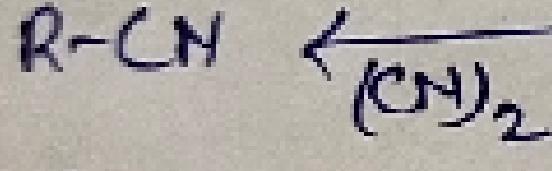
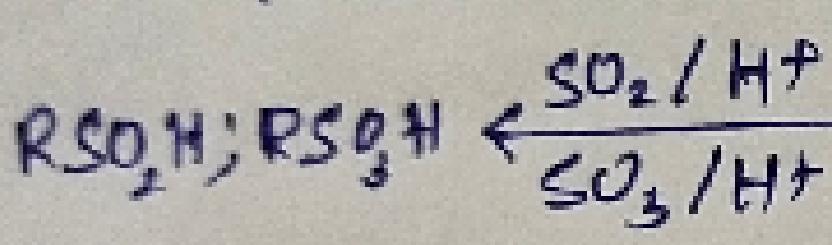
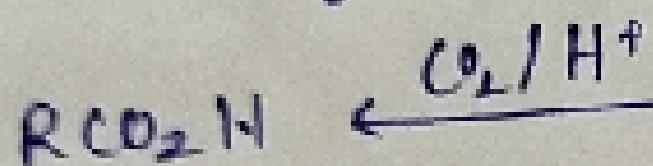
v) Diethyl lithium cuprate.

All have C-M linkage. All are good sources of carbanion.

no reaction
All are
example

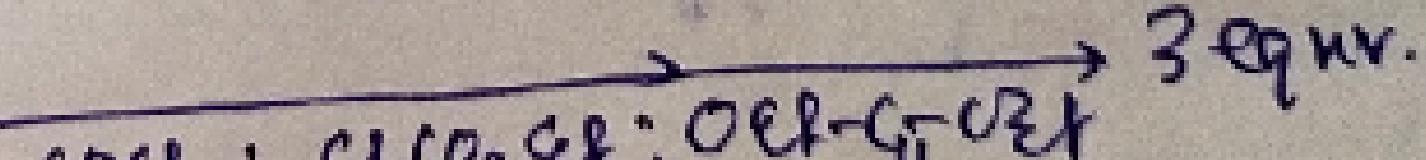
of
nucleo

phile & also
does not have RMgX
acidic hydrogen.



R-Sg-O-Sg-R is consumed.

R-Sg-OR See the final
 R-Sg-MR_2 product is
 $\text{R}_3\text{C-OH}$



of RMgX is consumed.

$\text{R}_3\text{C-OH.}$ is formed.