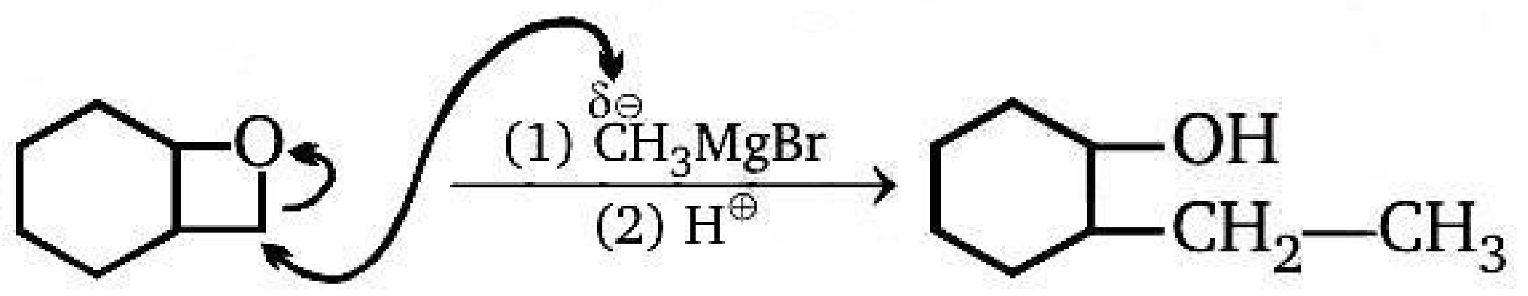
3 Grignard Reagent

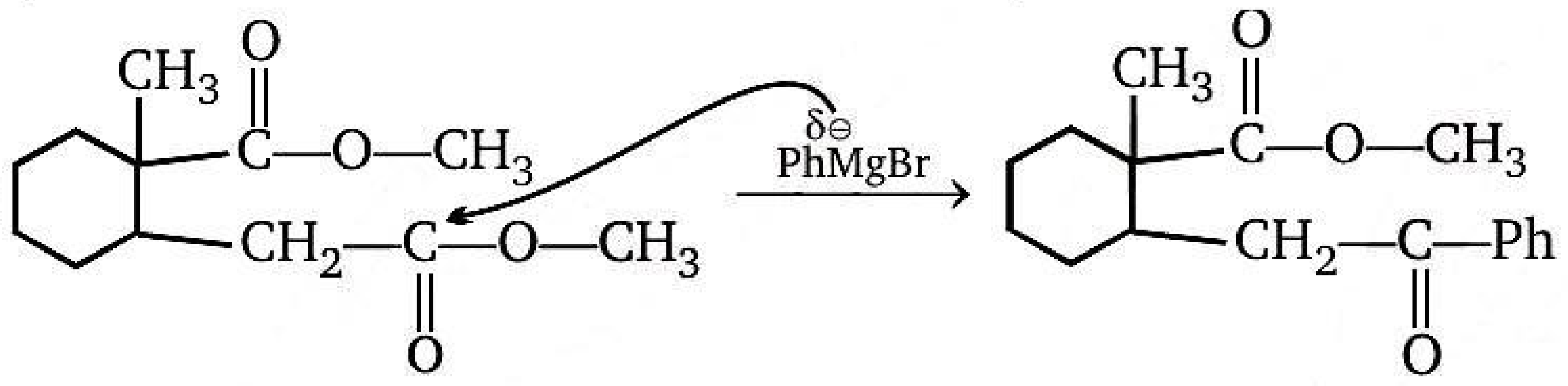
Level - 1

1. (b)



(Less steric hindered carbon will attack) 'Me' attack at less hindered 'C' atom

2. (d)



less steric hindered ester will be attacked.

3. (b) Reaction (1) $x = 6$

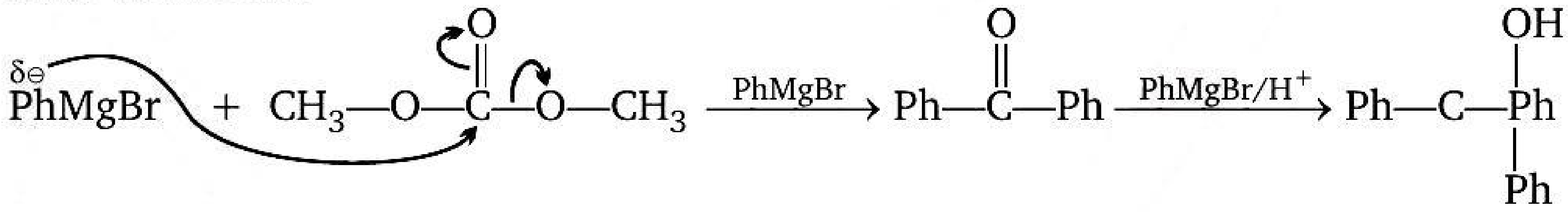
2 mole of CH_3MgBr act as a base 4 mole of CH_3MgBr act as a nucleophile

Reaction (2) $y = 3$

3 mole of CH_3MgBr act as a nucleophile.

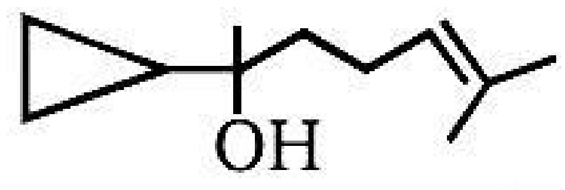
4. (d) (a), (b) are example of nucleophilic addition reaction of GR on aldehyde while in (c) GR adds on ketone.

5. (c)

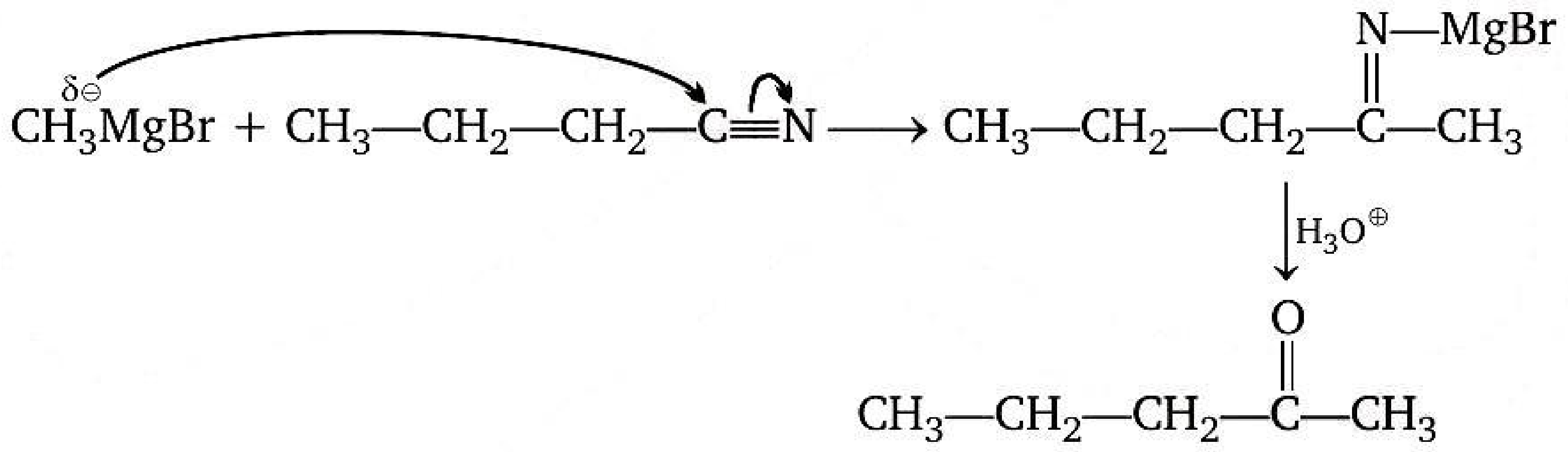


$$\overset{\delta\ominus}{Ph}MgBr + CH_3-O-\overset{O}{\overset{\|}{C}}-O-CH_3 \xrightarrow{PhMgBr} Ph-\overset{O}{\overset{\|}{C}}-Ph \xrightarrow{PhMgBr/H^+} Ph-\underset{Ph}{\overset{OH}{C}}-Ph$$

6. (d) In (i), (ii) and (iii), nucleophilic - addition take place to form compound

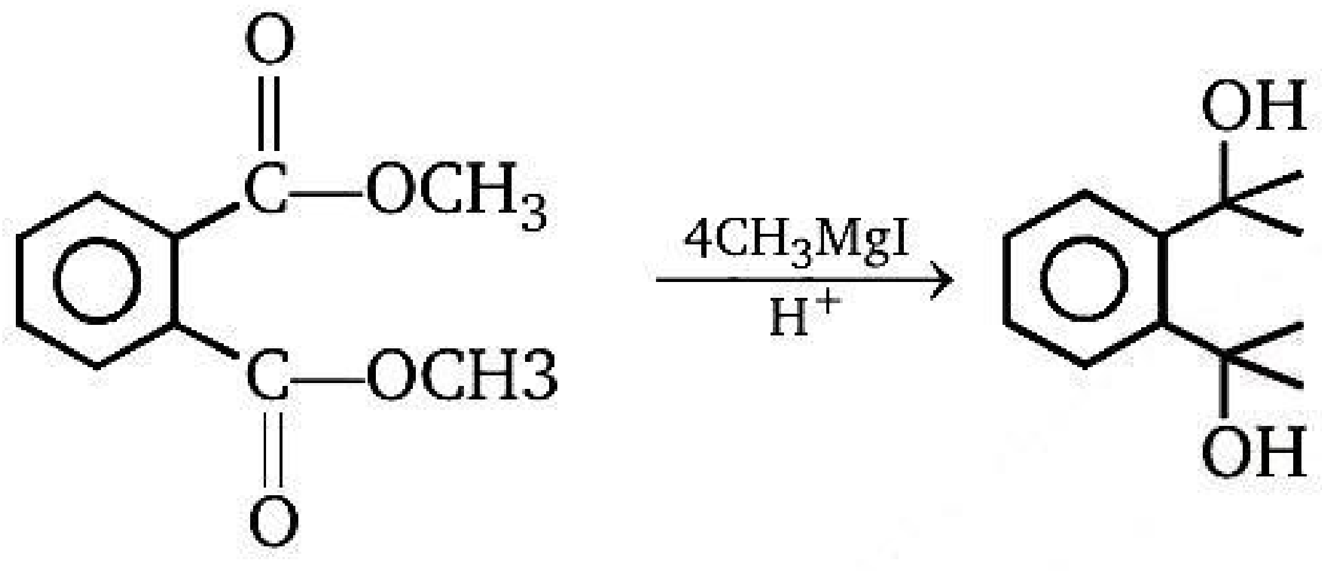


7. (c)

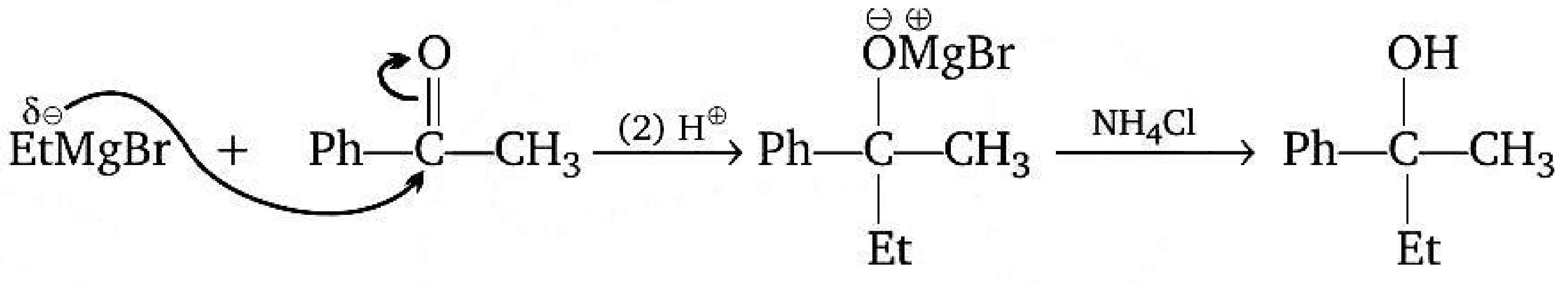


$$\overset{\delta\ominus}{CH_3}MgBr + CH_3-CH_2-CH_2-C\equiv N \longrightarrow CH_3-CH_2-CH_2-\overset{N-MgBr}{\overset{\|}{C}}-CH_3 \xrightarrow{H_3O^{\oplus}} CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

8. (c)

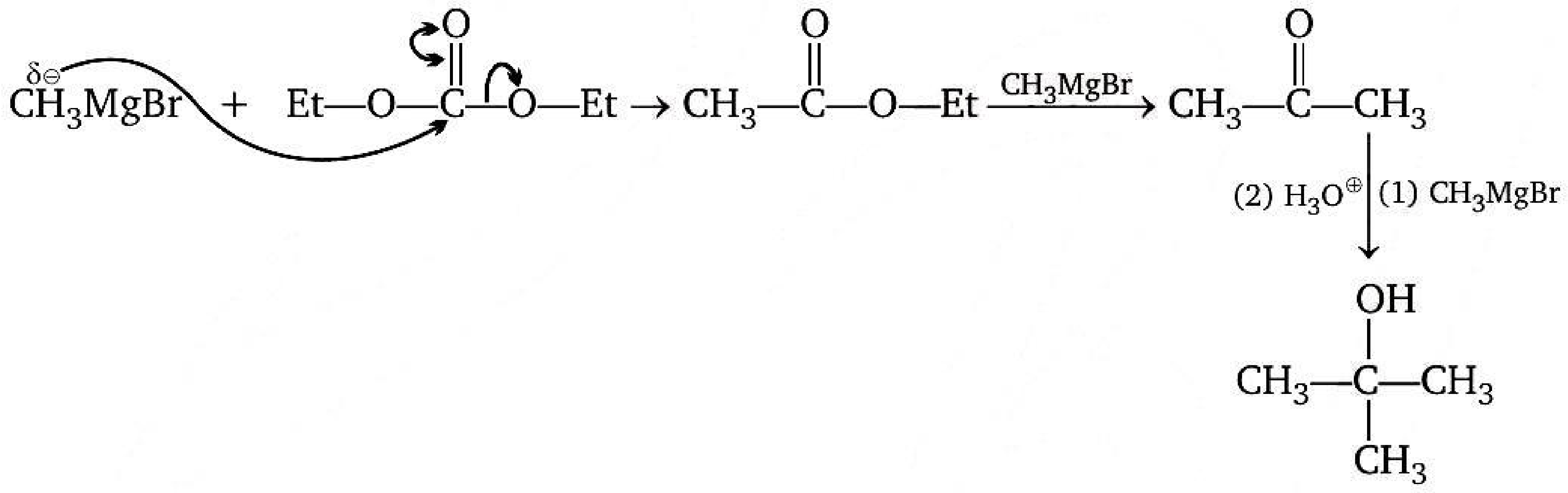


9. (b)



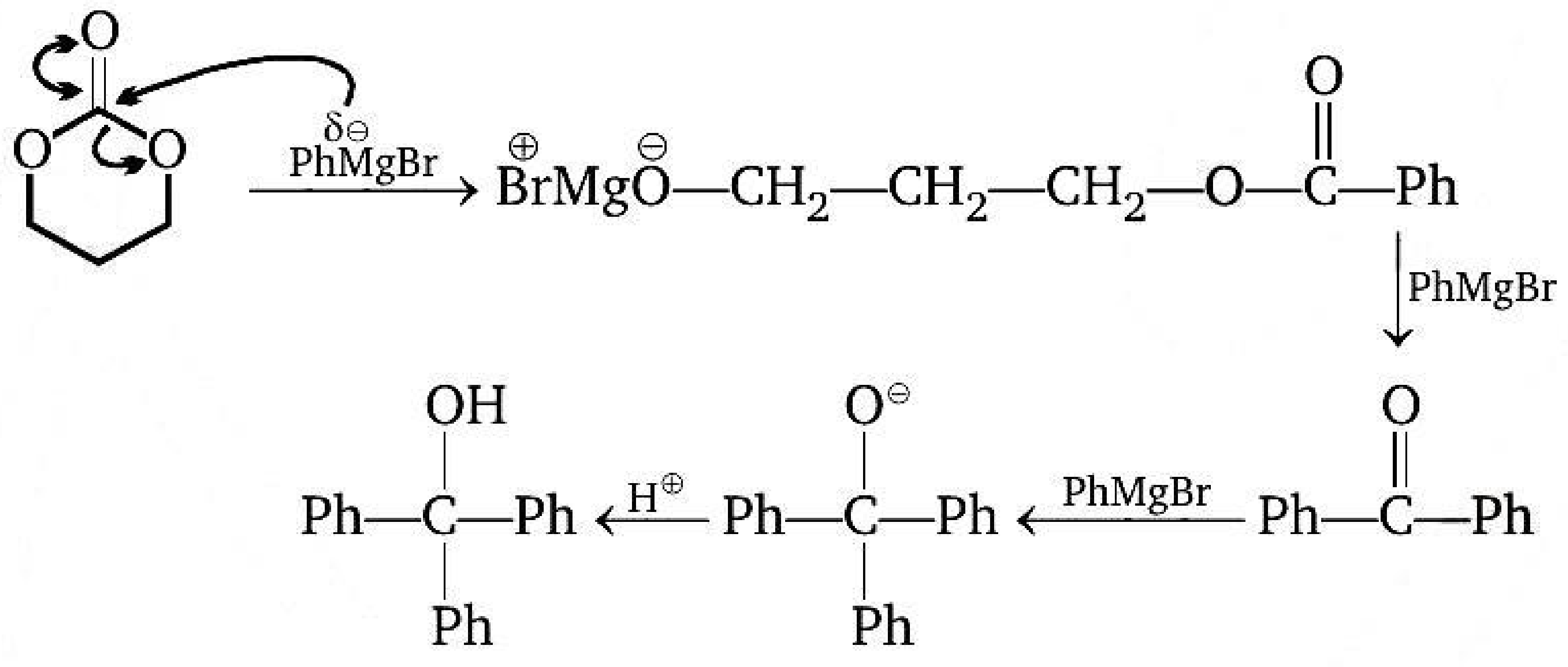
$$\overset{\delta\ominus}{\text{EtMgBr}} + \text{Ph—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—CH}_3 \xrightarrow{(2)\ \text{H}^{\oplus}} \text{Ph—}\underset{\text{Et}}{\underset{|}{\overset{\overset{\ominus\ \oplus}{\text{OMgBr}}}{\overset{|}{\text{C}}}}}\text{—CH}_3 \xrightarrow{\text{NH}_4\text{Cl}} \text{Ph—}\underset{\text{Et}}{\underset{|}{\overset{\text{OH}}{\overset{|}{\text{C}}}}}\text{—CH}_3$$

10. (c)



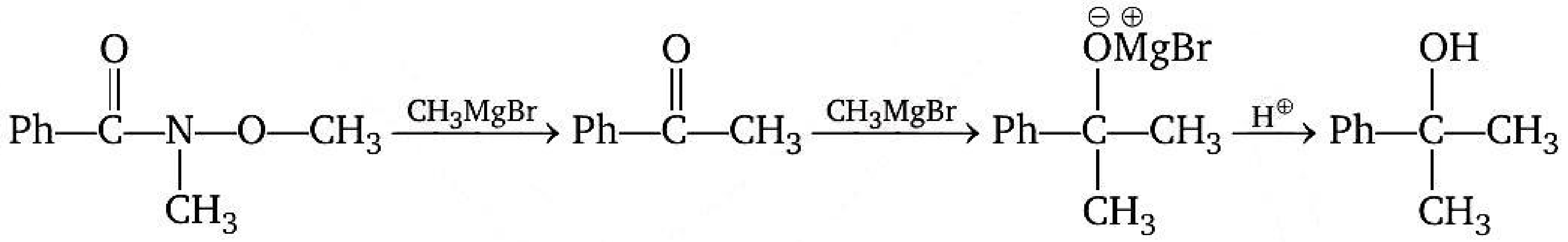
$$\overset{\delta\ominus}{\text{CH}_3\text{MgBr}} + \text{Et—O—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—O—Et} \rightarrow \text{CH}_3\text{—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—O—Et} \xrightarrow{\text{CH}_3\text{MgBr}} \text{CH}_3\text{—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—CH}_3 \xrightarrow[(2)\ \text{H}_3\text{O}^{\oplus}]{(1)\ \text{CH}_3\text{MgBr}} \text{CH}_3\text{—}\underset{\text{CH}_3}{\underset{|}{\overset{\text{OH}}{\overset{|}{\text{C}}}}}\text{—CH}_3$$

11. (b)



$$\xrightarrow{\overset{\delta\ominus}{\text{PhMgBr}}} \overset{\oplus}{\text{BrMg}}\overset{\ominus}{\text{O}}\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—O—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—Ph} \xrightarrow{\text{PhMgBr}} \text{Ph—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—Ph} \xrightarrow{\text{PhMgBr}} \text{Ph—}\underset{\text{Ph}}{\underset{|}{\overset{\text{O}^{\ominus}}{\overset{|}{\text{C}}}}}\text{—Ph} \xrightarrow{\text{H}^{\oplus}} \text{Ph—}\underset{\text{Ph}}{\underset{|}{\overset{\text{OH}}{\overset{|}{\text{C}}}}}\text{—Ph}$$

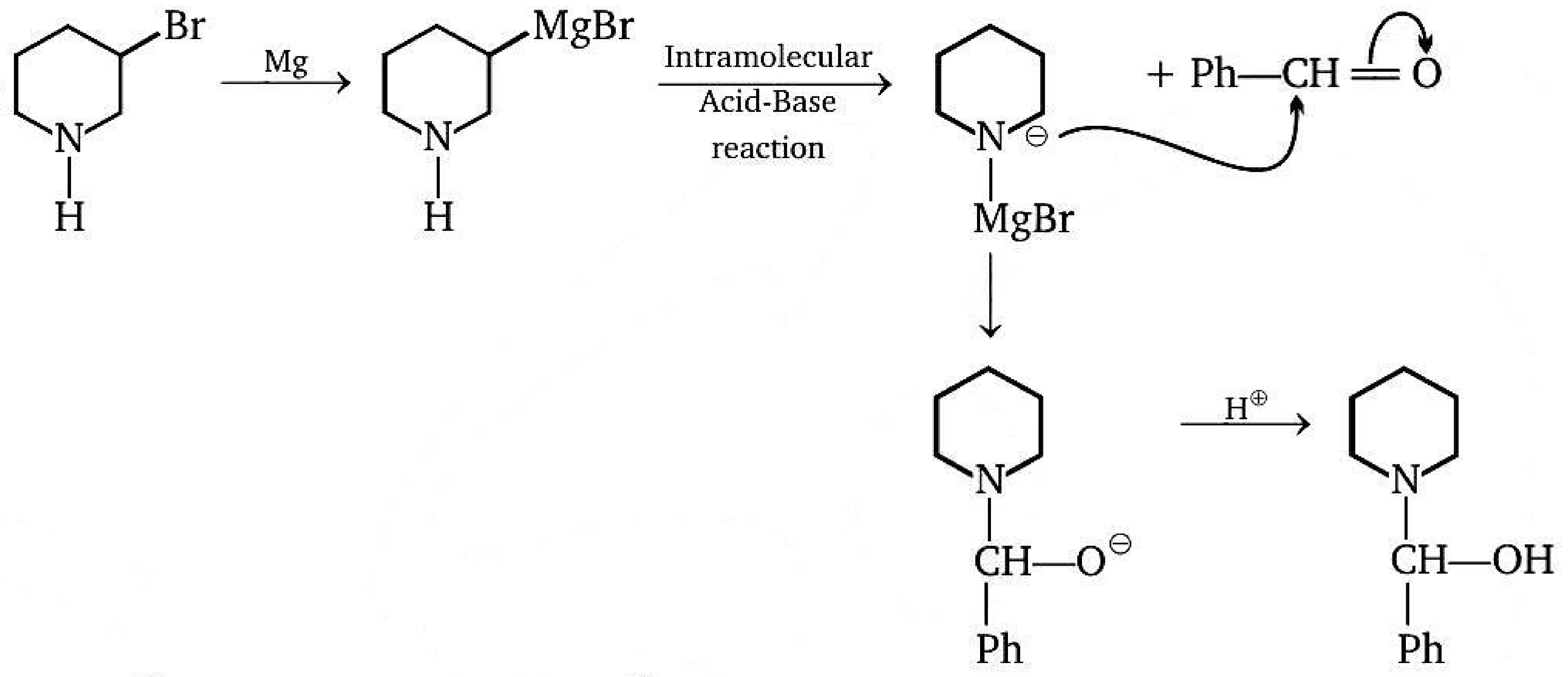
12. (b)



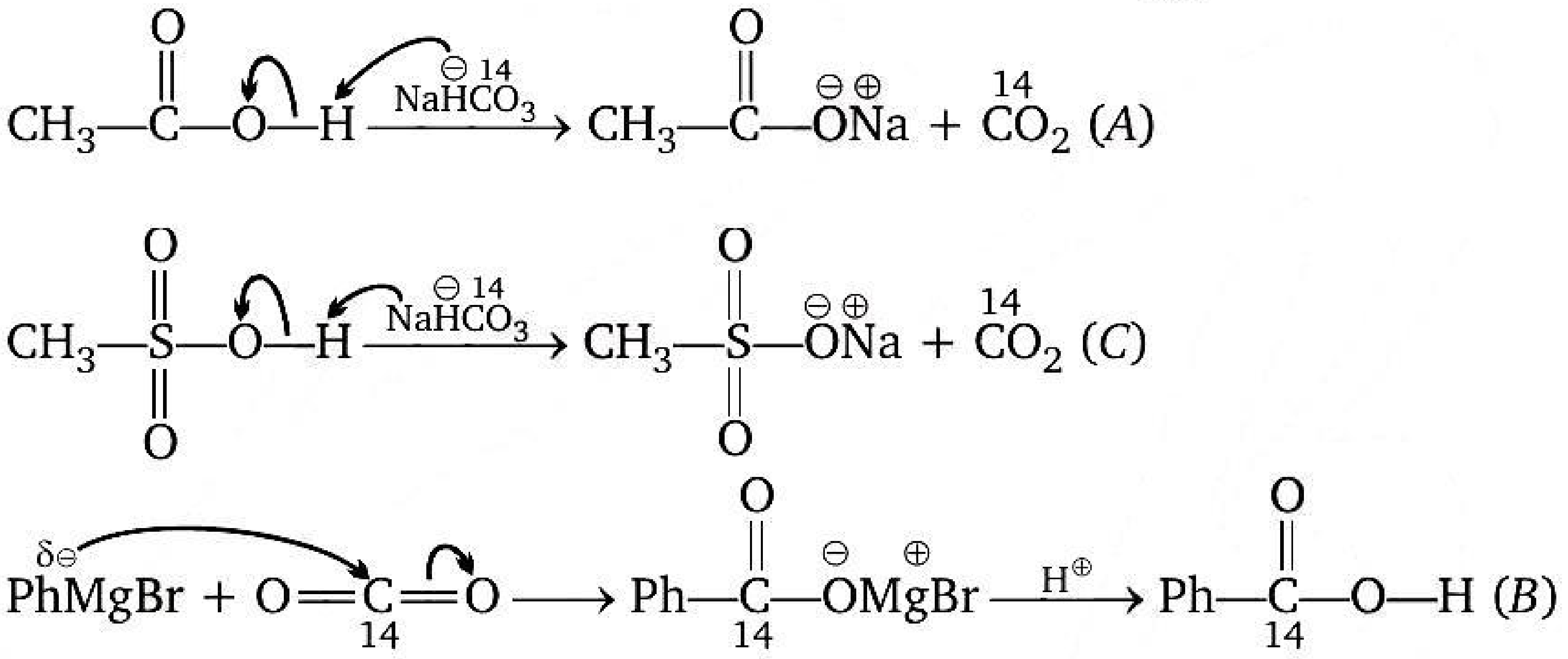
$$\text{Ph—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—}\underset{\text{CH}_3}{\underset{|}{\text{N}}}\text{—O—CH}_3 \xrightarrow{\text{CH}_3\text{MgBr}} \text{Ph—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—CH}_3 \xrightarrow{\text{CH}_3\text{MgBr}} \text{Ph—}\underset{\text{CH}_3}{\underset{|}{\overset{\overset{\ominus\ \oplus}{\text{OMgBr}}}{\overset{|}{\text{C}}}}}\text{—CH}_3 \xrightarrow{\text{H}^{\oplus}} \text{Ph—}\underset{\text{CH}_3}{\underset{|}{\overset{\text{OH}}{\overset{|}{\text{C}}}}}\text{—CH}_3$$

excess of CH_3MgBr is used to maximise the yield.

13. (b)



14. (c)

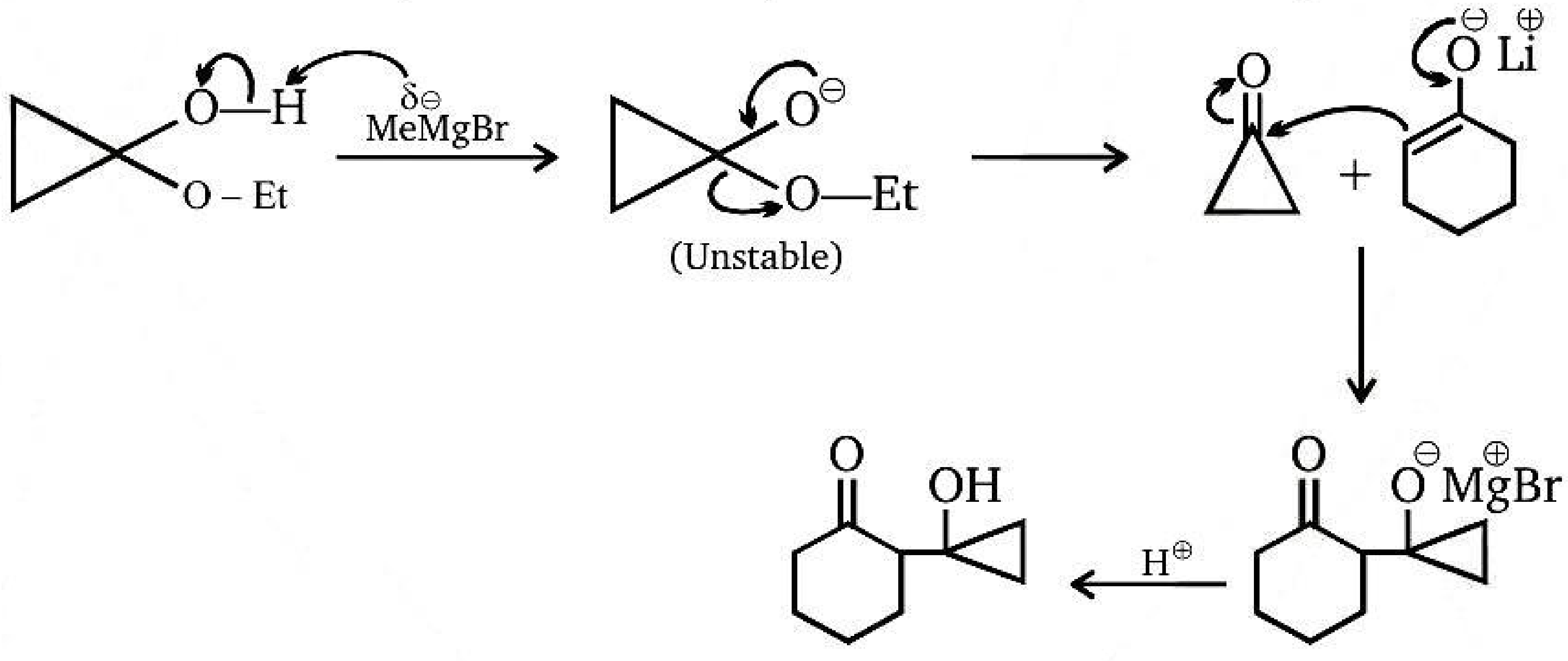


$$CH_3-\overset{\overset{O}{\|}}{C}-O-H \xrightarrow{\overset{\ominus\ 14}{NaHCO_3}} CH_3-\overset{\overset{O}{\|}}{C}-\overset{\ominus\oplus}{ONa} + \overset{14}{CO_2}\ (A)$$

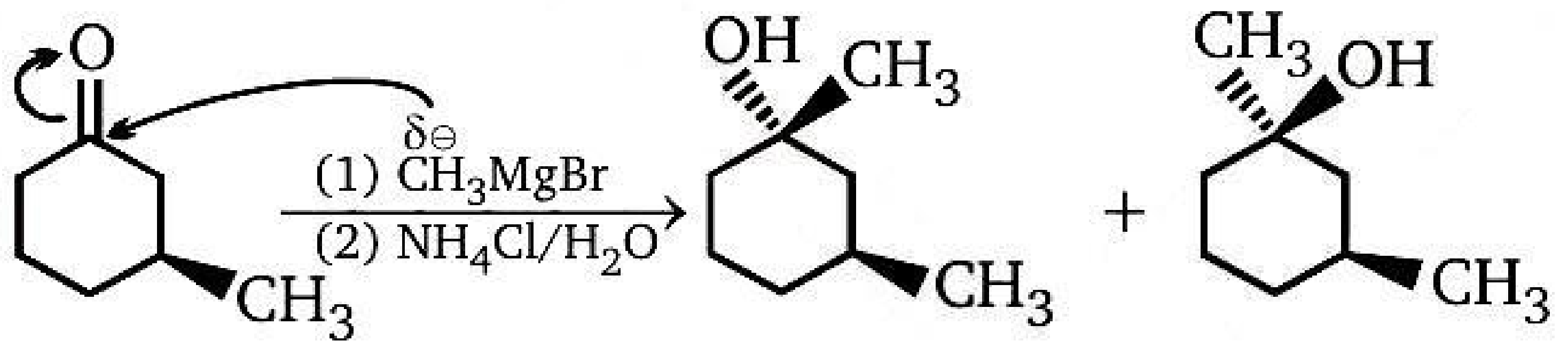
$$CH_3-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-H \xrightarrow{\overset{\ominus\ 14}{NaHCO_3}} CH_3-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-\overset{\ominus\oplus}{ONa} + \overset{14}{CO_2}\ (C)$$

$$\overset{\delta\ominus}{PhMgBr} + O=\underset{14}{C}=O \longrightarrow Ph-\underset{14}{\overset{\overset{O}{\|}}{C}}-\overset{\ominus}{O}\overset{\oplus}{MgBr} \xrightarrow{H^{\oplus}} Ph-\underset{14}{\overset{\overset{O}{\|}}{C}}-O-H\ (B)$$

15. (b)



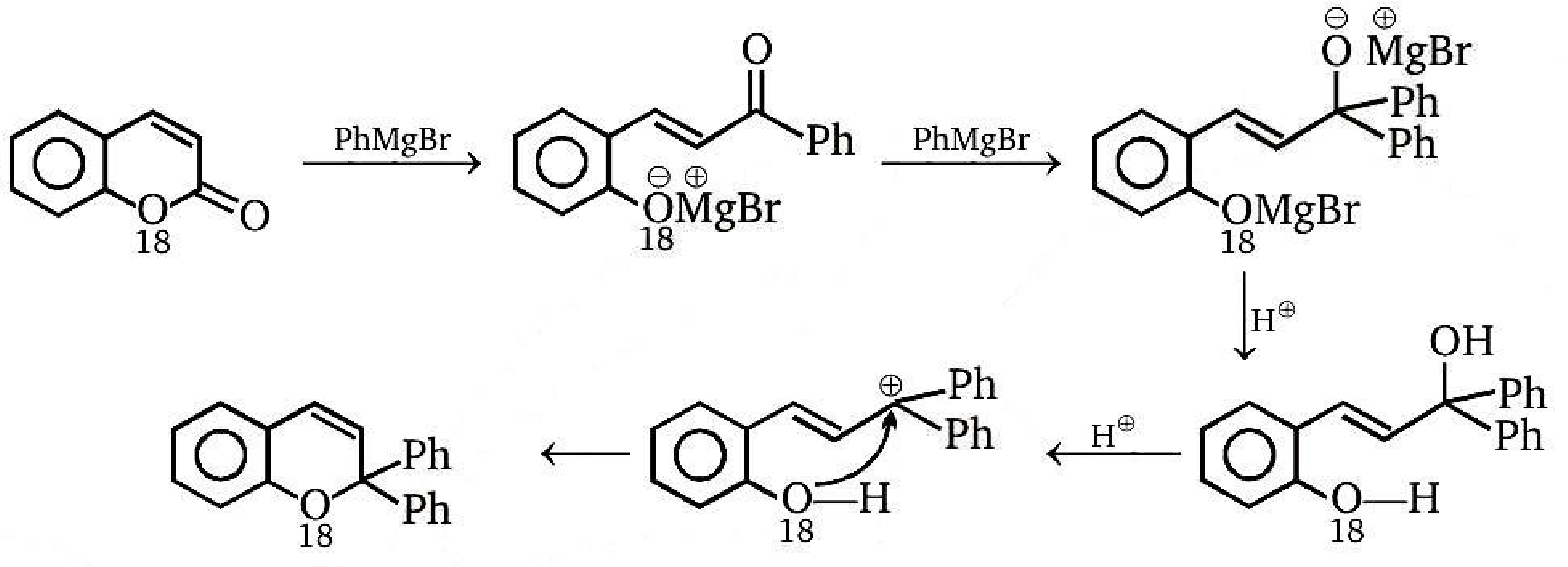
16. (b)



Diastereomers

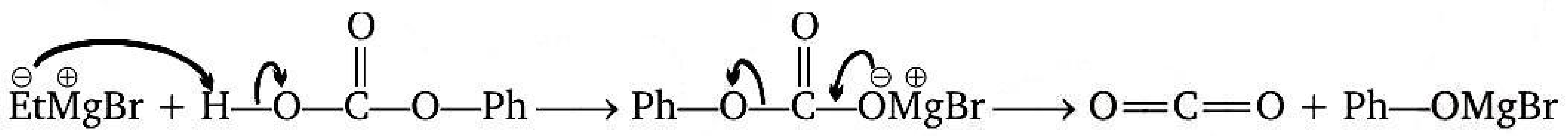
17. (d) All reactions are between Girgnard reagent and the reagents having ‘H’ or ‘D’
∴ all are acid-base reactions.

18. (d)



(B)

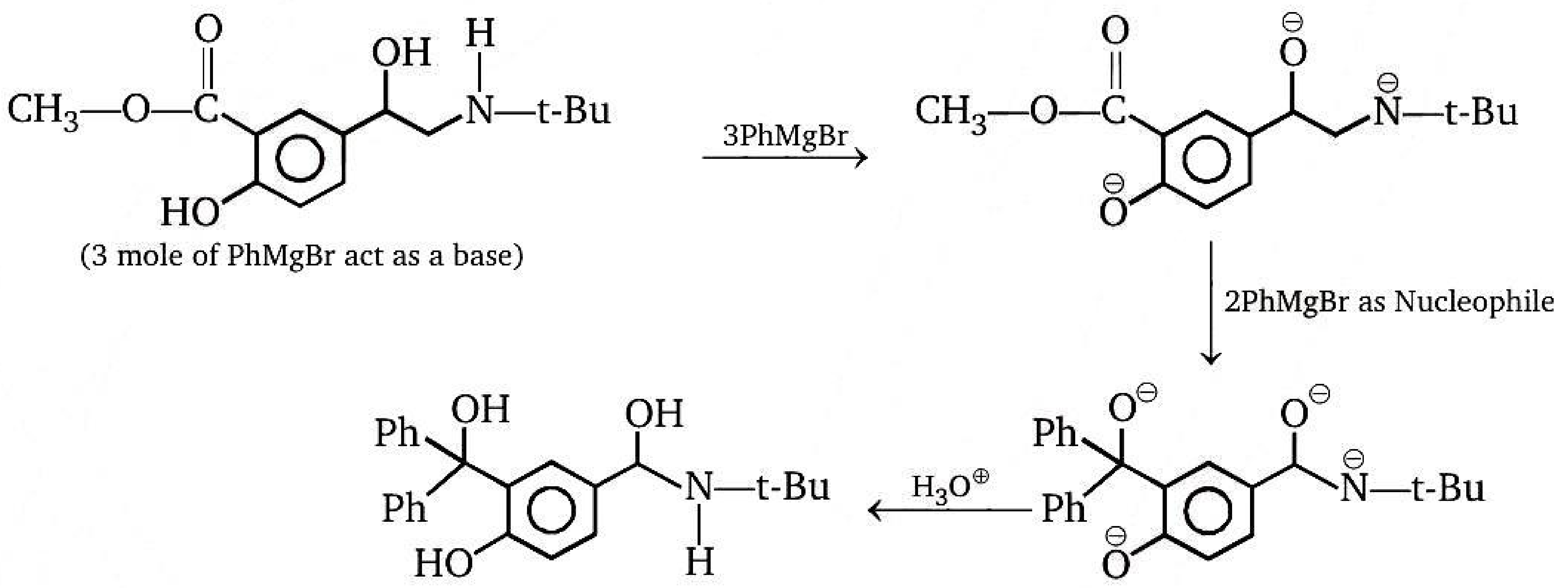
19. (d)



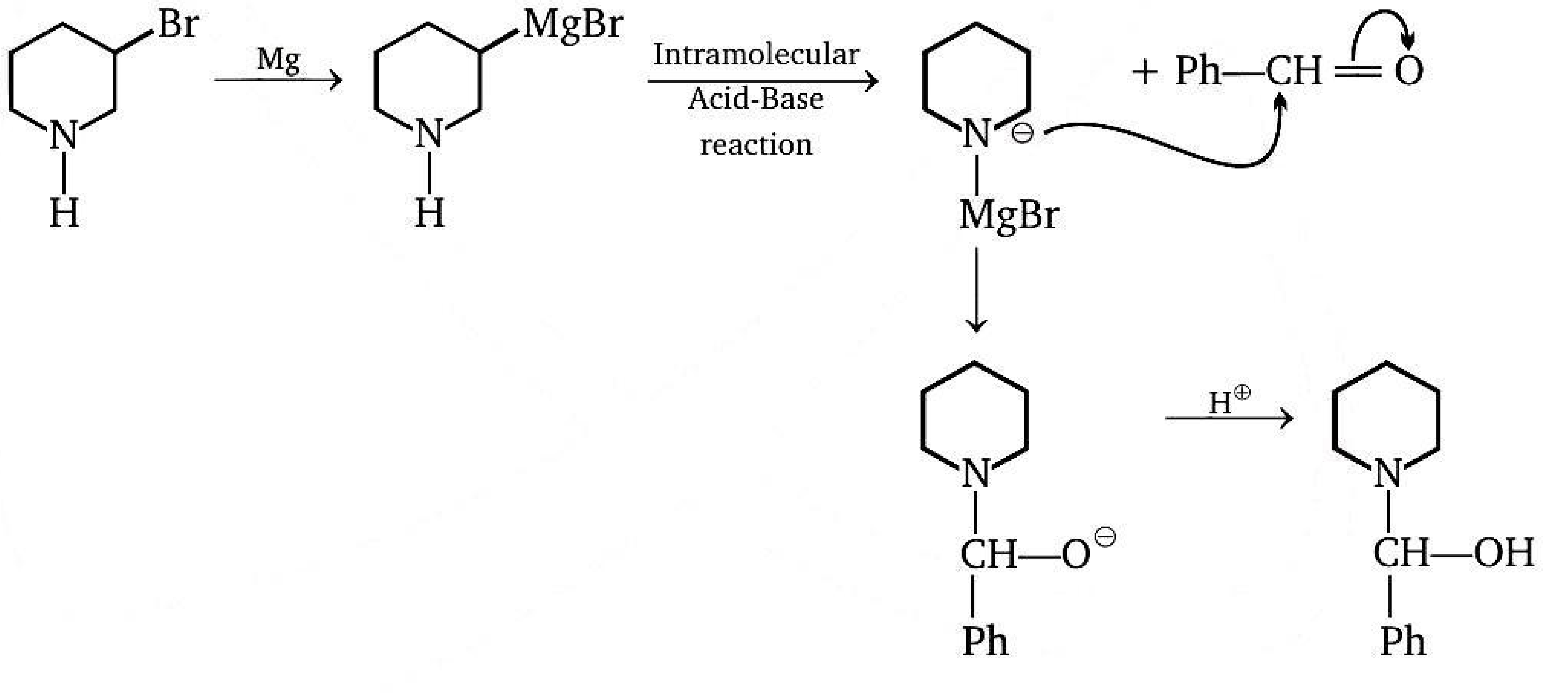
$$\overset{\ominus}{\text{Et}}\overset{\oplus}{\text{MgBr}} + \text{H}-\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{O}-\text{Ph} \longrightarrow \text{Ph}-\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\overset{\ominus}{\text{O}}\overset{\oplus}{\text{MgBr}} \longrightarrow \text{O}=\text{C}=\text{O} + \text{Ph}-\text{OMgBr}$$

20. (d) Benzene will not react with Grignard reagent.

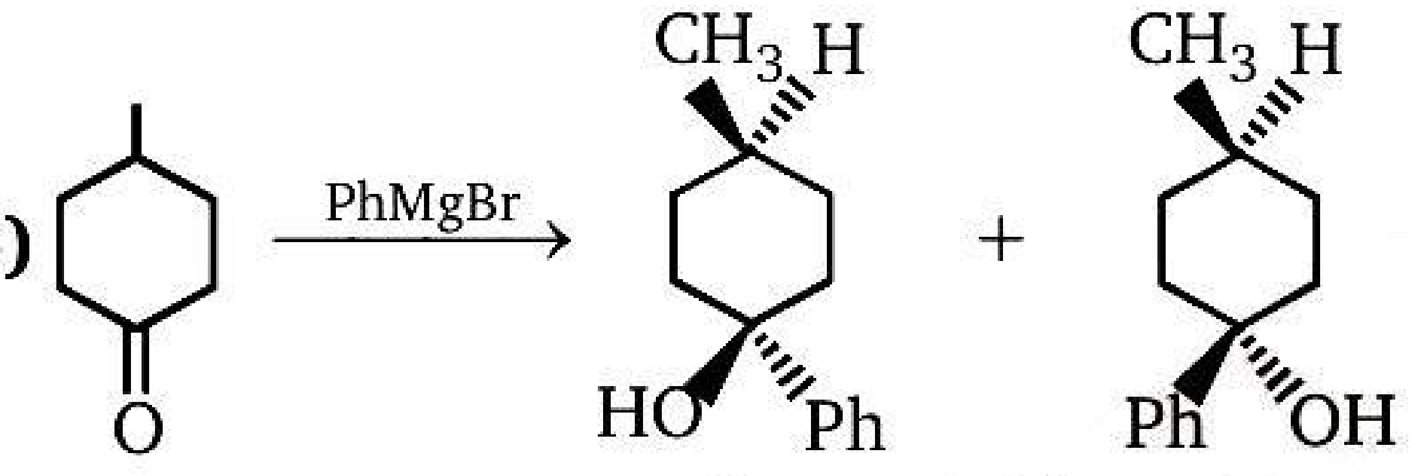
21. (c)



22. (b)

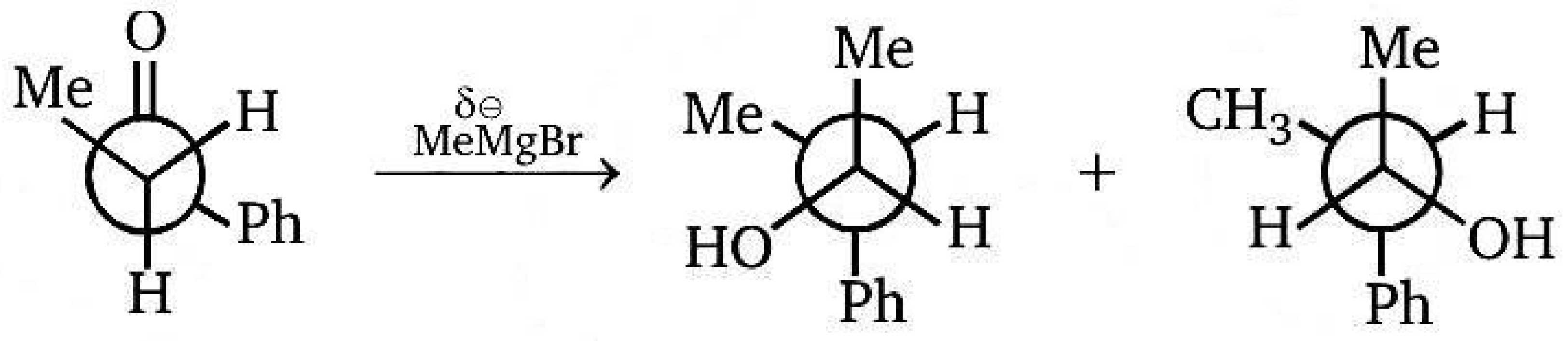


23. (b)

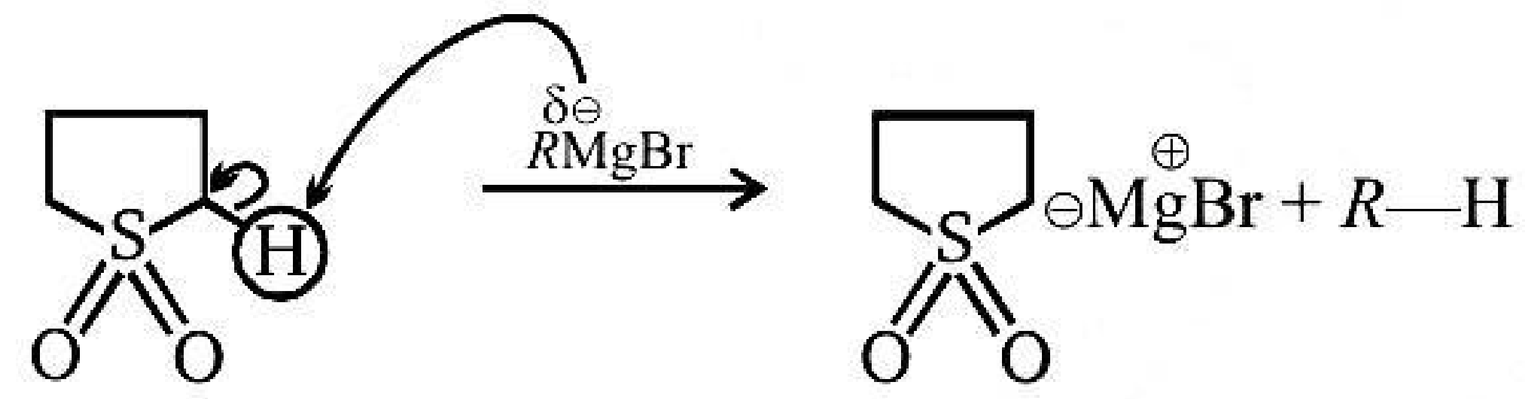


(Geometrical isomers)

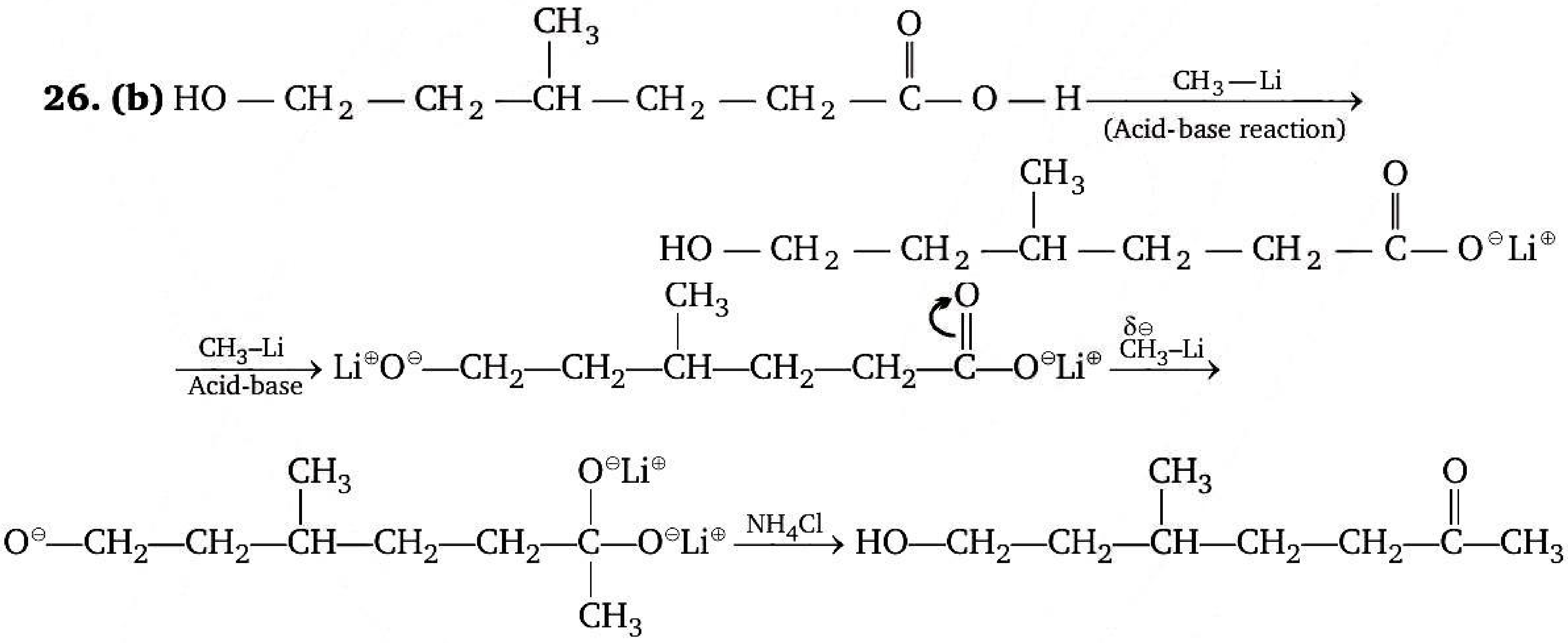
24. (c)



25. (c)



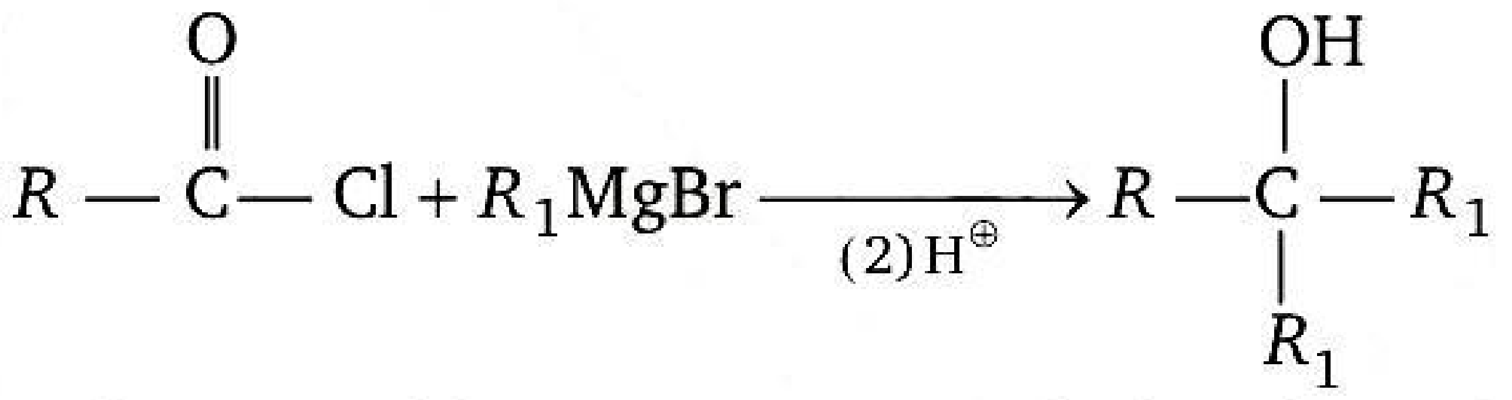
(Acid -base reaction)



$$\textbf{26. (b)}\ HO-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-H\xrightarrow[\text{(Acid-base reaction)}]{CH_3-Li}HO-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O^{\ominus}Li^{\oplus}$$

$$\xrightarrow[\text{Acid-base}]{CH_3\text{–}Li}Li^{\oplus}O^{\ominus}-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O^{\ominus}Li^{\oplus}\xrightarrow{\overset{\delta\ominus}{CH_3\text{–}Li}}$$

$$O^{\ominus}-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{O^{\ominus}Li^{\oplus}}{|}}{C}}-O^{\ominus}Li^{\oplus}\xrightarrow{NH_4Cl}HO-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

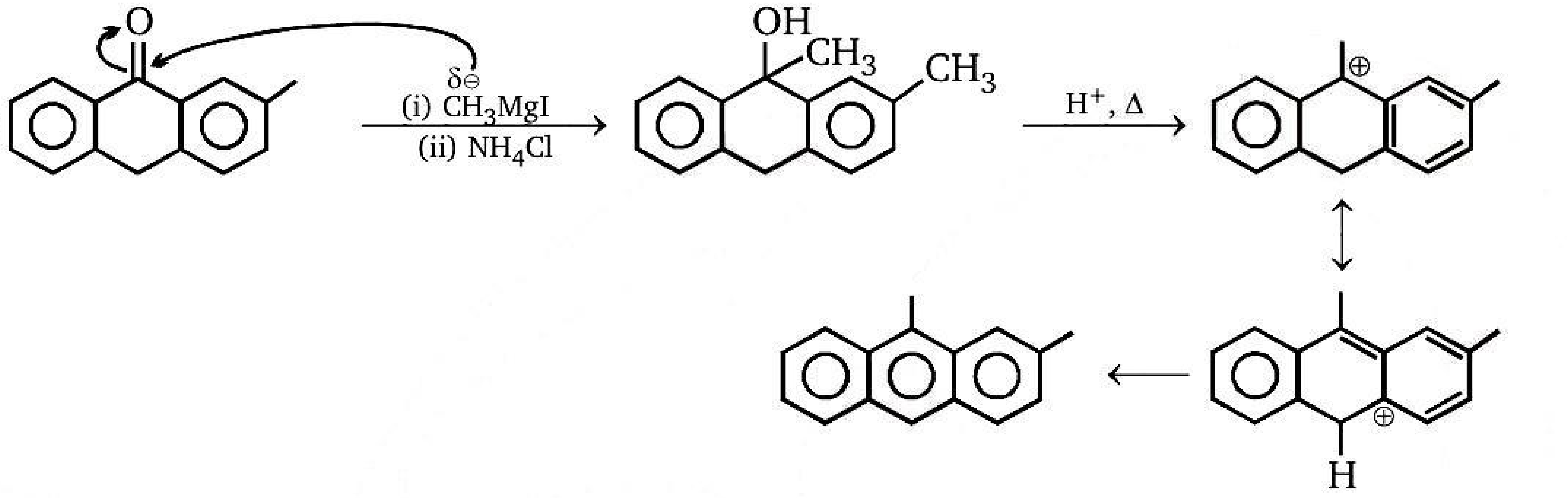


$$\textbf{27. (d)}\ R-\overset{\overset{O}{\|}}{C}-Cl+R_1MgBr\xrightarrow[(2)H^{\oplus}]{}R-\underset{\underset{R_1}{|}}{\overset{\overset{OH}{|}}{C}}-R_1$$

at least two like group are attached with 3° alcohol then that alcohol can be prepared.

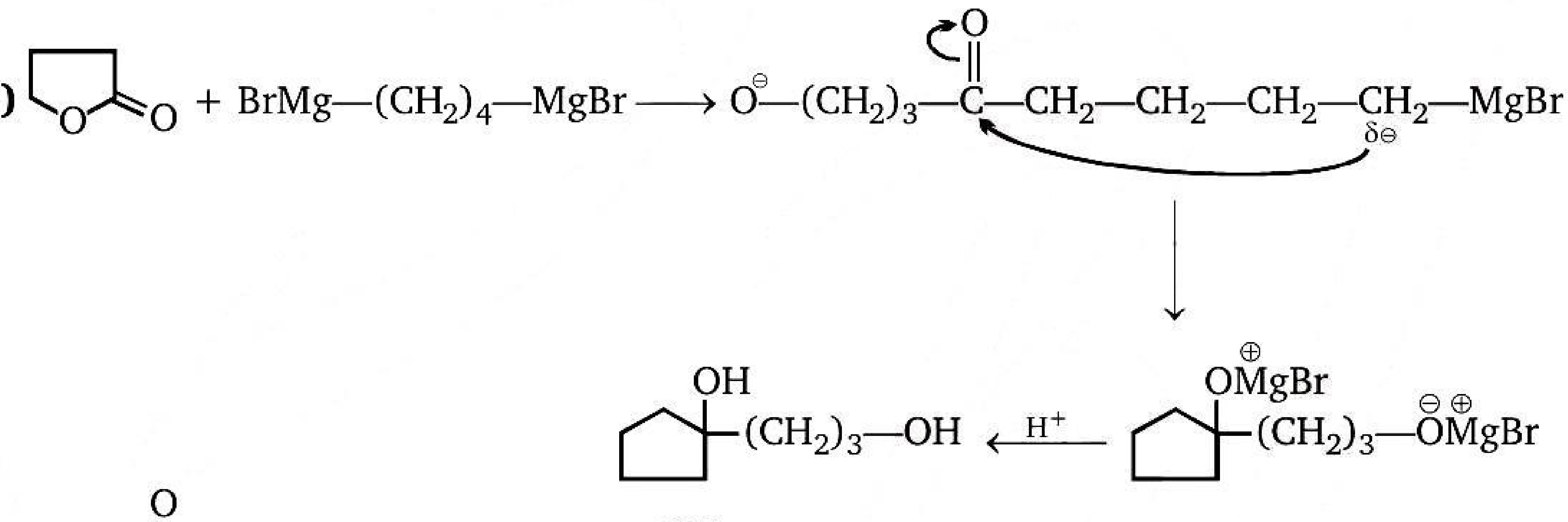
(d) has three unlike group : it cannot be prepared.

28. (d)

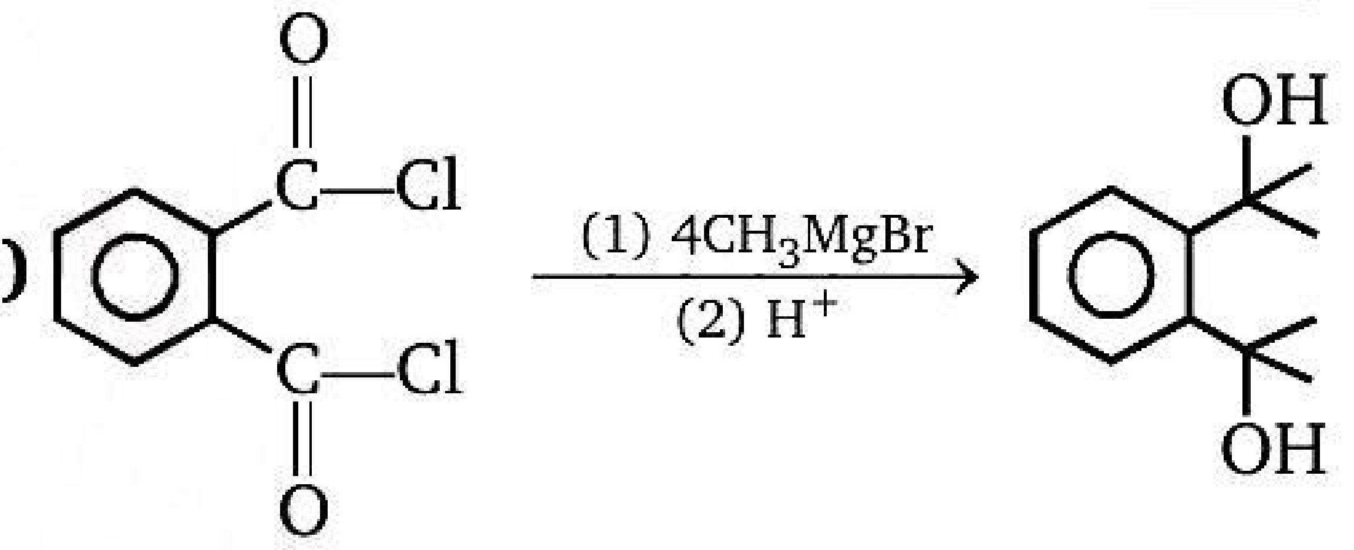


29. (a) $\overset{\delta\ominus}{R}MgBr + S \longrightarrow R—\overset{\ominus\,\oplus}{S}MgBr \xrightarrow{H^+} R—S—H$

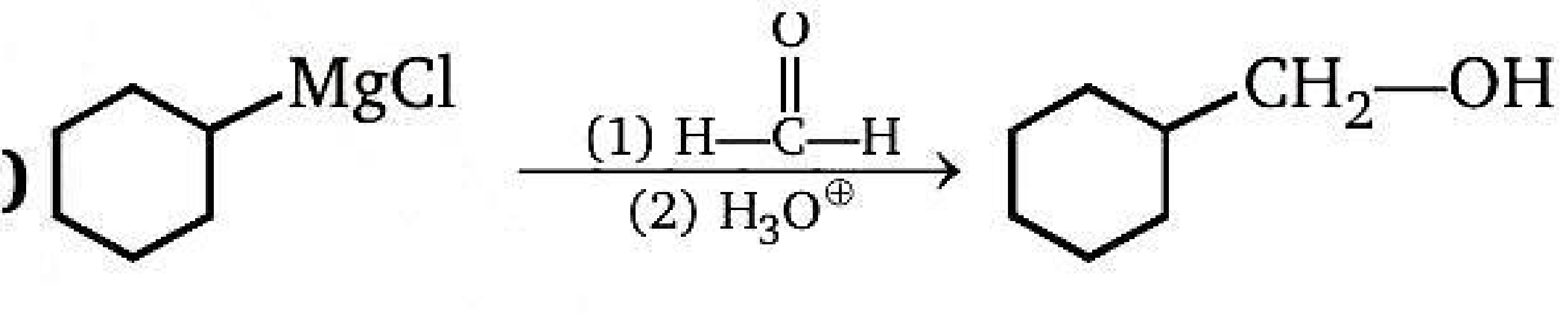
30. (b)



31. (b)

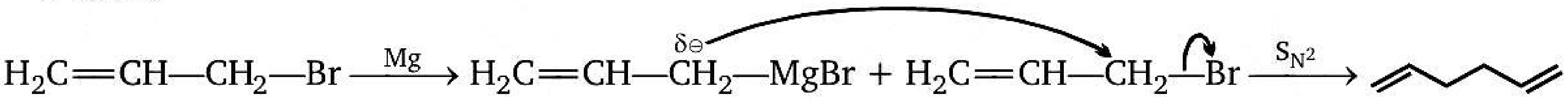


32. (b)

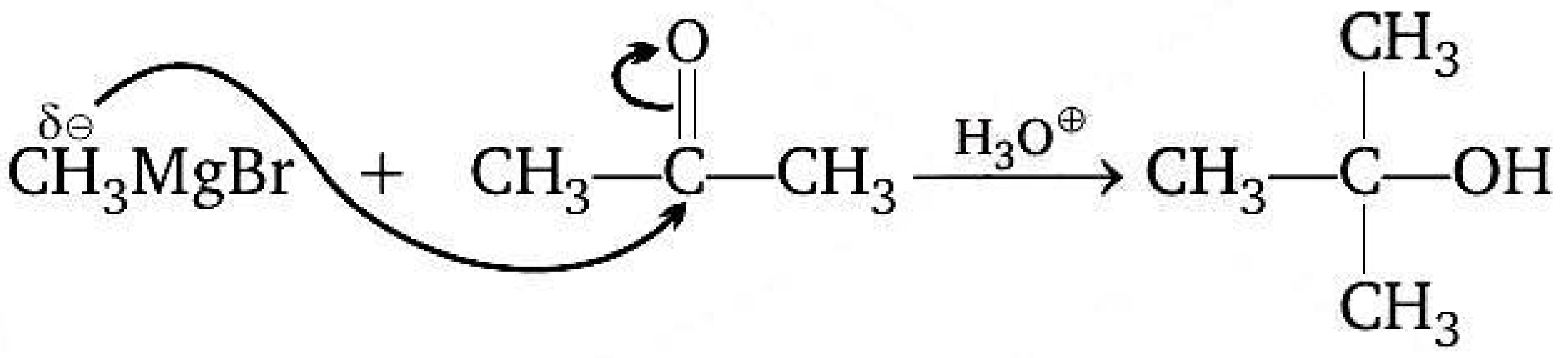


33. (d) In non-polar solvent solution of Grignard reagent is possible.

34. (b)

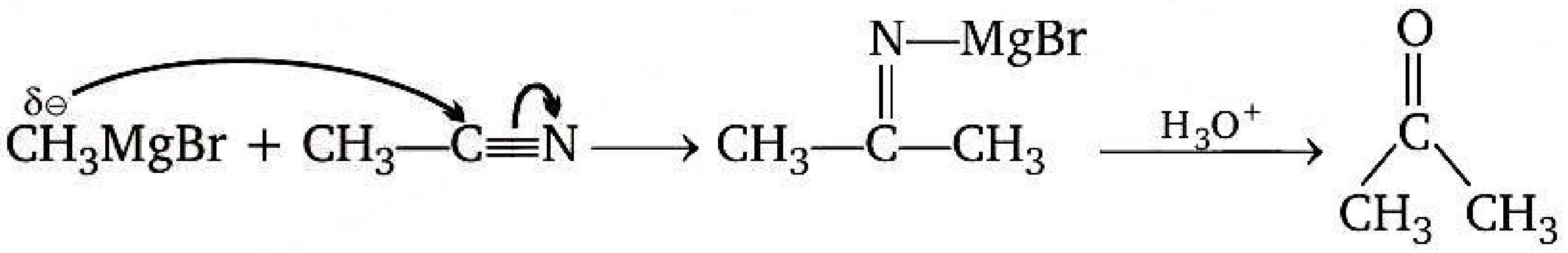


35. (c)



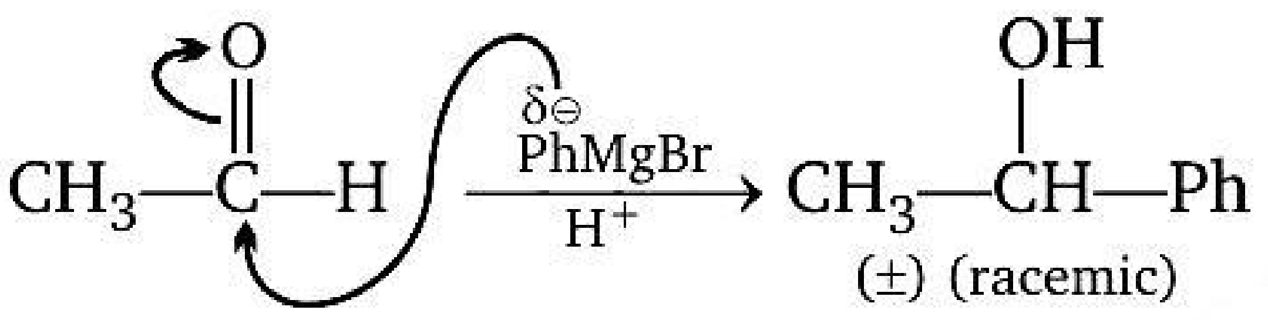
$$\overset{\delta\ominus}{CH_3}MgBr + CH_3—\overset{\overset{O}{\|}}{C}—CH_3 \xrightarrow{H_3O^{\oplus}} CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—OH$$

36. (c)

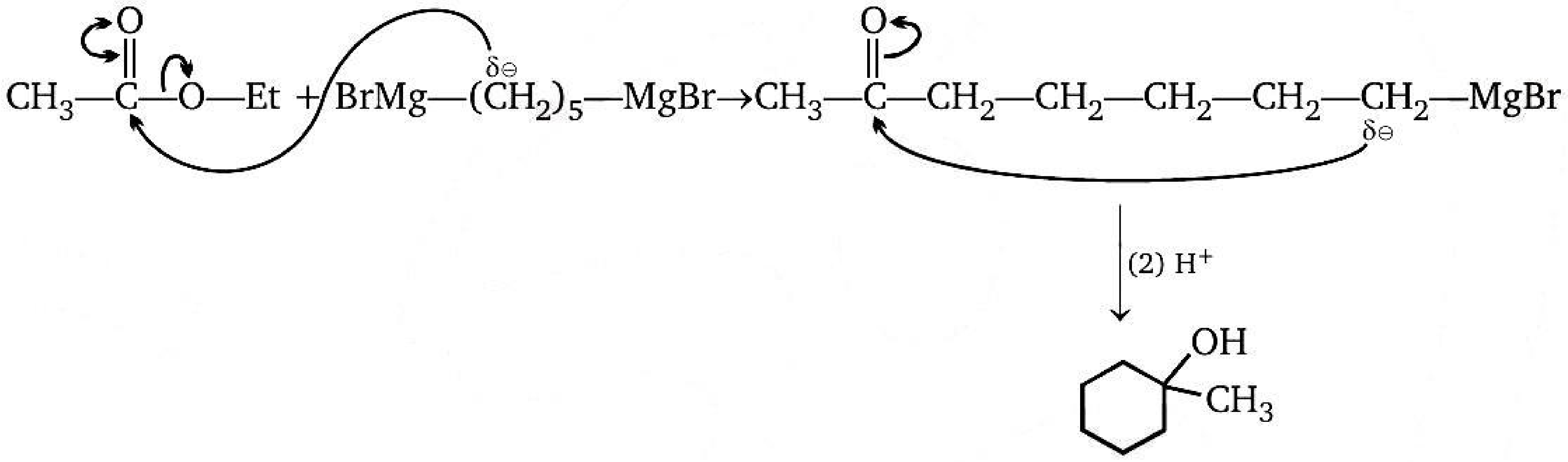


$$\overset{\delta\ominus}{CH_3}MgBr + CH_3—C{\equiv}N \longrightarrow CH_3—\overset{\overset{N—MgBr}{\|}}{C}—CH_3 \xrightarrow{H_3O^+} \underset{CH_3\quad CH_3}{\overset{\overset{O}{\|}}{C}}$$

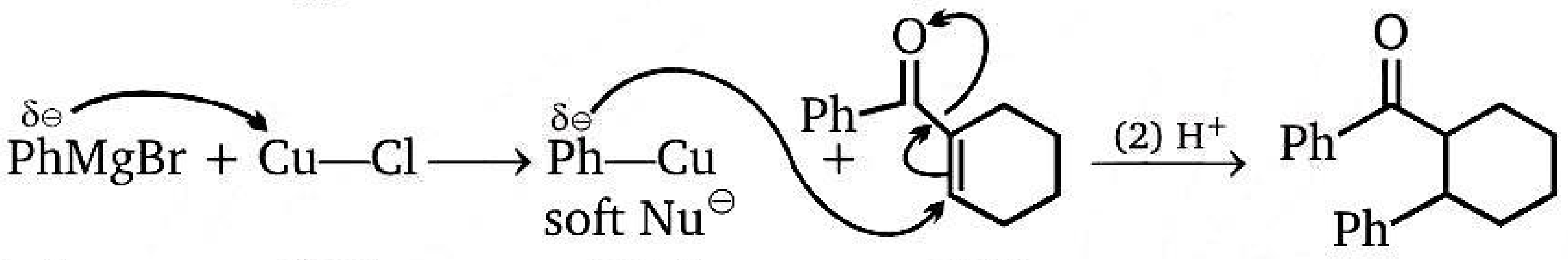
37. (b)



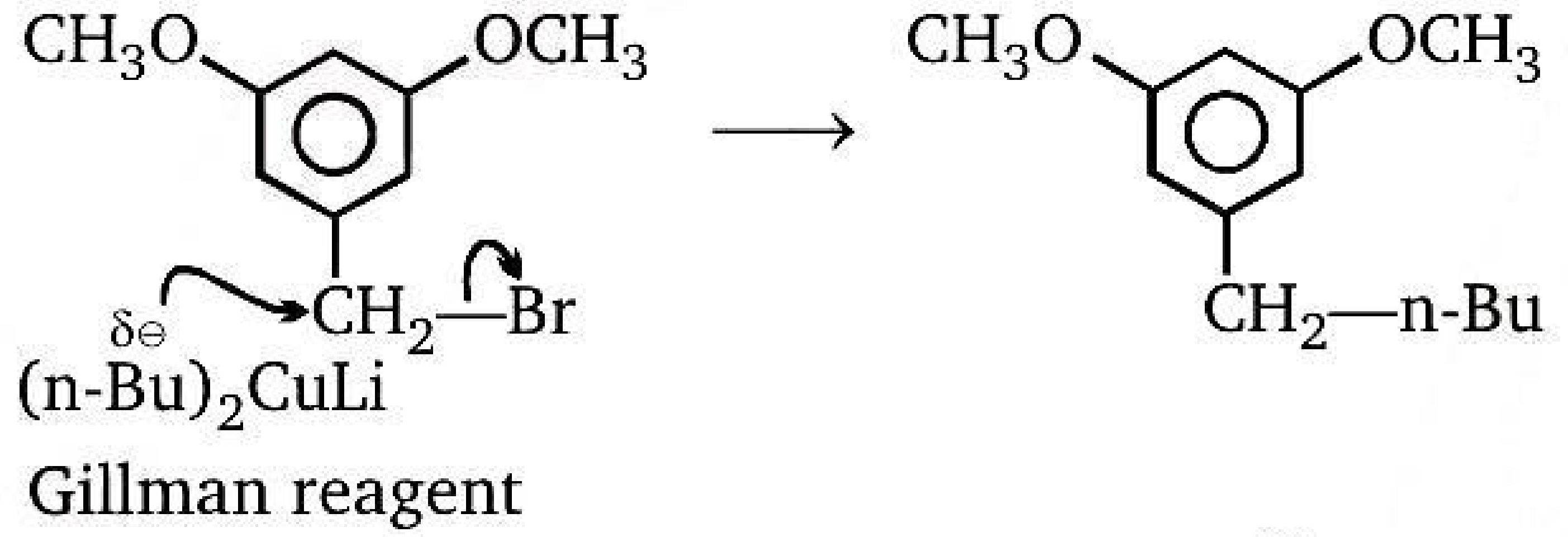
38. (b)



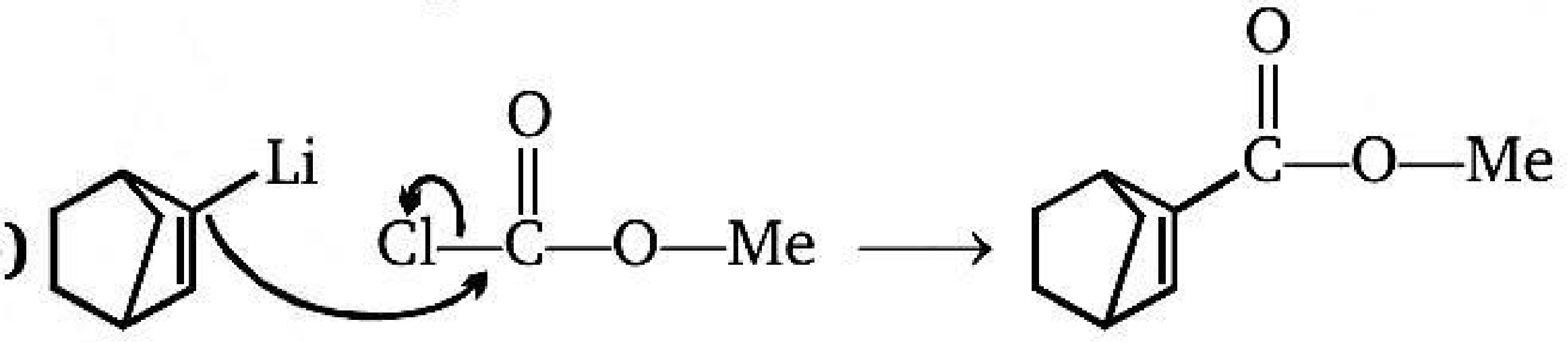
39. (b) In presence of copper salt 1, 4-addition take place.



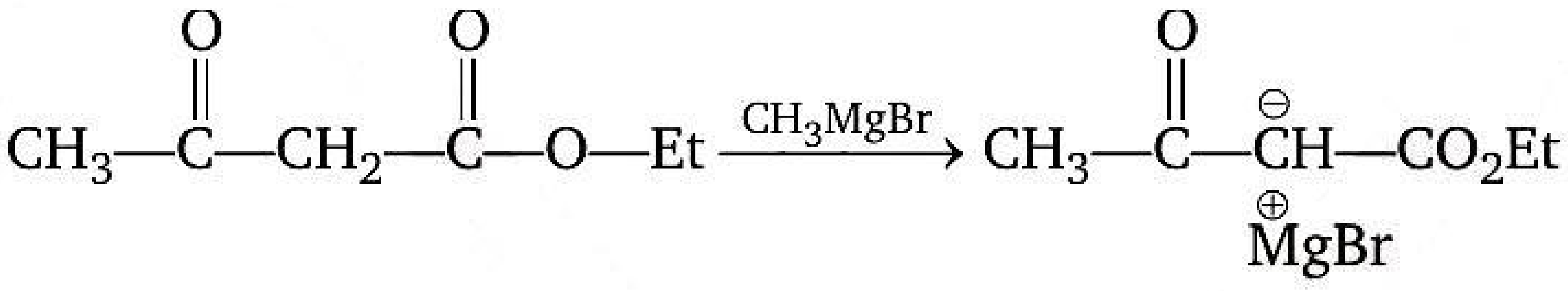
40. (a)



41. (b)



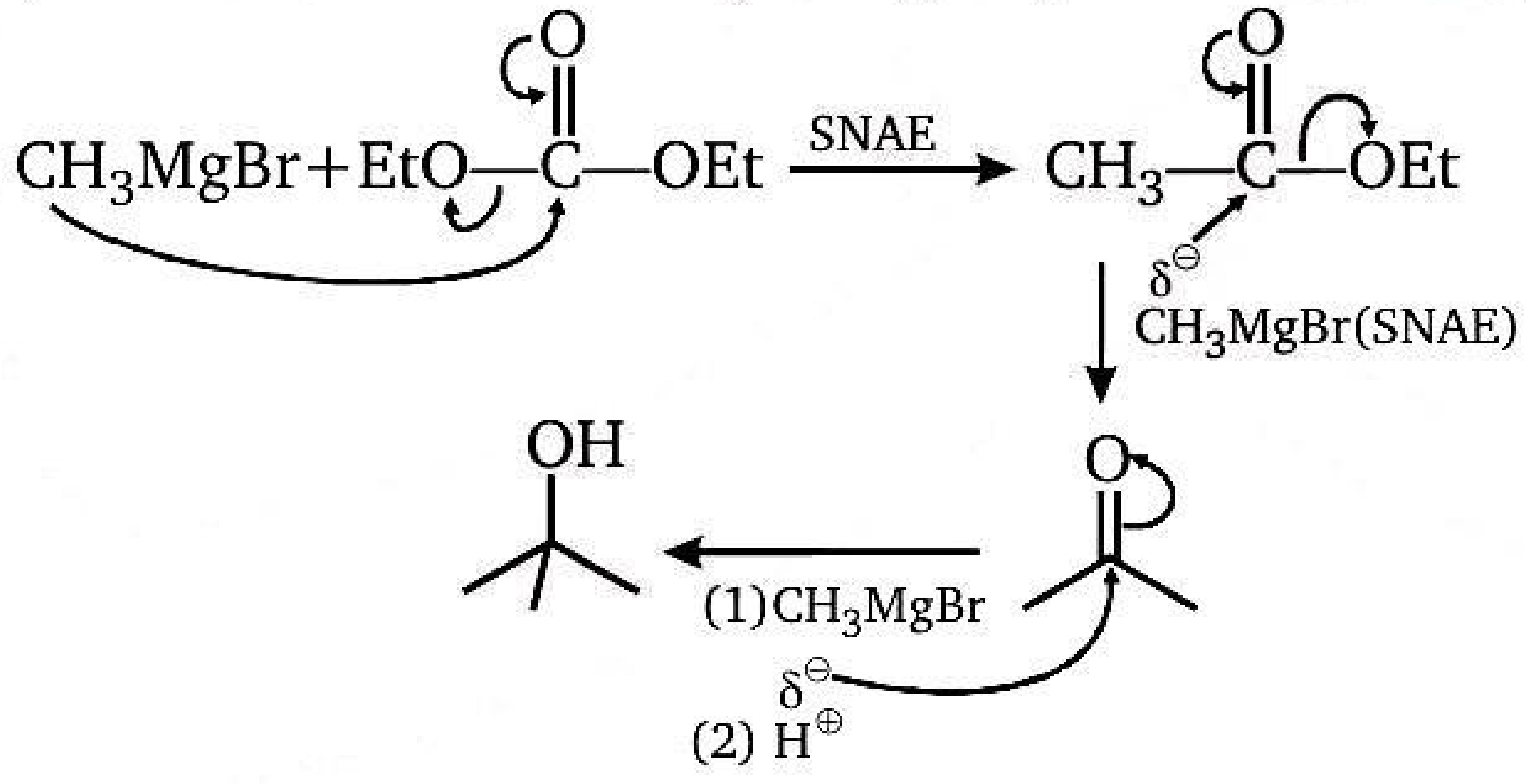
42. (c)



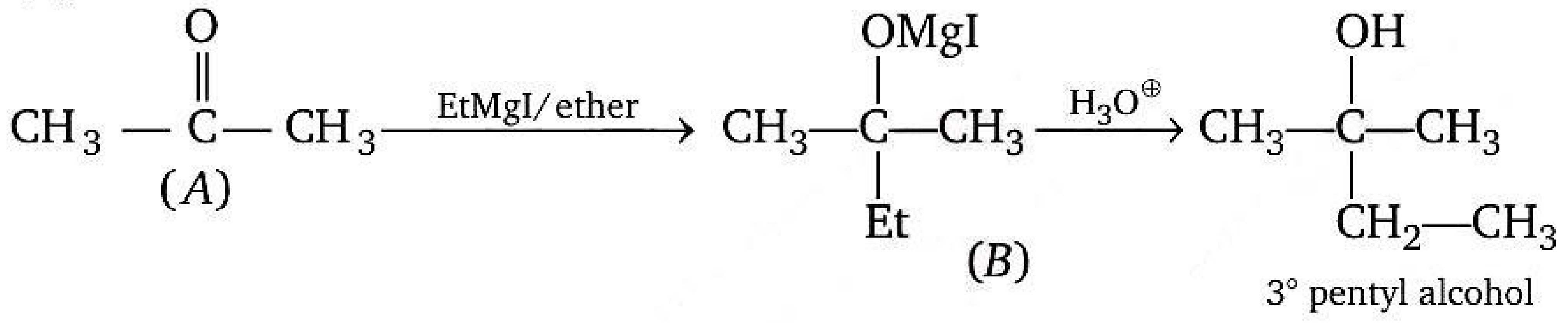
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O-Et \xrightarrow{CH_3MgBr} CH_3-\overset{O}{\overset{\|}{C}}-\underset{\overset{\oplus}{MgBr}}{\overset{\ominus}{C}H}-CO_2Et$$

(because of active methylene group acid-base take place).

43. (b)



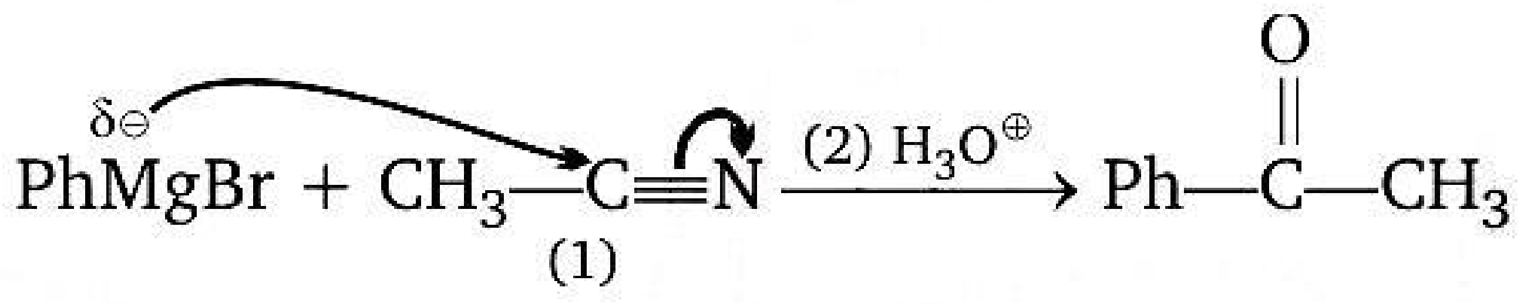
44. (c)



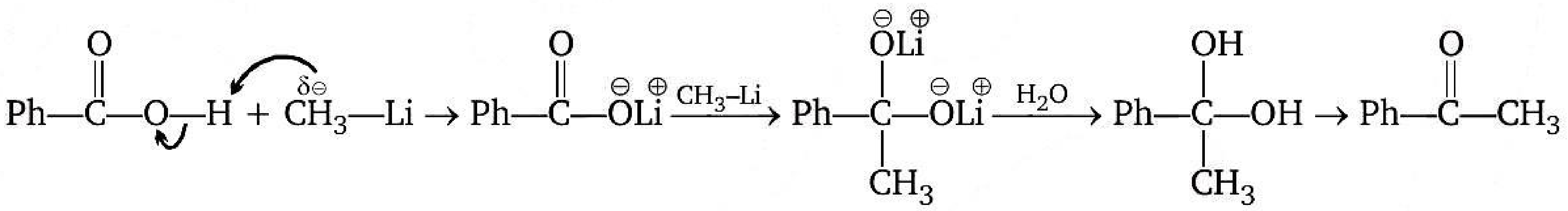
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{EtMgI/ether} CH_3-\underset{\underset{Et}{|}}{\overset{\overset{OMgI}{|}}{C}}-CH_3 \xrightarrow{H_3O^{\oplus}} CH_3-\underset{\underset{CH_2-CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

(A) (B) 3° pentyl alcohol

45. (c)



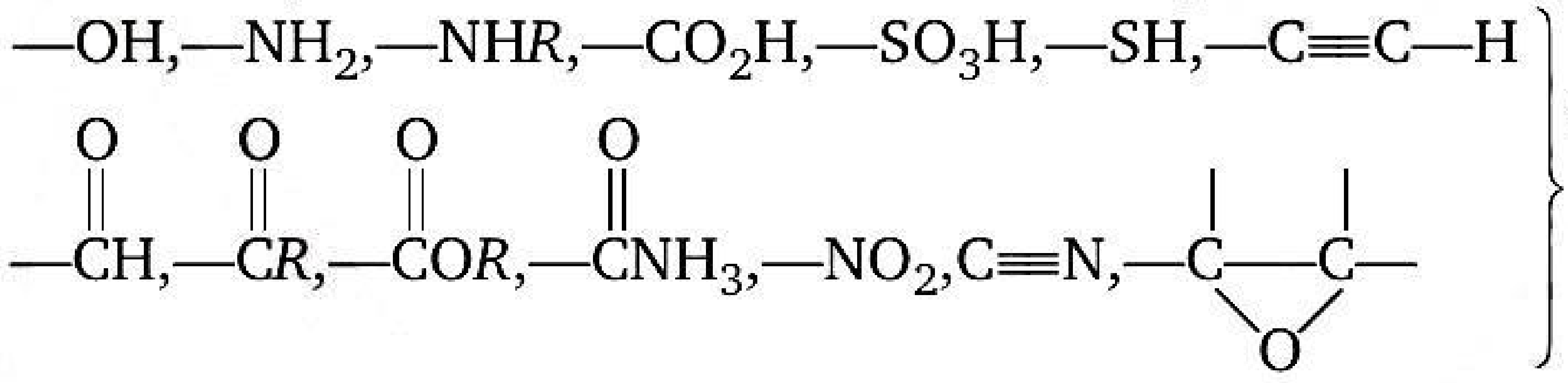
$$\overset{\delta\ominus}{PhMgBr} + CH_3-\underset{(1)}{C}\equiv N \xrightarrow{(2)\ H_3O^{\oplus}} Ph-\overset{\overset{O}{\|}}{C}-CH_3$$



$$Ph-\overset{\overset{O}{\|}}{C}-O-H + \overset{\delta\ominus}{CH_3}-Li \rightarrow Ph-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O}\overset{\oplus}{Li} \xrightarrow{CH_3-Li} Ph-\underset{\underset{CH_3}{|}}{\overset{\overset{\overset{\ominus}{O}\overset{\oplus}{Li}}{|}}{C}}-\overset{\ominus}{O}\overset{\oplus}{Li} \xrightarrow{H_2O} Ph-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-OH \rightarrow Ph-\overset{\overset{O}{\|}}{C}-CH_3$$

46. (d) The Grignard reagent is a very powerful base ; in effect it contains a carbanion. Thus, it is not possible to prepare a Grignard reagent from an organic group that contains an acidic hydrogen ; by an acidic hydrogen, we mean any hydrogen more acidic than the hydrogen atoms of an alkane or alkene. We cannot, for example, prepare a Grignard reagent from a compound containing an — OH group, an — NH – group, an — SH group, a — CO_2H group, or an — SO_3H group. If we were to attempt to prepare a Grignard reagent from an organic halide containing any of these groups, the formation of the Grignard reagent would simply fail to take place. (Even if a Grignard reagent were to form, it would immediately react with the acidic group.)

Since Grignard reagents are powerful nucleophiles, we cannot prepare a Grignard reagent from any organic halide that contains a carbonyl, epoxy, nitro, or cyano (– CN) group. If we were to attempt to carry out this kind of reaction, any Grignard reagent that formed would only react with the unreacted starting material :



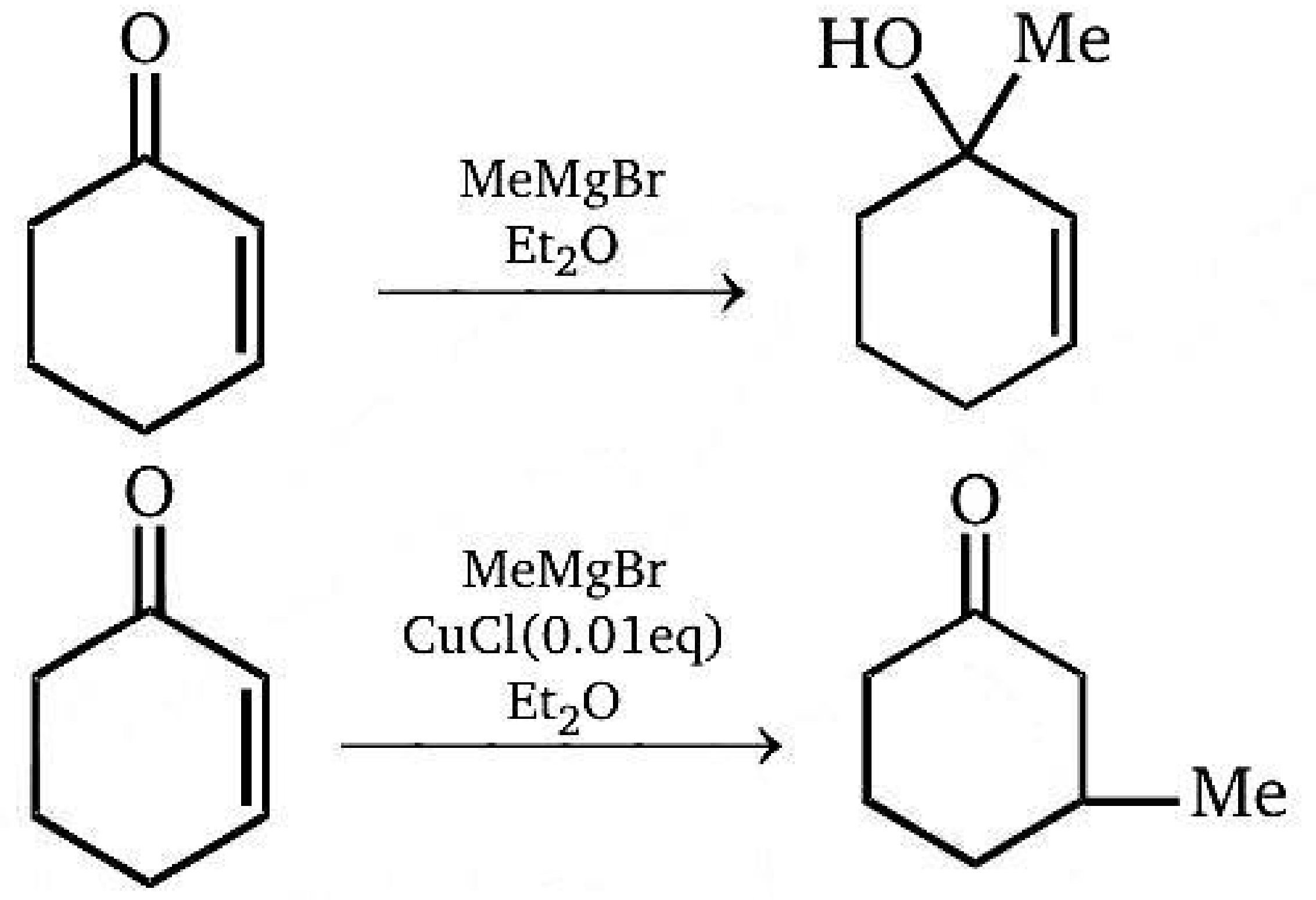
$$\left.\begin{array}{l} -OH, -NH_2, -NHR, -CO_2H, -SO_3H, -SH, -C\equiv C-H \\ -\overset{\overset{O}{\|}}{C}H, -\overset{\overset{O}{\|}}{C}R, -\overset{\overset{O}{\|}}{C}OR, -\overset{\overset{O}{\|}}{C}NH_3, -NO_2, C\equiv N, -\underset{\diagdown O \diagup}{\overset{|}{C}-\overset{|}{C}}- \end{array}\right\}$$

Grignard reagents containing these groups cannot be prepared.

This means that when we prepare Grignard reagents, we are effectively limited to alkyl halides or to analogous organic halides containing carbon - carbon double bonds, internal triple bonds, ether linkages, and $—NR_2$ groups.

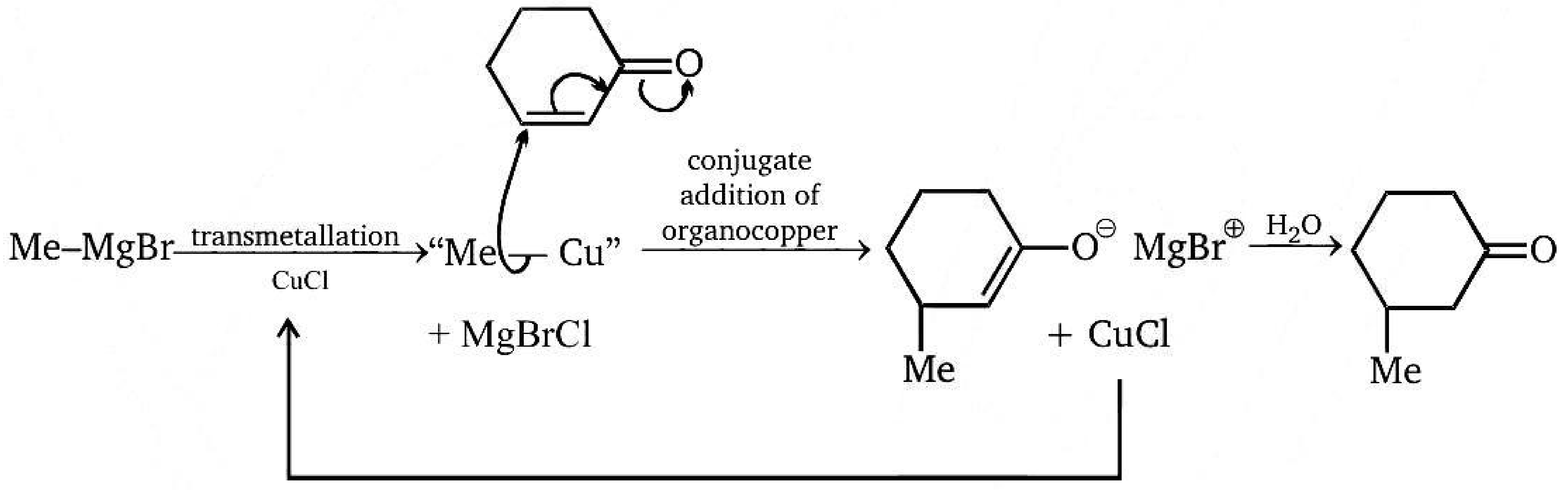
47. (b) Copper (I) salts have a remarkable effect on organometallic reagents.

Grignard reagents add directly to the carbonyl group of α,β-unsaturated aldehydes and ketones to give allylic alcohols : you have seen several examples of this, and you can now explain it by saying that the hard Grignard reagent prefers to attack the harder $C=O$ rather than the softer $C=C$ electrophilic centre. Here is a further example - the addition of MeMgBr to a cyclic ketone to give an allylic alcohol, plus, as it happens, some of a diene that arises from this alcohol by loss of water (dehydration). Below this example is the same reaction to which a very small amount (just 0.01 equivalents, that is 1%) of copper(I) chloride has been added. The effect of the copper is dramatic : it makes the Grignard reagent undergo conjugate addition, with only a trace of the diene.



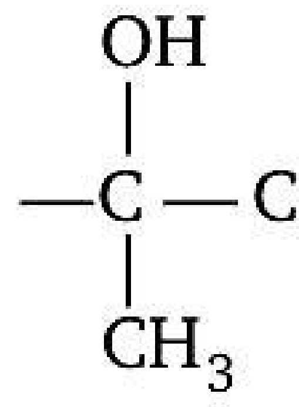
Organocopper reagents undergo conjugate addition:

The copper works by transmetallating the Grignard reagent to give an organocopper reagent. Organocoppers are softer than Grignard reagents, and add in a conjugate fashion to the softer $C=C$ double bond. Once the organocopper had added, the copper salt is available to transmetallate some more Grignard, and only a catalytic amount is required.



copper(I) recycled : only a catalytic quantity is required

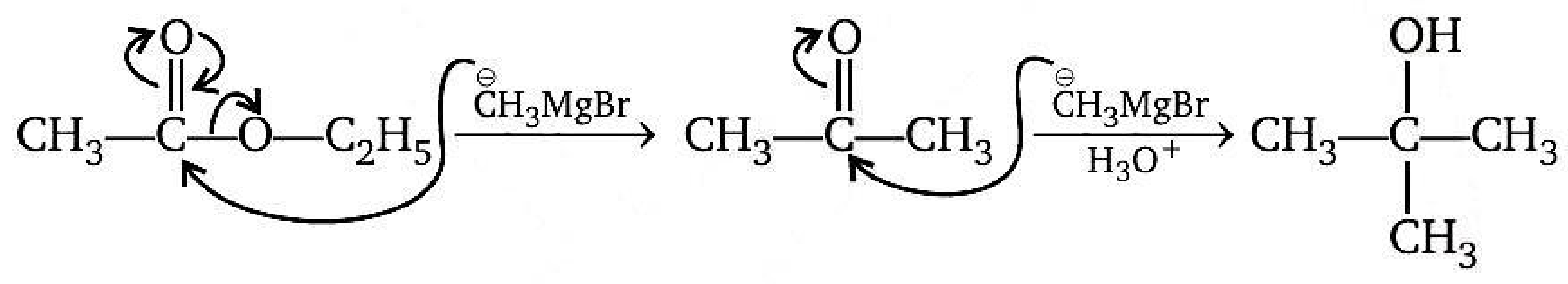
48. (d) Compound (A) is



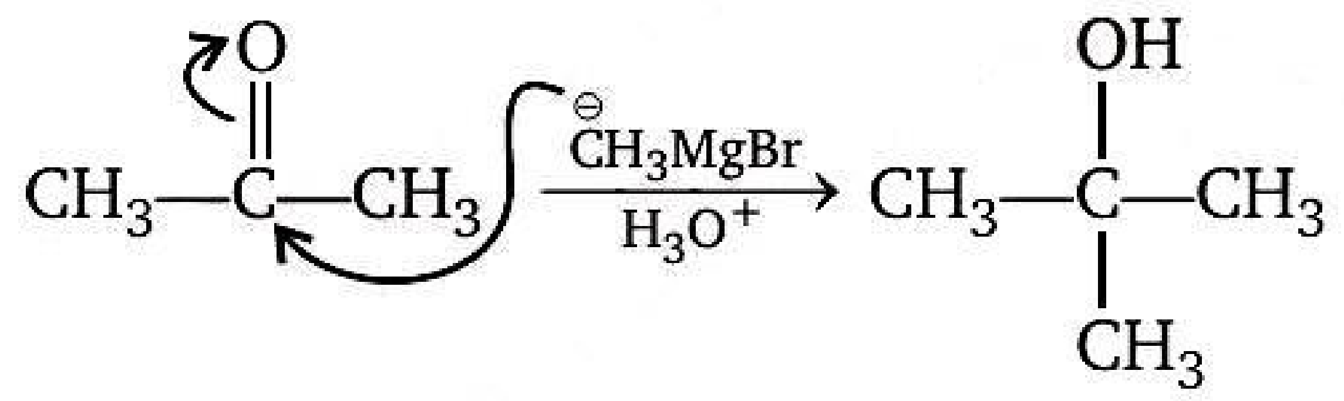
$$CH_3-\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}}-CH_3,$$

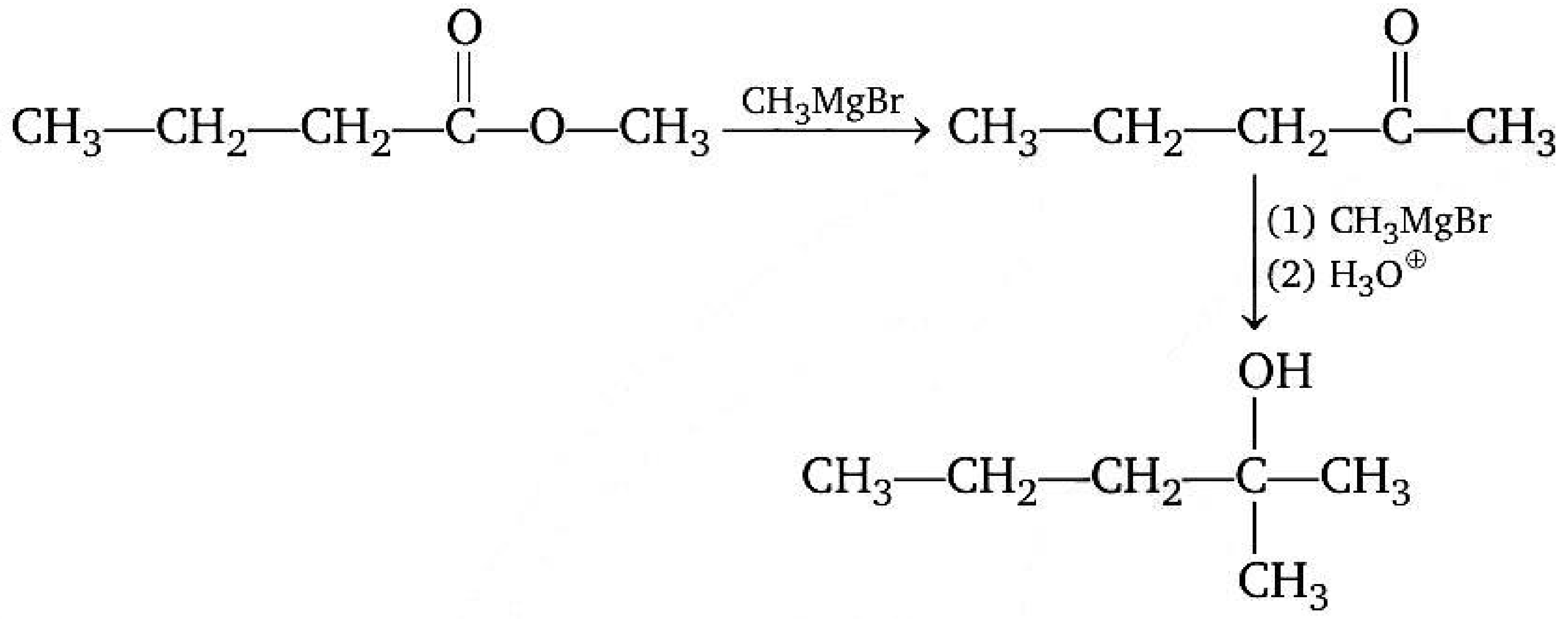
(b) & (c) give (A)

(b)

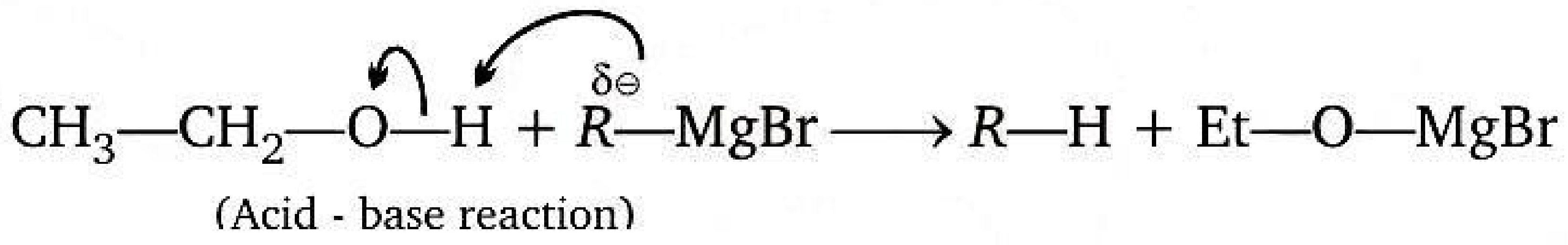


(c)



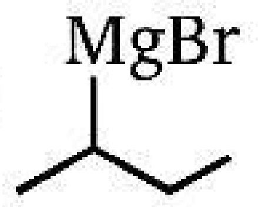
49. (b)


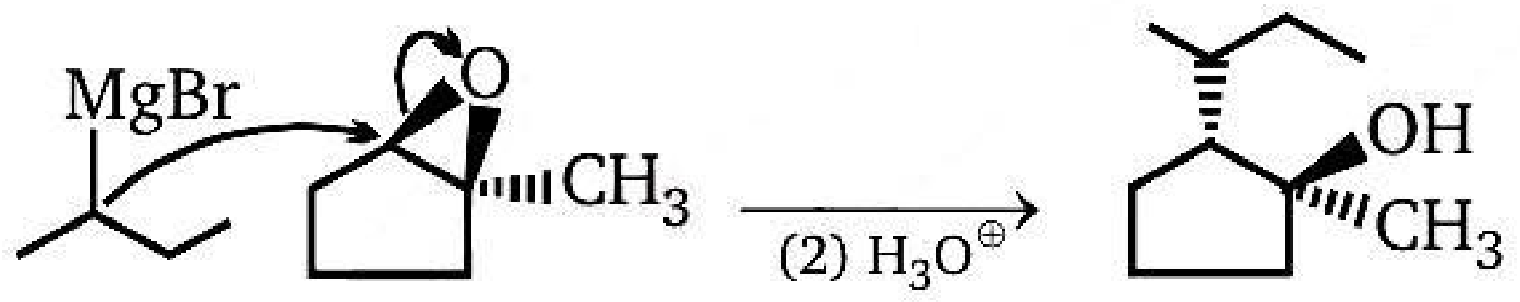
$$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_3 \xrightarrow{CH_3MgBr} CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[(2)\ H_3O^{\oplus}]{(1)\ CH_3MgBr} CH_3-CH_2-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

50. (a)


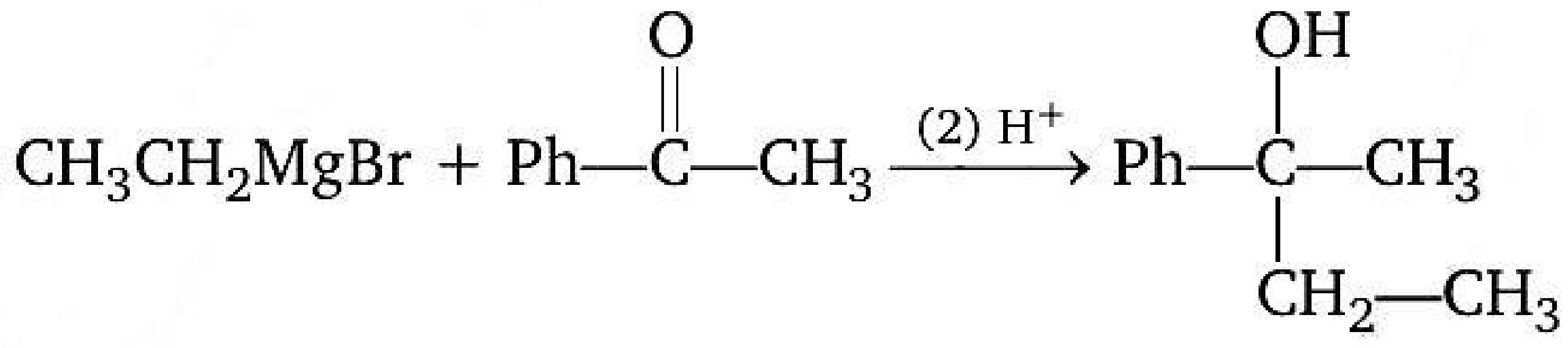
$$CH_3-CH_2-O-H + \overset{\delta\ominus}{R}-MgBr \longrightarrow R-H + Et-O-MgBr$$

(Acid - base reaction)

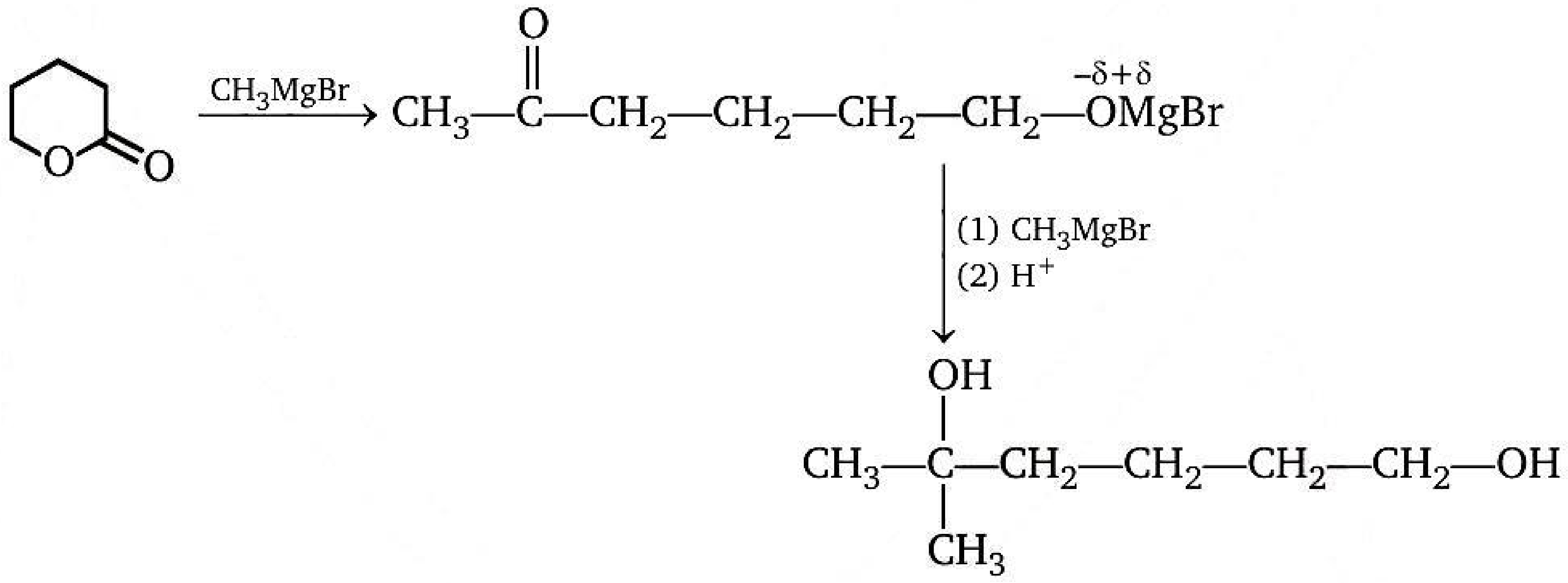
51. (a)




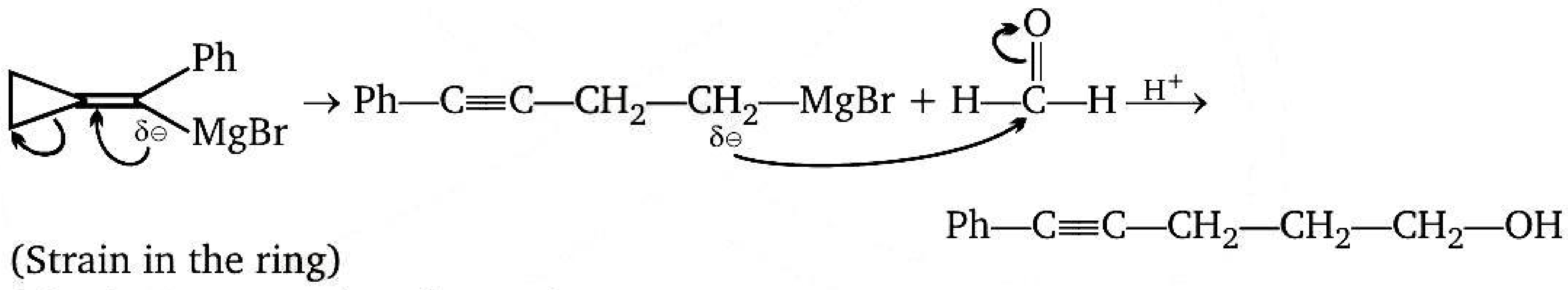
In basic medium less sterichindered carbon will be attacked.

52. (a)


$$CH_3CH_2MgBr + Ph-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{(2)\ H^+} Ph-\underset{\underset{CH_2-CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

53. (c)


$$\xrightarrow{CH_3MgBr} CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_2-CH_2-\overset{-\delta+\delta}{O}MgBr \xrightarrow[(2)\ H^+]{(1)\ CH_3MgBr} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-CH_2-CH_2-CH_2-OH$$

54. (b)


$$\rightarrow Ph-C\equiv C-CH_2-\underset{\delta\ominus}{CH_2}-MgBr + H-\overset{\overset{O}{\|}}{C}-H \xrightarrow{H^+} Ph-C\equiv C-CH_2-CH_2-CH_2-OH$$

(Strain in the ring)

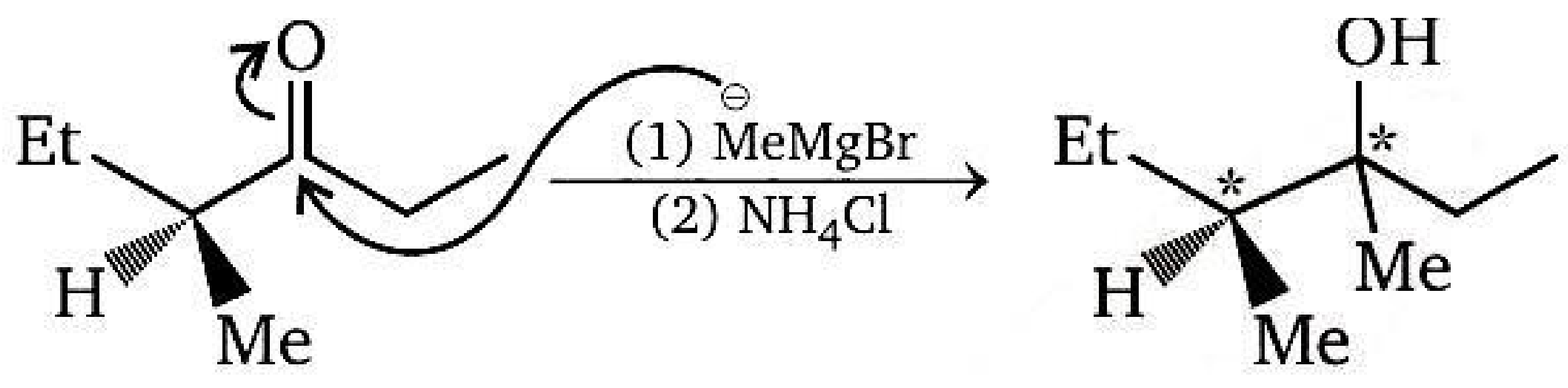
55. (b) (a) Gives 1-Butanol as the product

(c) Gives 2-methyl-2-hexanol as the product

(d) Gives 2-propyl-1-pentanol as the product

only (b) gives 4-heptanol as the product.

56. (a) attack of Nucleophilic on sp^2 carbon.



Two chiral carbons in the product. Configuration of one carbon is fixed.

Attack on the carbonyl carbon can be from two sides. Hence products obtained will be diastereomers.

57. (c) Because 3 acidic H are present.

58. (c) mol. mass of $A = 12 \times 5 + 8 + 16 = 84\,\text{g}$

moles of $A = \dfrac{0.40\,\text{g}}{84\,\text{g}} = 0.005$ moles

moles of gas released at STP $= \dfrac{224\,\text{mL}}{22.4\,\text{L}} = 0.01$ moles

$\therefore$ 0.005 moles of A release 0.01 moles of gas.

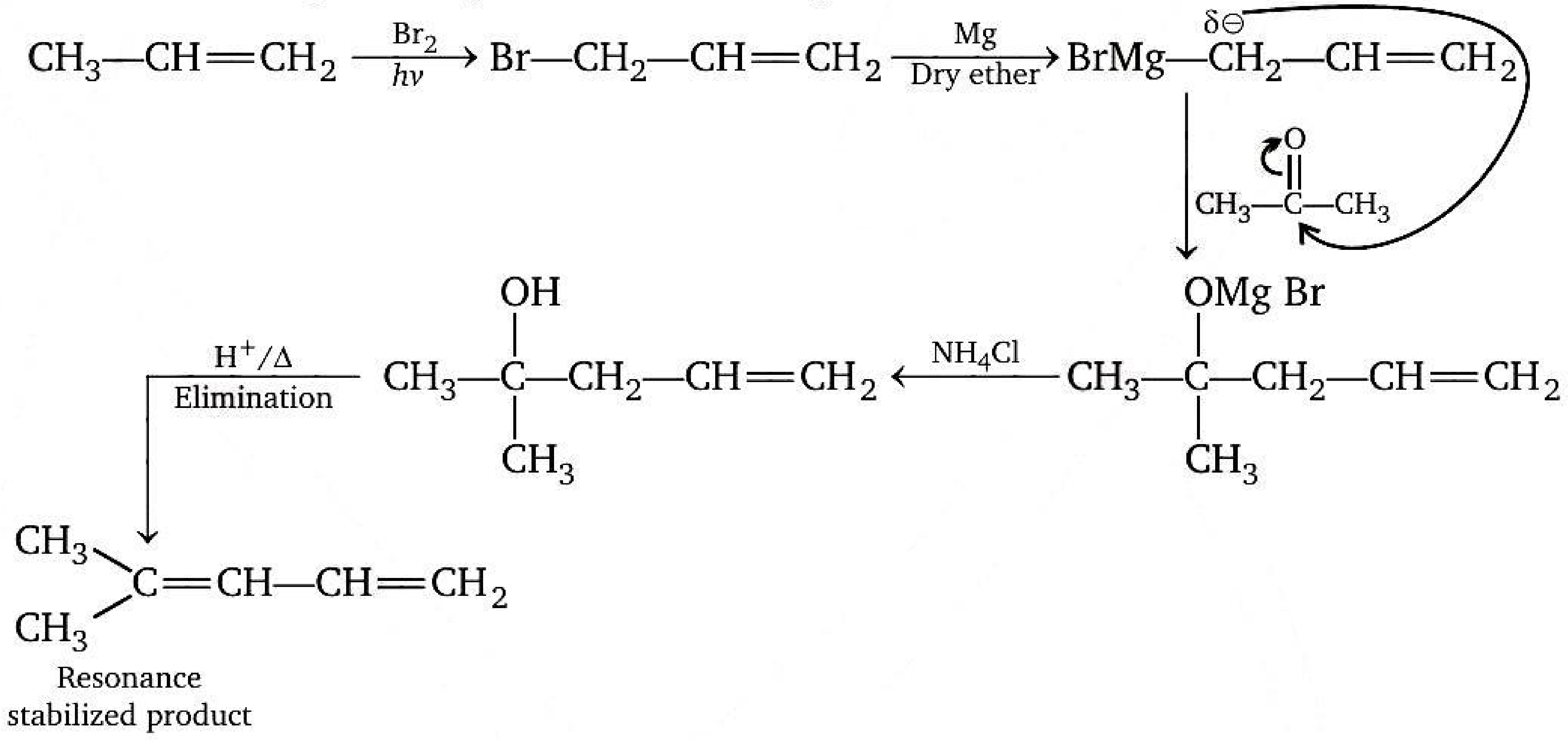
i.e., ratio of 1 : 2.

Hence there must be two acidic H in the compound A. One acidic H is from alcohol the other must be terminal alkyne as only the H attached to terminal alkynes are acidic.

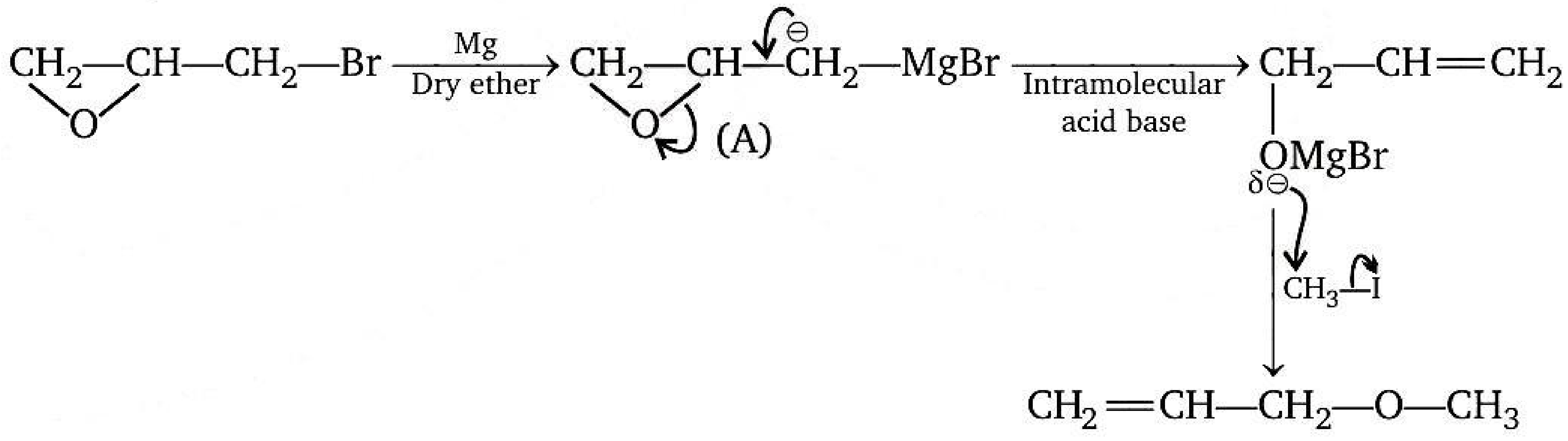
$A \xrightarrow{\text{Excess } H_2}$ pentan-1-ol

Hence option (d) is incorrect.

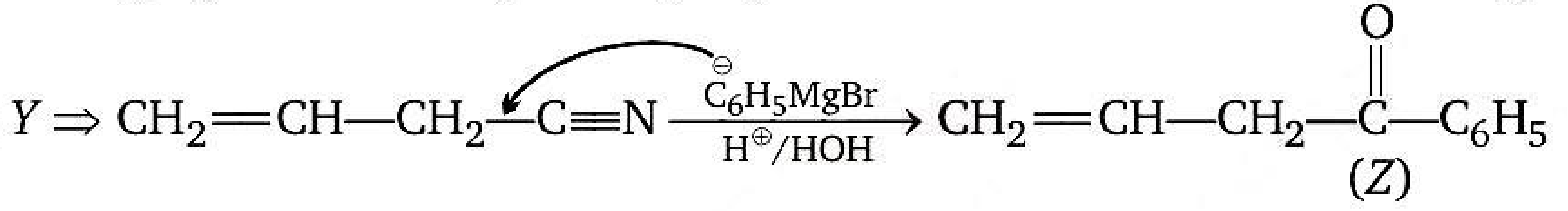
59. (b) 3° alcohol undergoes dehydration on heating with acid.



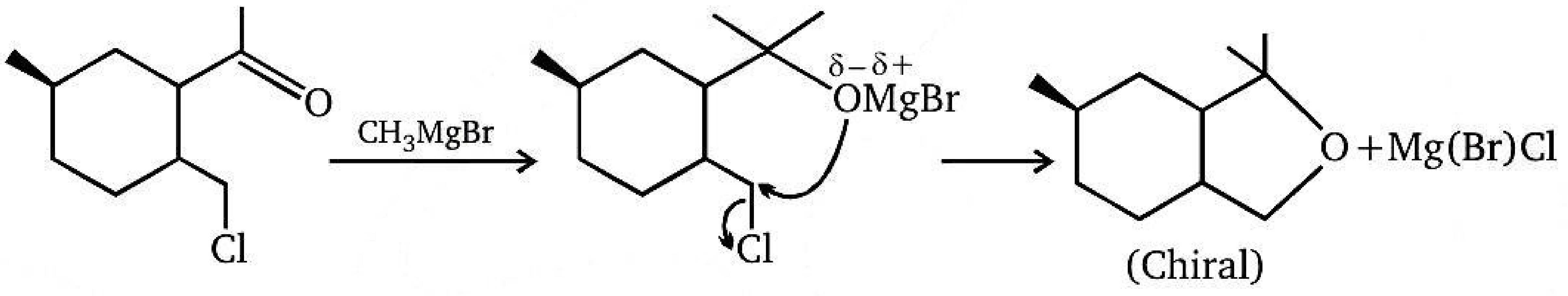
60. (c)

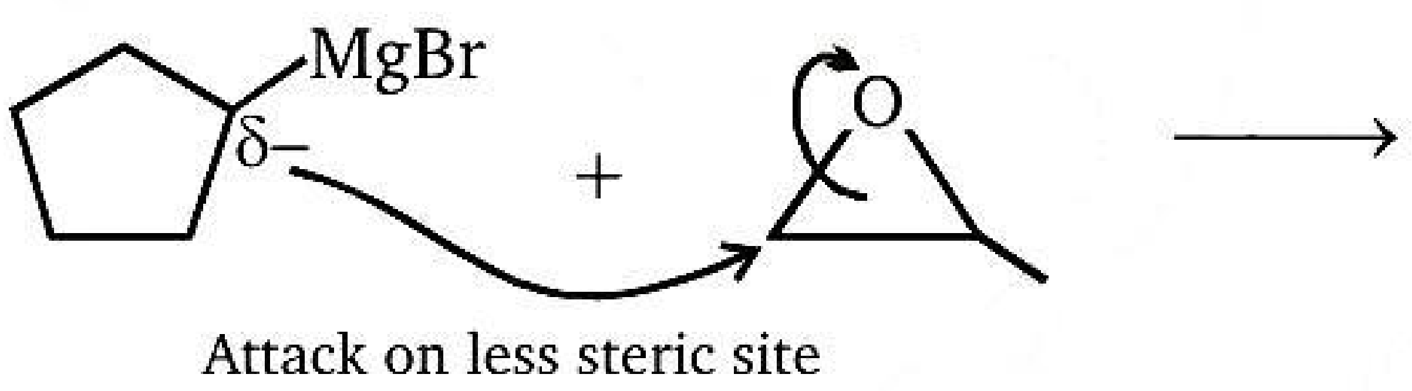


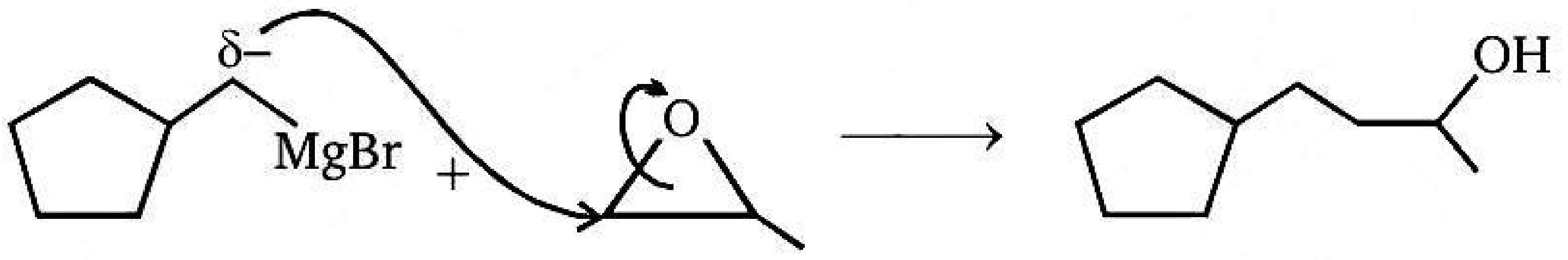
61. (d) $POCl_3$/Pyridine is dehydrating agent. It will cause elimination of H_2O to give alkene.

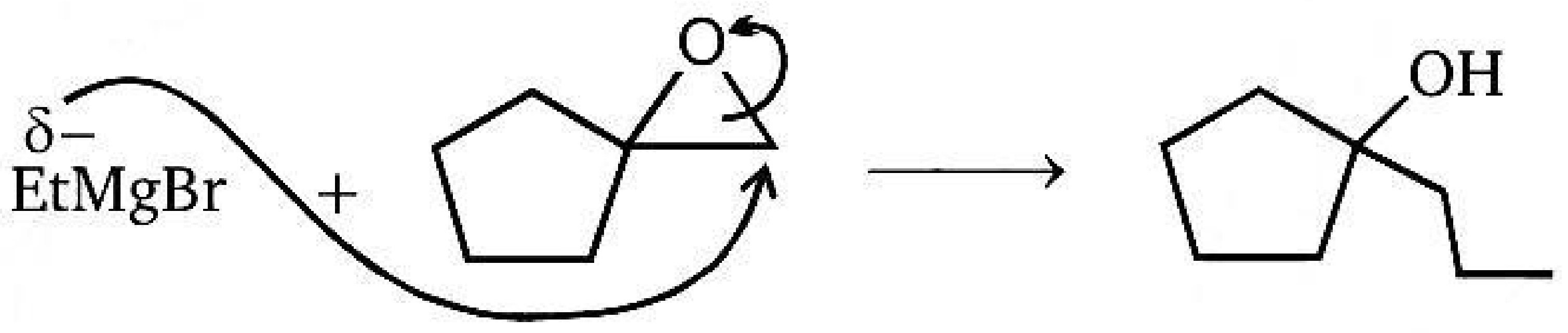
62. (a) 

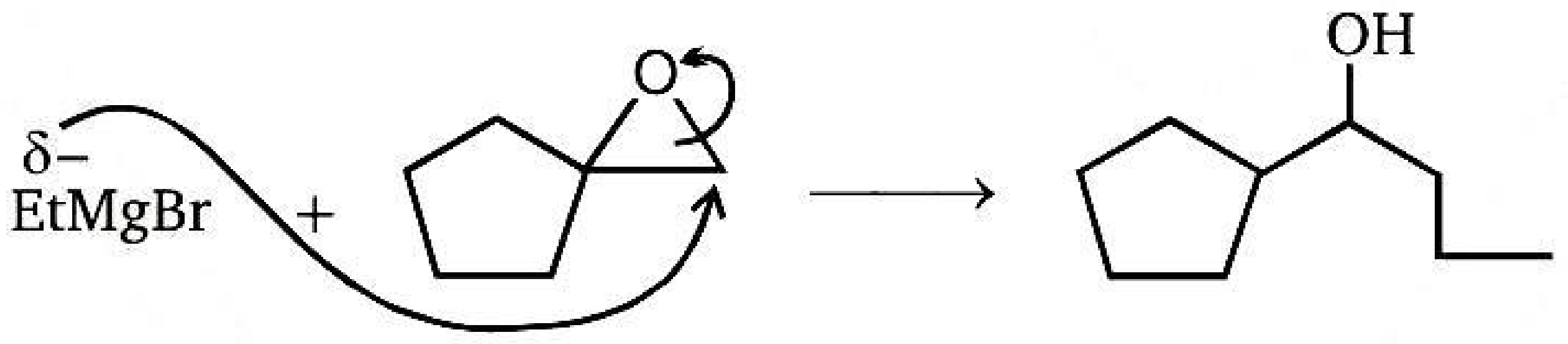
$Y \Rightarrow CH_2{=}CH{-}CH_2{-}\overset{\ominus}{C}{\equiv}N \xrightarrow[H^{\oplus}/HOH]{C_6H_5MgBr} CH_2{=}CH{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}C_6H_5$ (Z)

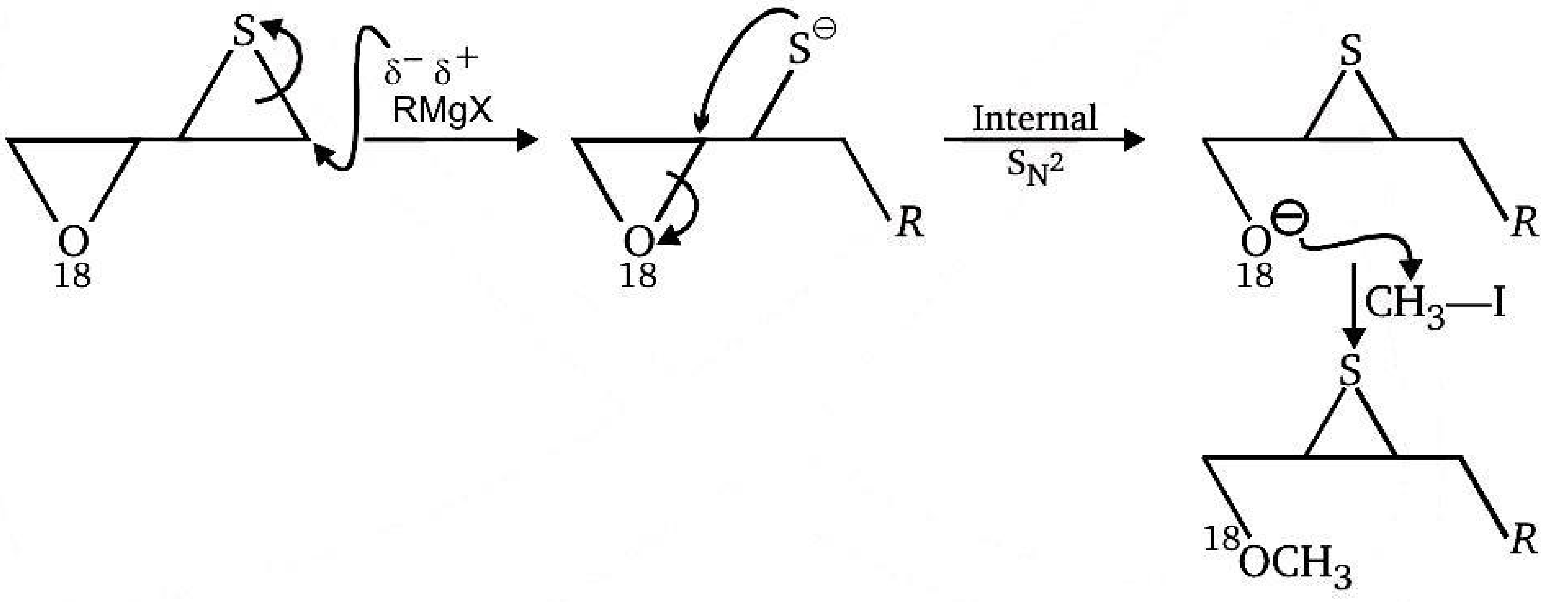
63. (d) 

64. (b) (a) 

(b) 

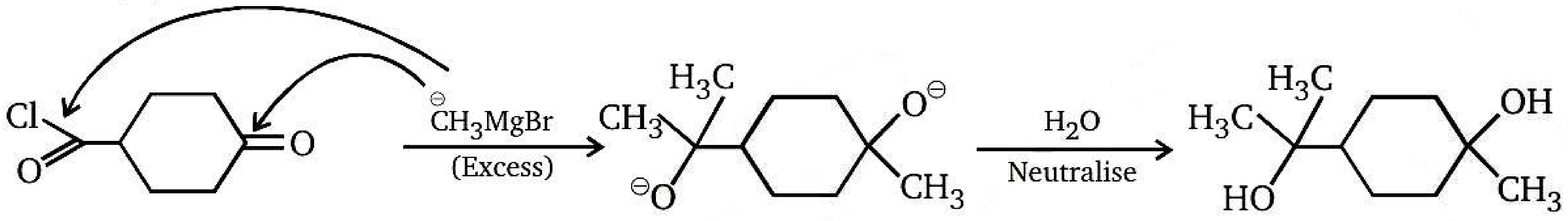
(c) 

(d) 

65. (c) 

Ring containing sulphur is more strained.

66. (d)


Cl
O
O
$\ominus$
CH$_3$MgBr
(Excess)
H$_3$C
CH$_3$
$\ominus$O
O$^\ominus$
CH$_3$
H$_2$O
Neutralise
H$_3$C
H$_3$C
HO
OH
CH$_3$

Level - 2

1. Grignard reagents are usually prepared by the reaction of an organic halide and magnesium metal (turnings) in an ether solvent.

$$\left.\begin{array}{l} RX + \text{Mg} \xrightarrow{\text{Et}_2\text{O}} R\text{Mg}X \\ \text{Ar}X + \text{Mg} \xrightarrow{\text{Et}_2\text{O}} \text{ArMg}X \end{array}\right\} \text{Grignard reagents}$$

The order of reactivity of halides with magnesium is also $RI > RBr > RCl$. Very few organomagnesium fluorides have been prepared. Aryl Grignard reagents are more easily prepared from aryl bromides and aryl iodides than from aryl chlorides, which react very sluggishly.

Grignard reagents are seldom isolated but are used for further reactions in ether solution. The ether solutions can be analyzed for the content of the Grignard reagent, however, and the yields of Grignard reagents are almost always very high (85–95%). Two examples are shown here :

$$CH_3I + Mg \xrightarrow[35°C]{Et_2O} \underset{\substack{\text{Methylmagnesium iodide} \\ (95\%)}}{CH_3MgI}$$

$$C_6H_5Br + Mg \xrightarrow[35°C]{Et_2O} \underset{\substack{\text{Phenylmagnesium bromide} \\ (95\%)}}{C_6H_5MgBr}$$

2. Reaction of Grignard reagent with aldehyde or ketone is an example of nucleophilic addition.

a – r ; b – q ; c – p ; d – s

3. Reaction of Grignard reagent with aldehyde or ketone is an example of nucleophilic addition.

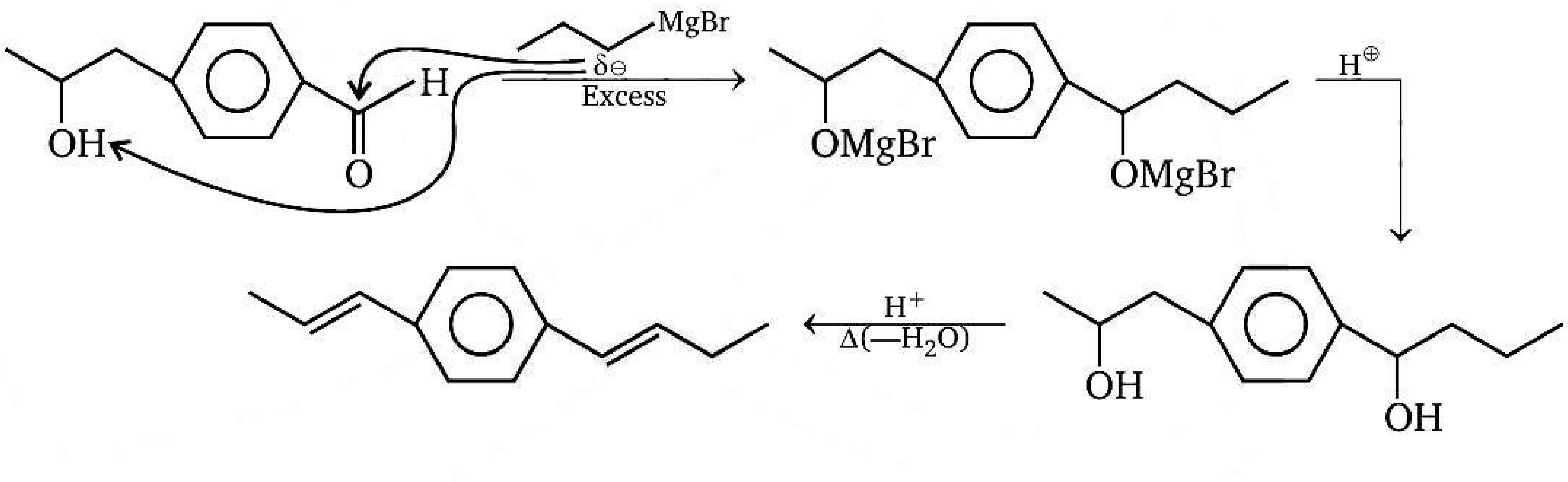
a – s ; b – r ; c – q ; d – p

4. a – r ; b – q ; c – p ; d – s

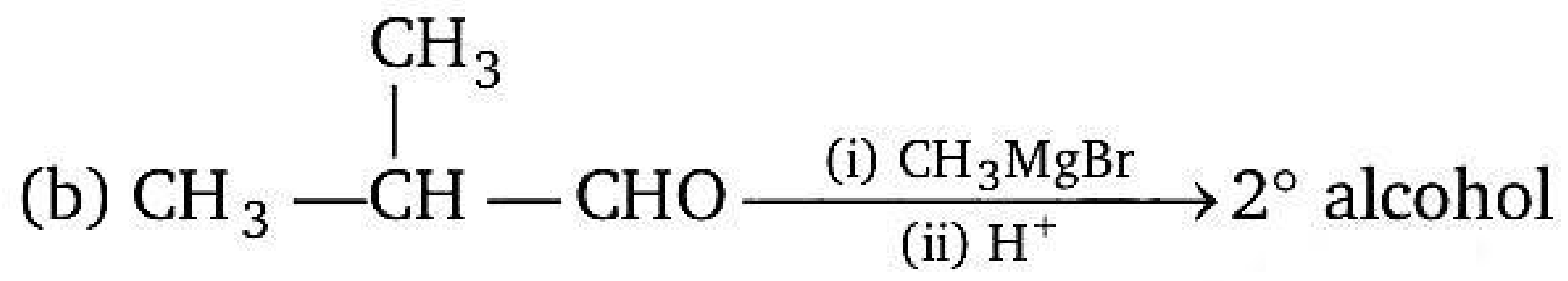
5. Number of active hydrogen present in organic compound will be four based on mole concept calculation so the answer will be (a) and (b).

Subjective Problems

1.



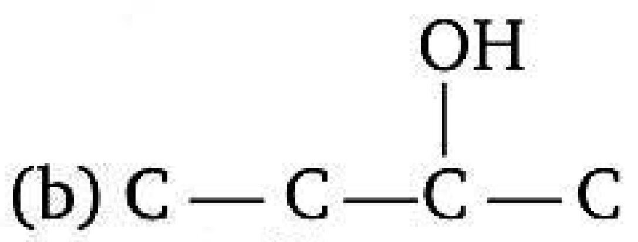
2. (a) $CH_3 — CH_2 — CH_2CHO \xrightarrow[\text{(ii) } H^+]{\text{(i) } CH_3MgBr} 2°$ alcohol



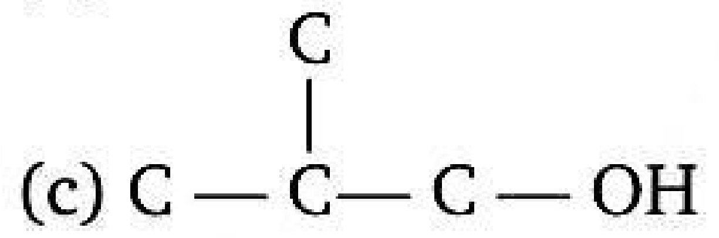
$$\text{(b) } CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CHO \xrightarrow[\text{(ii) } H^+]{\text{(i) } CH_3MgBr} 2^\circ \text{ alcohol}$$

3. Esters and nitrile will consume 2 moles *R*Mg*X* each.
Ketone will consume only one mole.

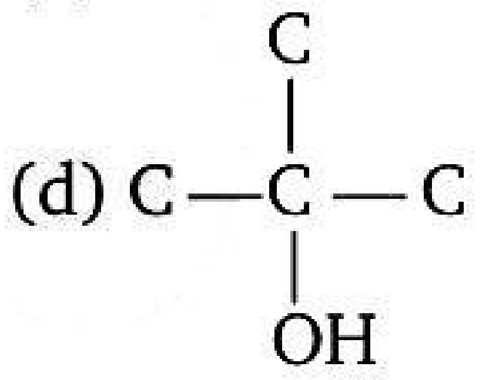
4. (a) C — C — C — C — OH



$$\text{(b) } C-C-\overset{\displaystyle OH}{\overset{|}{C}}-C$$



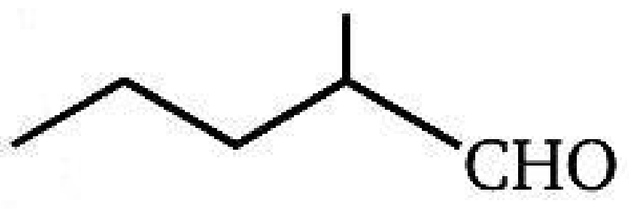
$$\text{(c) } C-\overset{\displaystyle C}{\overset{|}{C}}-C-OH$$

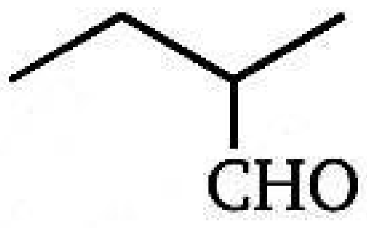


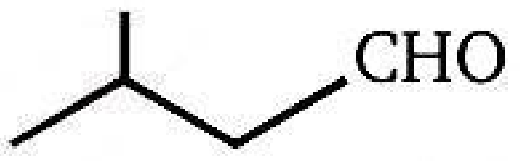
$$\text{(d) } C-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle C}{\overset{|}{C}}}}-C$$

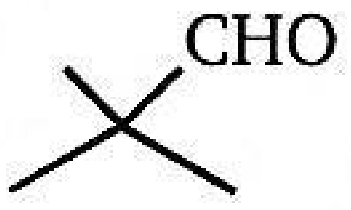
All these alcohol have active hydrogen so these are capable to react with CH_3MgBr to evolve CH_4 gas.

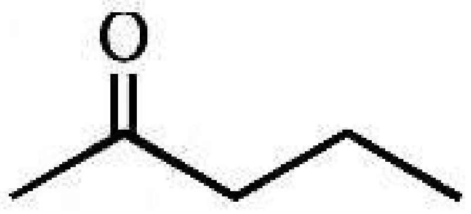
5. Carbonyl isomers of $C_5H_{10}O$ that will give racemic mixture when react with PhMgBr are :

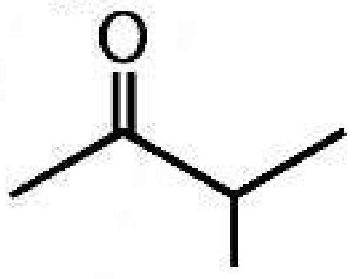












6. Moles consumed in ↗ Acid-base reaction = 2
↘ $Nu^\ominus$ Addition reaction = 6
Total = 8