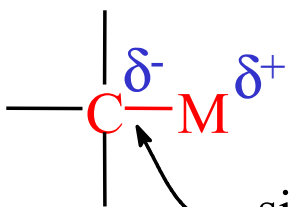
Composti Organometallici

Metallo legato a **carbonio**.

es. CH_3CH_2MgBr (non $CH_3O^-Na^+$)

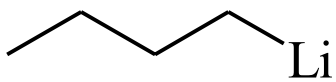
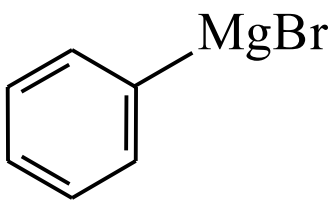
In generale: 

legame **covalente** ma **polare**

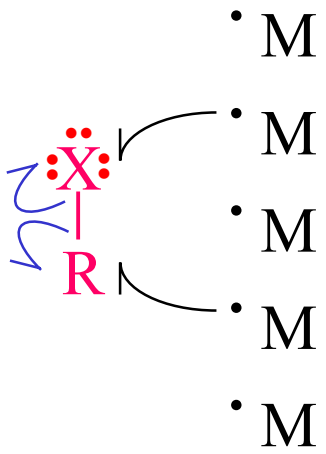
significativo carattere **carbanionico**

- base forte e buon nucleofilo

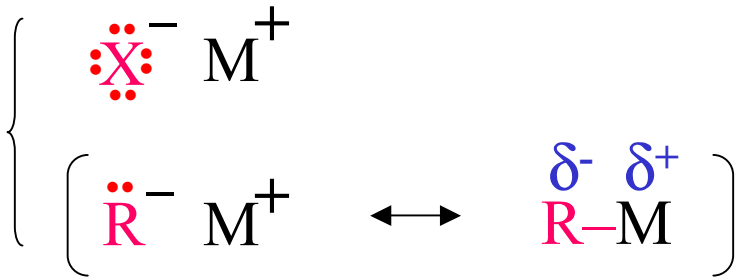
I. Nomenclatura

R—M	R—M—X
alchilmetallo	alchilmetallo alogenuro
	*n*-butillitio
	fenilmagnesio bromuro
$(CH_3CH_2)_4Pb$	tetraetilpiombo

II. Struttura di R-M



2e- trasferiti all'alogenuro dalla superficie metallica in 1 o 2 stadi



forma ionica

forma covalente

R porta carica negativa nucleofilo e base forte

	% ionico
C-K	51
C-Na	47
C-Li	43
C-Mg	35
C-Zn	18
C-Cd	15
C-Cu	9

base più forte
più reattivo

Li e Mg sono i metalli più usati

nucleofilo migliore
meno reattivo

III. Preparazione di Composti Organometallici

Metalli del Gruppo I: Li, Na, K

$$R{-}X + 2M \longrightarrow R{-}M + M^{+}X^{-}$$

Metalli del Gruppo II: Mg, Cu

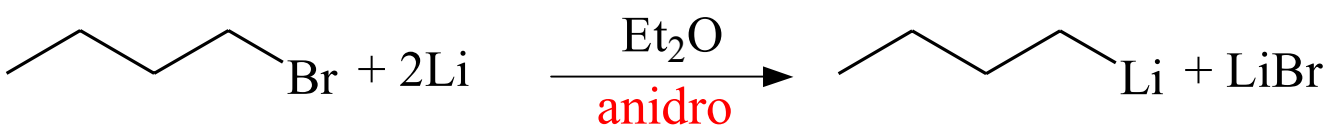
$$R{-}X + M \longrightarrow R{-}M^{+}X^{-}$$

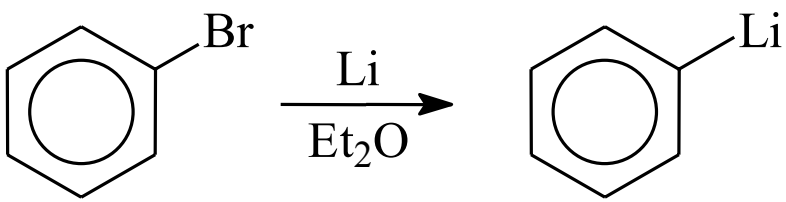
R = 1°, 2°, alcuni 3°, vinile, fenile

velocità: X = I > Br > Cl

solventi: eteri, pentano, benzene

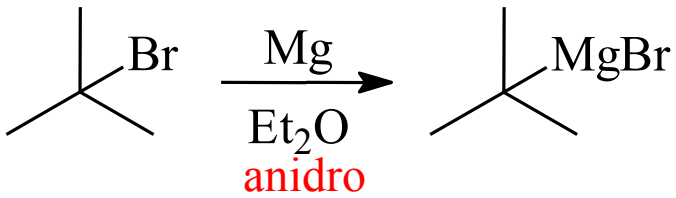
A. Composti Organolitio



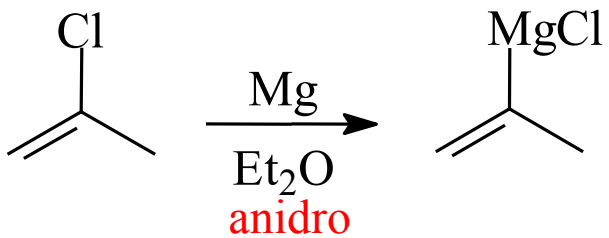


III. Preparazione di Composti Organometallici

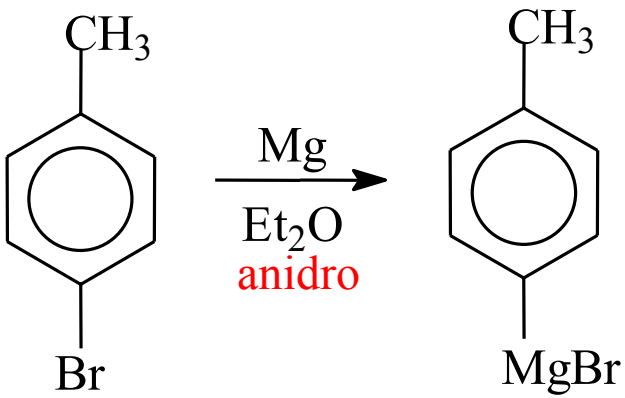
B. Reattivi di Grignard (organomagnesiaci)



t-butilmagnesio bromuro



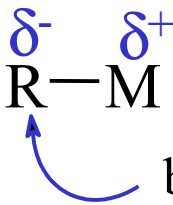
isopropenilmagnesio bromuro



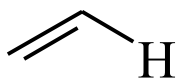
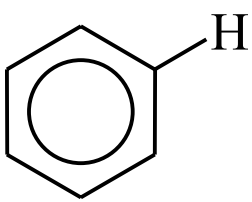
p-tolilmagnesio bromuro

III. Preparazione di Composti Organometallici

C. I composti organometallici sono **basi forti**.

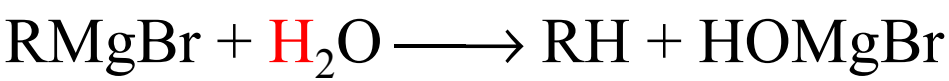


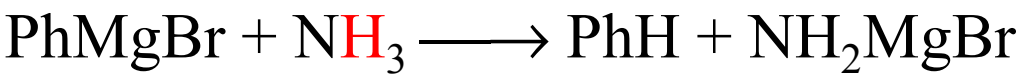
base **molto** forte (base coniugata di una acido **molto** debole)

	pK_a		pK_a
R–H	60	HC≡C–H	25
	45	ROH	16
	45	H_2O	16
NH_3	36	RCO_2H	5

III. C. Basi forti

∴ Bisogna evitare composti protici:





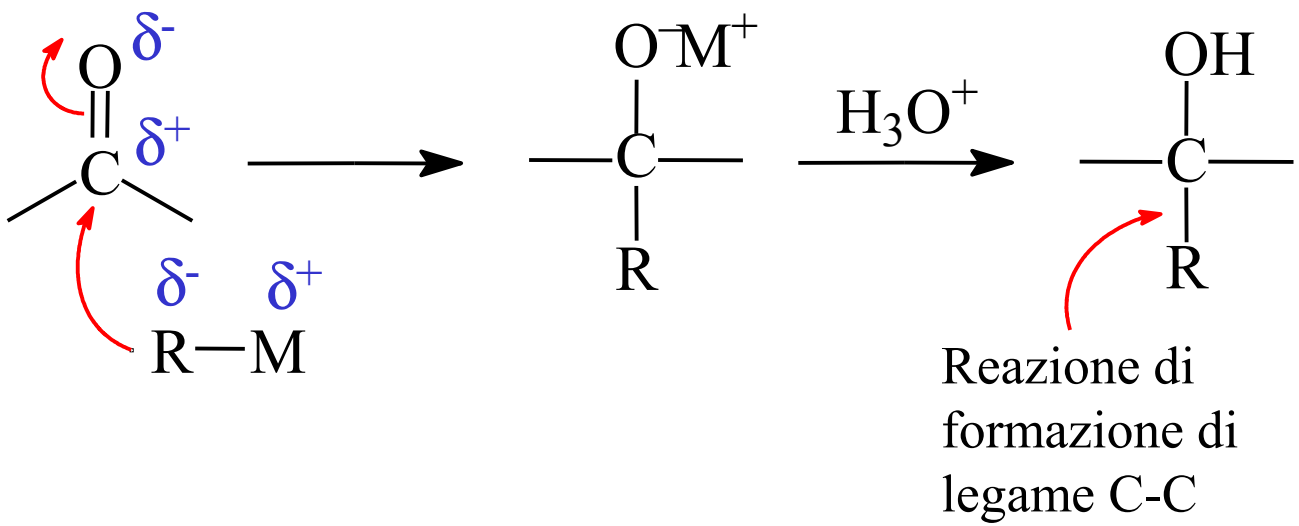
Ma può essere utile:

– Rimuovere un alogeno:

– Introdurre il deuterio:

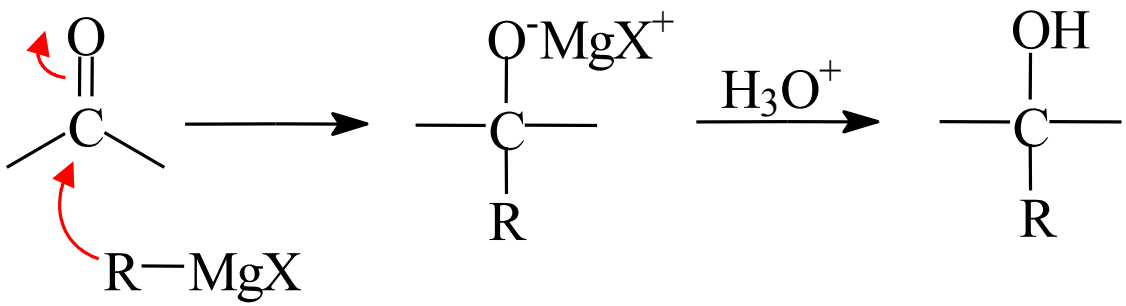
IV. Sintesi di Alcoli

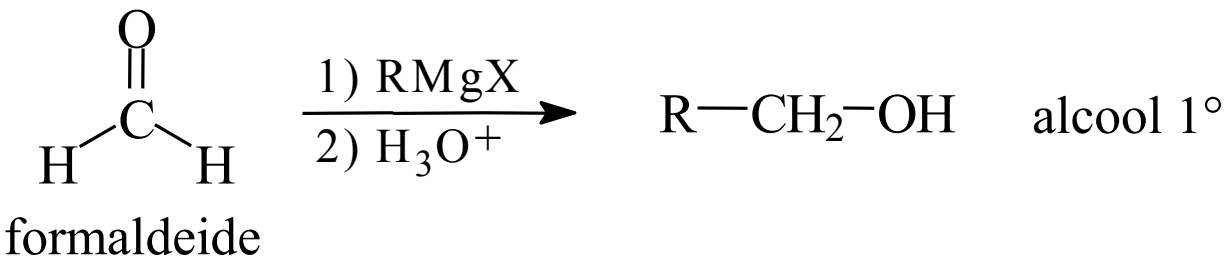
In generale:



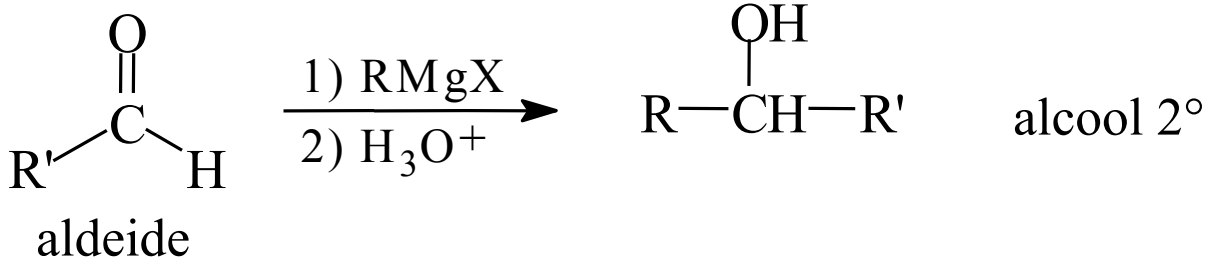
IV. Sintesi di Alcoli

A. Reattivi di Grignard e aldeidi e chetoni

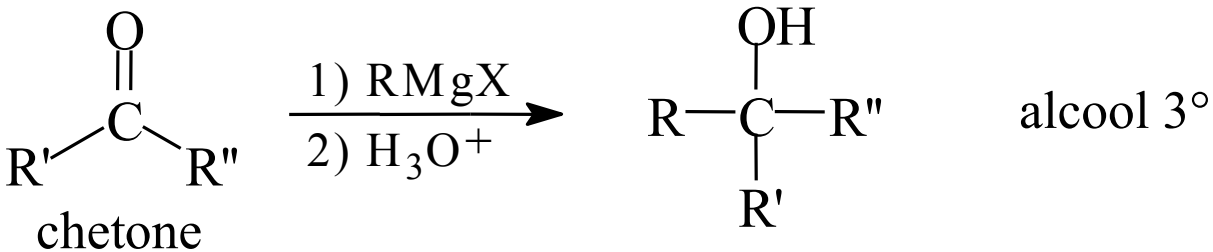




formaldeide



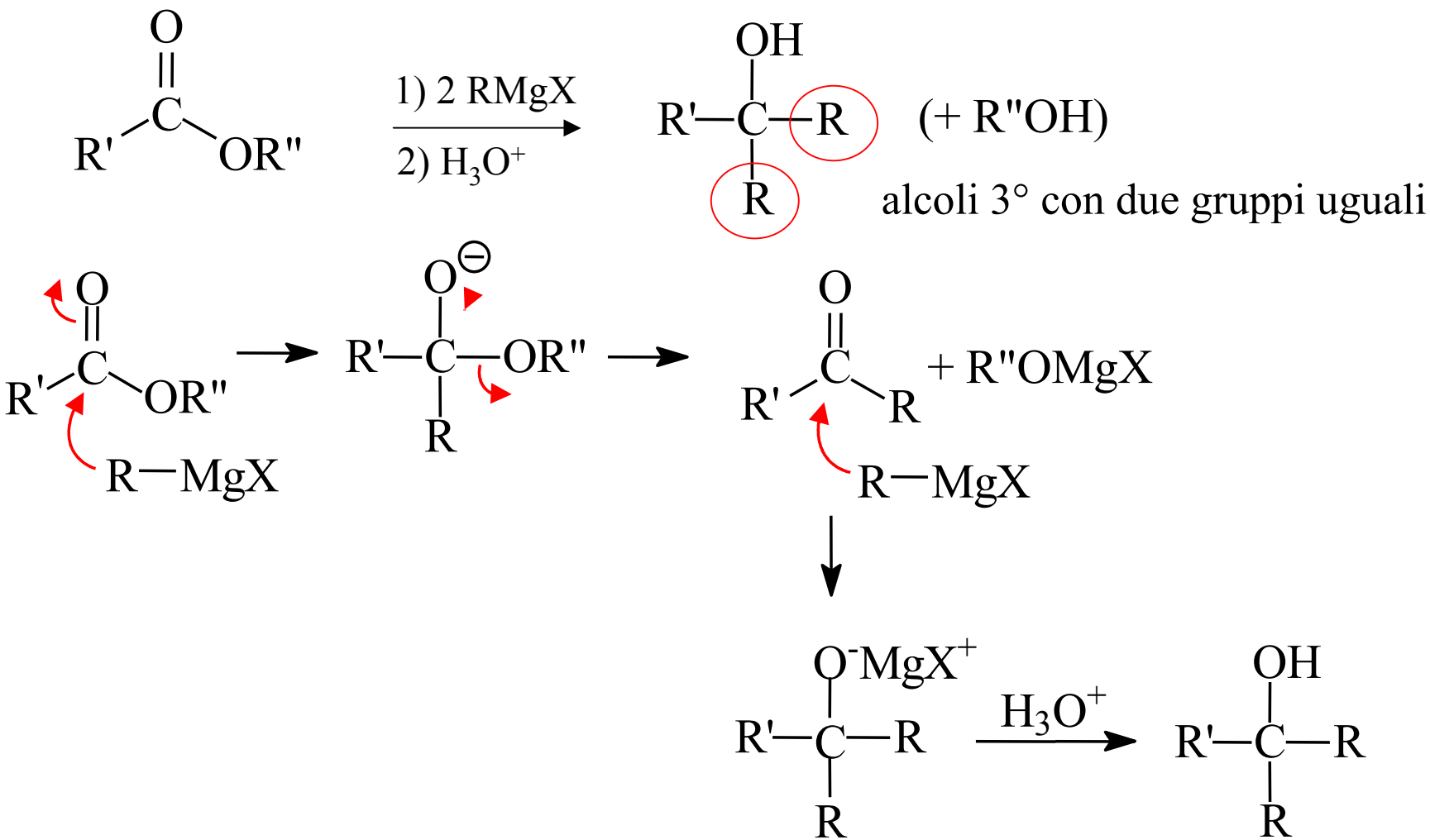
aldeide



chetone

IV. Sintesi di Alcoli

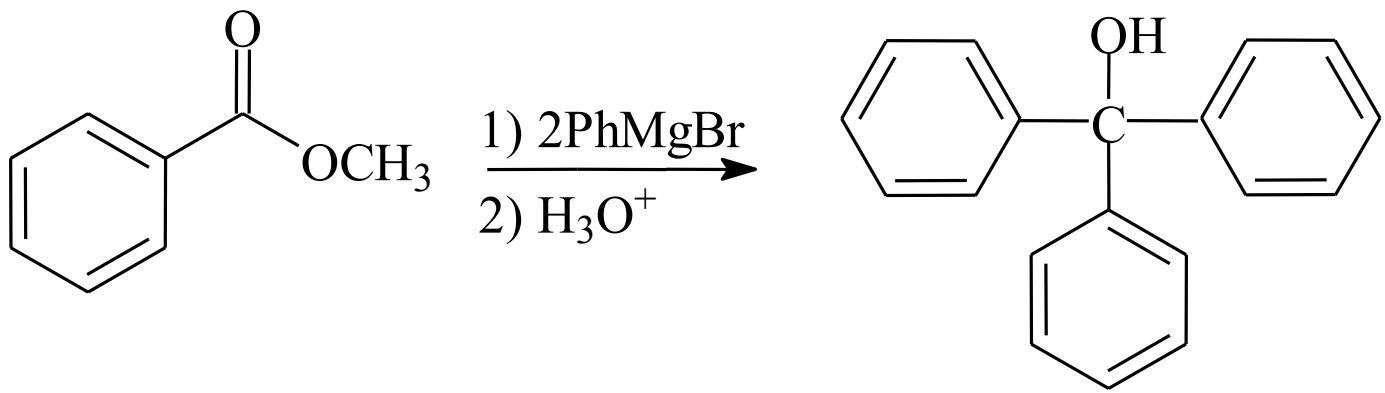
B. Reattivi di Grignard e esteri

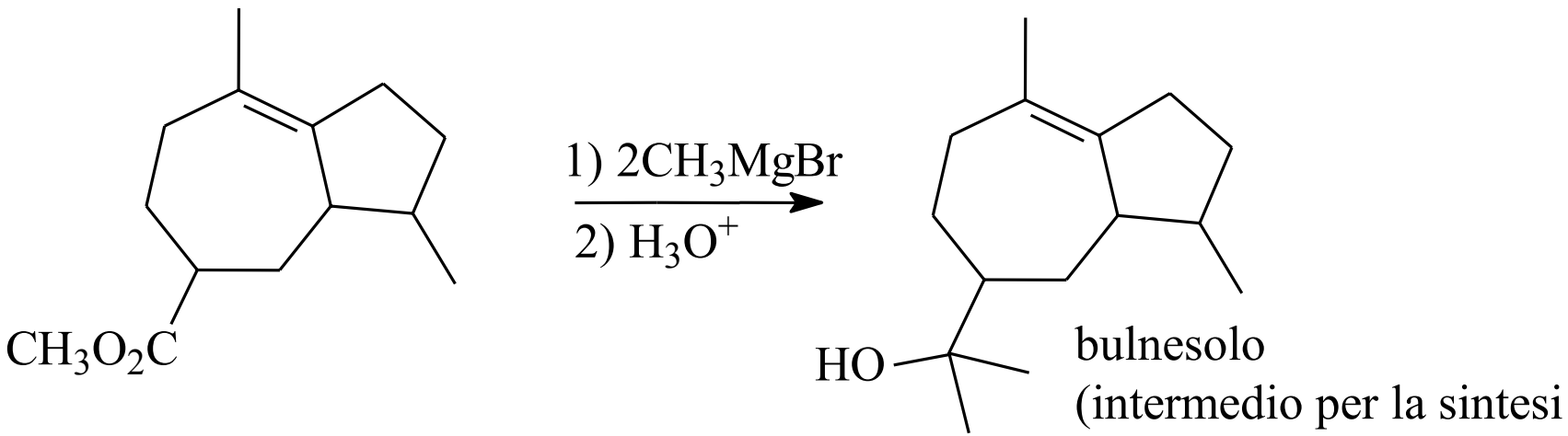


IV. Sintesi di Alcoli

B. Reattivi di Grignard e esteri

Esempi

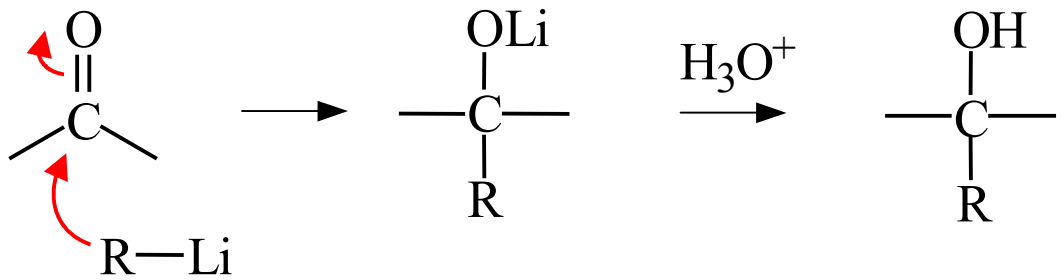


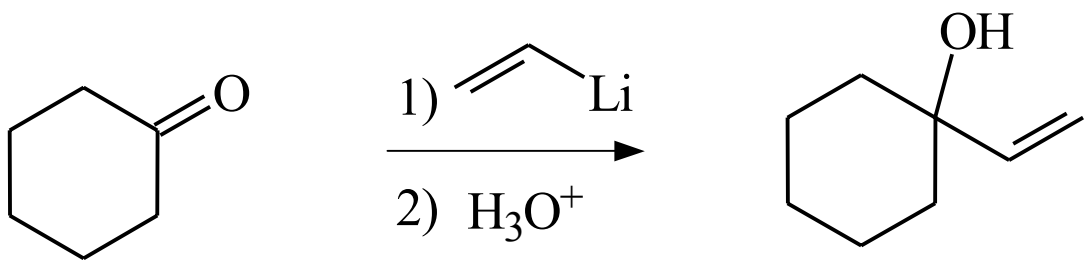


bulnesolo
(intermedio per la sintesi
di farmaci e insetticidi)

IV. Sintesi di Alcoli

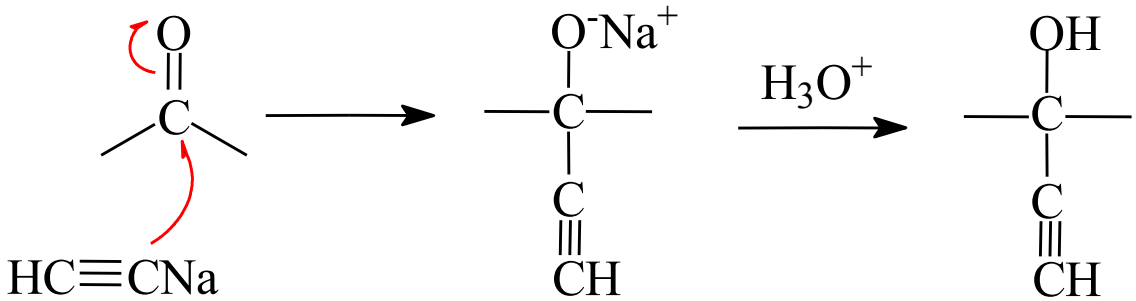
C. Reagenti Organolitio

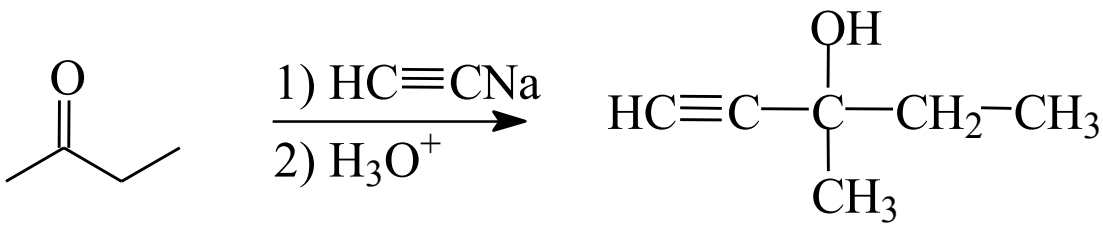


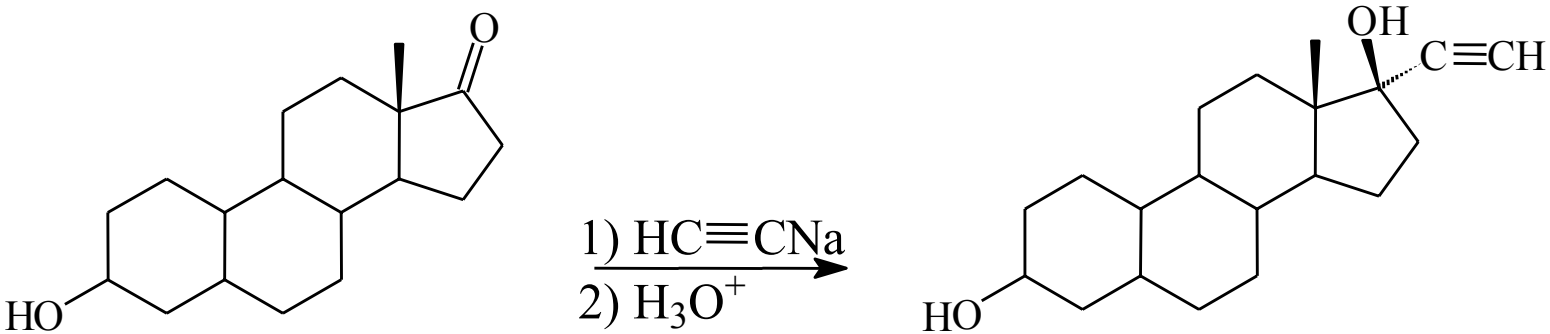


IV. Sintesi di Alcoli

D. Ioni acetiluro



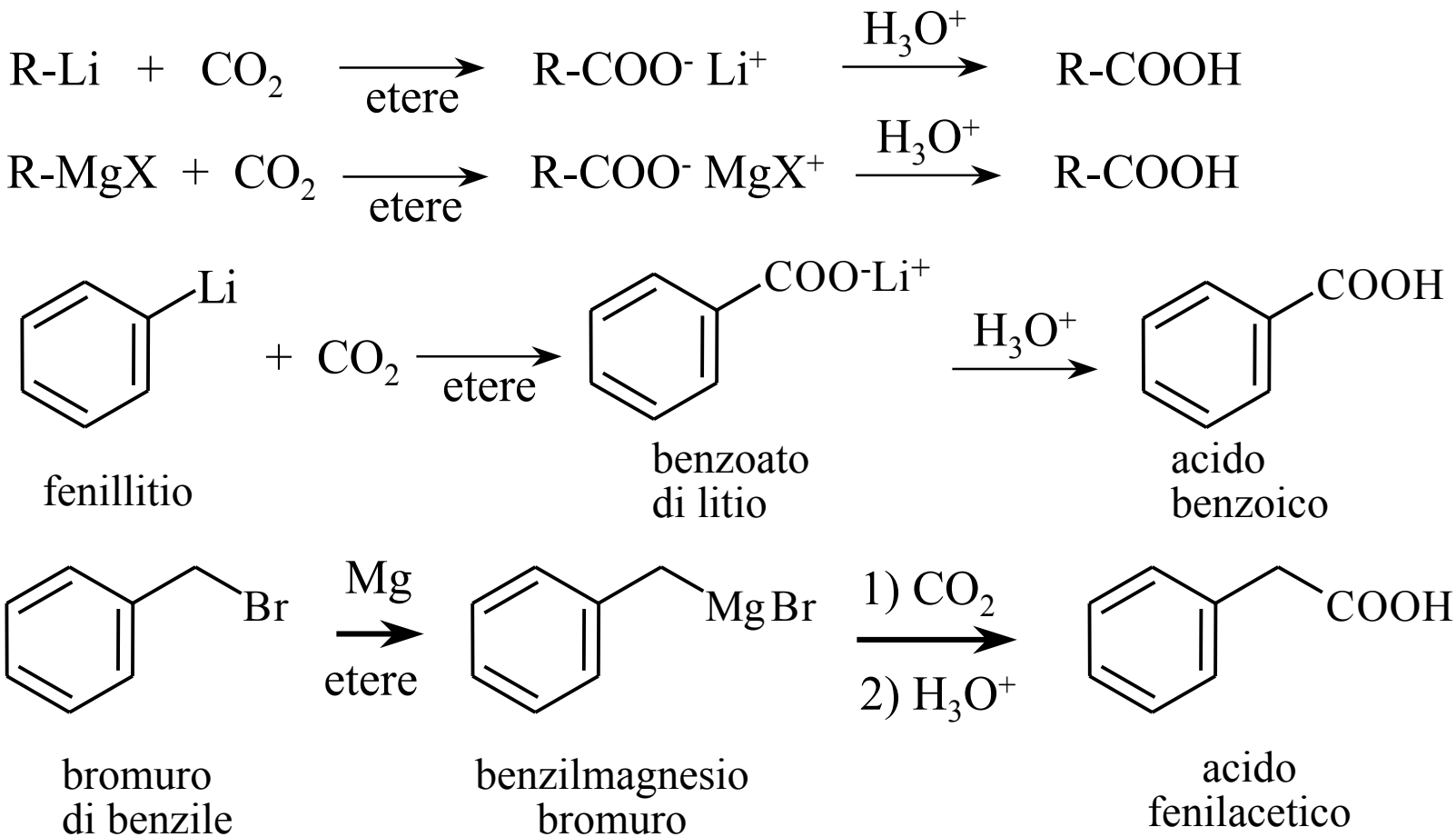




$$HC{\equiv}CH + NaNH_2 \longrightarrow HC{\equiv}CNa + NH_3$$

V. Sintesi di acidi

CO_2 solido (ghiaccio secco) reagisce con RLi e RMgX per dare acidi carbossilici.



VI. Reagenti Organorame

Sintesi di alcani

$$2RLi + CuX \xrightarrow{\text{etere}} R_2CuLi + LiX$$

litio dialchilcuprato

$$R_2CuLi + R'X \xrightarrow{\text{etere}} R{-}R' + RCu + LiX$$

solo 1°