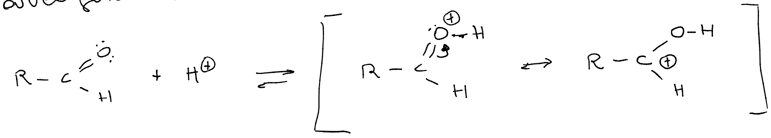
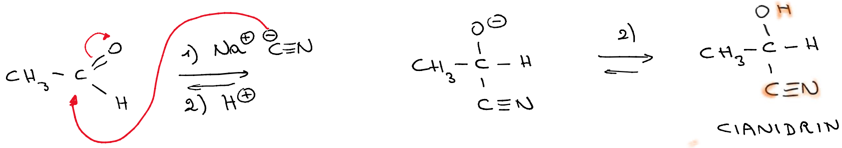
Sono le reazioni di addizione Nu al C carbonilico avvengono con catalisi acida :



SINTESI DELLE CIANIDRINE

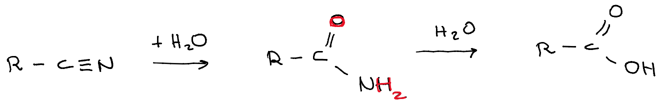


CIANIDRINA

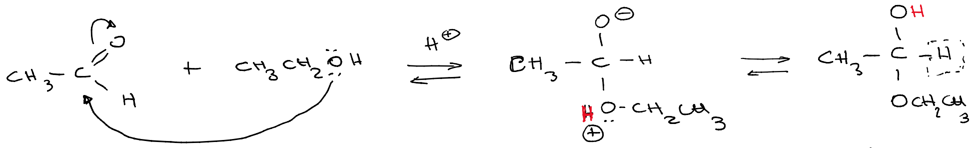
È stato aggiunto HCN

HCN non è acido forte pKa = 9,1

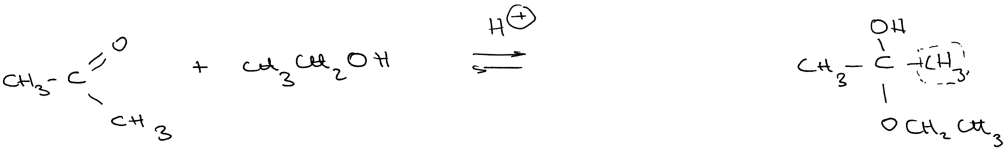
HCN è un gas tossico



SINTESI DI EMIACETALI / EMICHETALI



EMIACETALE

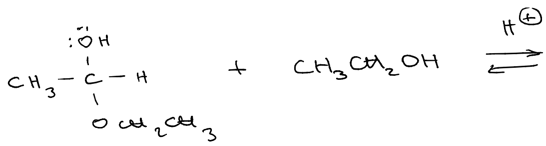


EMICHETALE

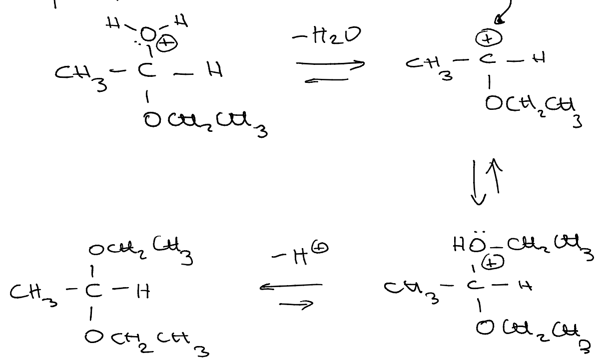
Se gli emiacetali reagiscono con una seconda molecola di ROH generano ACETALI

CHETONE + ROH → EMICHETALE

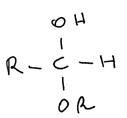
EMICHETALE + ROH → CHETALE



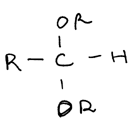
L'emiacetale si protona :



Acetale



Emiacetale

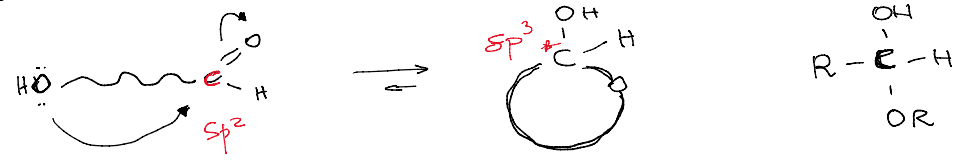


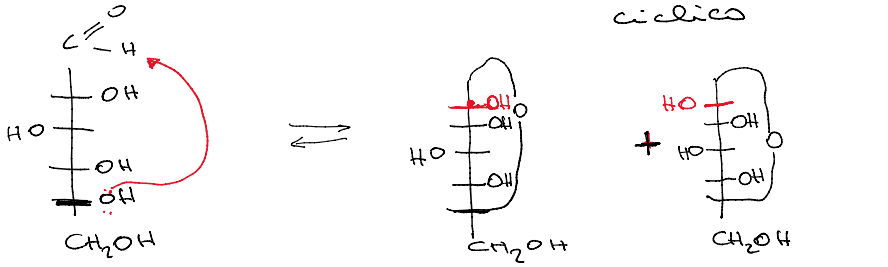
Acetale

... spostate a dx ad eccezione

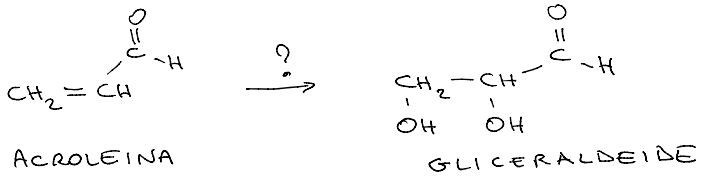
Acetale

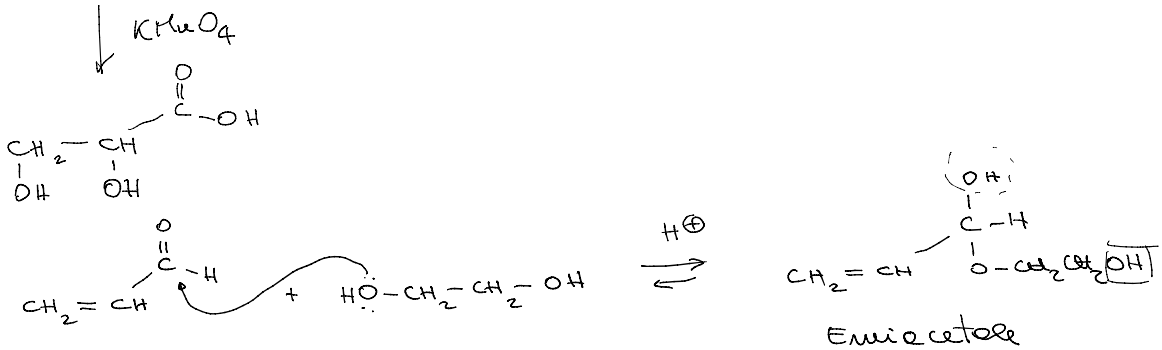
Queste reazioni sono poco spostate a dx ad eccezione delle reazioni INTRAMOLECOLARI

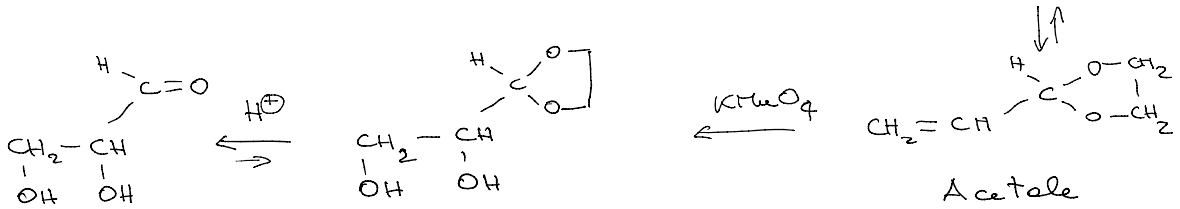




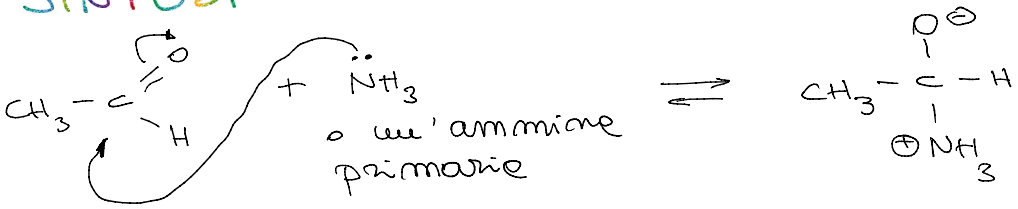
Acetali come gruppi protettori

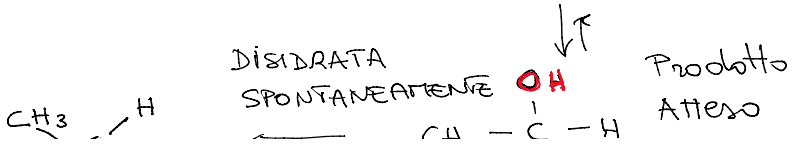


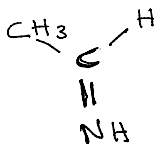




SINTESI DELLE IMMINE o BASI di SCHIFF

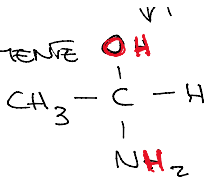






IMMINA

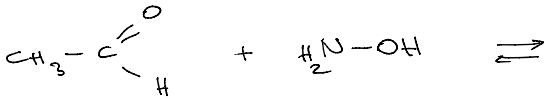
DISIDRATA SPONTANEAMENTE ←



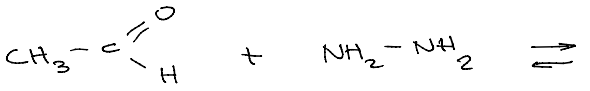
Prodotto Atteso

Aldimmine se uso una aldeide

Chetimmine se uso un chetone



IDROSSILAMMINA — OSSIMA



IDRAZINA — IDRAZONE

Reazioni condotte con $pH = 4 \div 5$

REAZIONE CON I REATTIVI DI GRIGNARD

I REATTIVI DI GRIGNARD SONO REATTIVI ORGANOMETALLICI (C — Metallo)

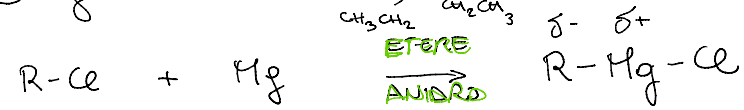
Il composto è tanto più reattivo quanto più grande è la % di carattere ionico del legame C – M ($-\overset{|}{C}\ominus \oplus M$)

Se M = Hg il legame ha il 9% di carattere ionico (91% covalente) ⇒ non reattivo

M = Na 47% di carattere ionico ⇒ Molto reattivo

M = Mg 35% " " " ⇒ Reattivo

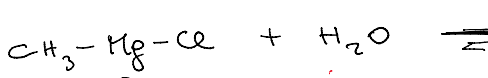
I reattivi organomagnesiaci si dicono reattivi di Grignard



ETERE ANIDRO

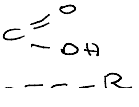
Alogenuro alchilico o Arilico — Magnesio Metallico — Reattivo di Grignard

Perché serve anidro:



per un 35%: $\ominus CH_3 \; \oplus MgCl$

Reagiscono così anche ROH



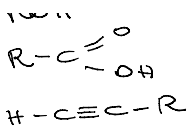
$CH_4 \rightleftharpoons {}^{\ominus}CH_3 + H^{\oplus}$

$K_a = 10^{-50}$

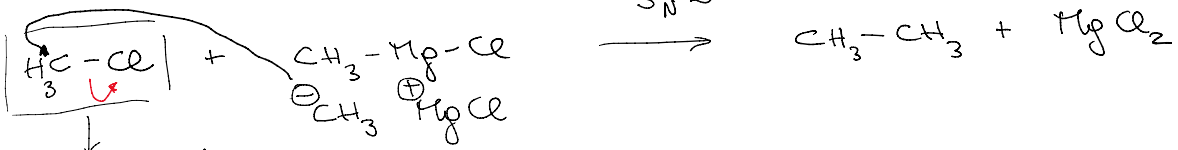
Base coniugata del metano

BASE FORTISSIMA

anche



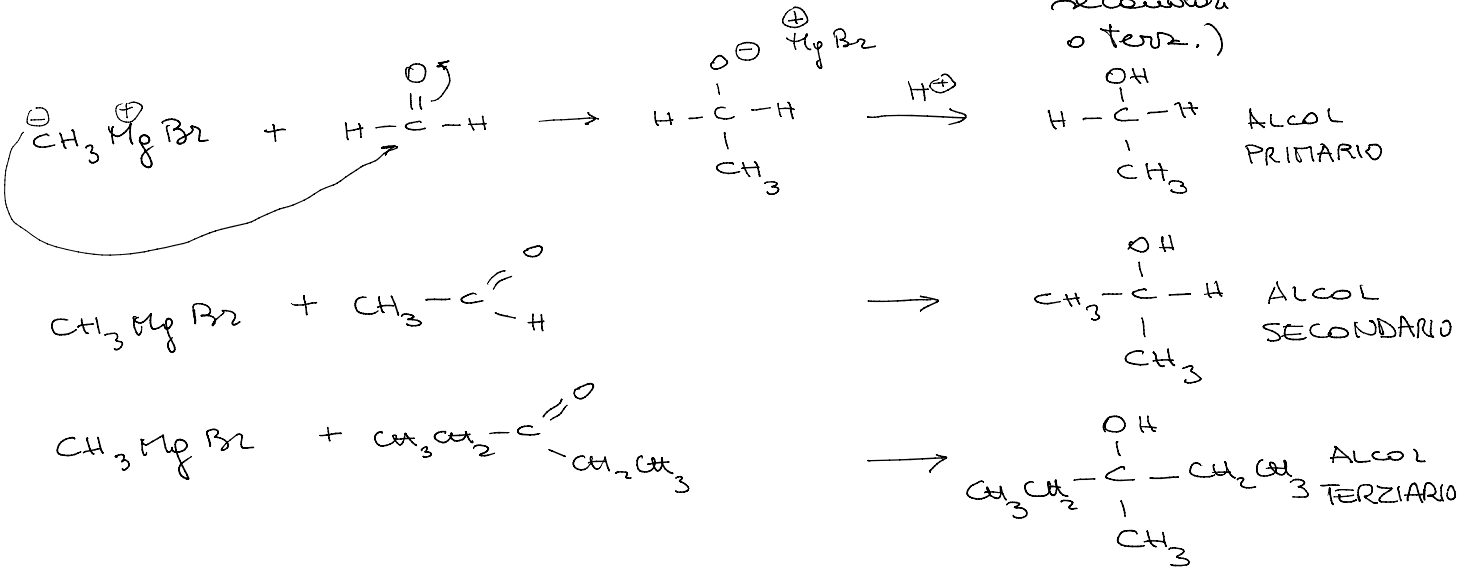
Perché serve l'etere?



Buon substrato per S_N

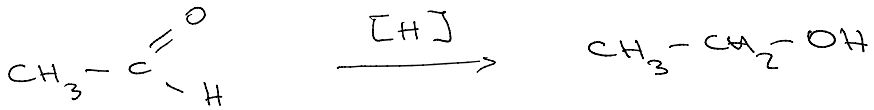
↑ L'etere si coordina attorno al Grignard e lo protegge dalla reazione con RCl

Reattivo di Grignard + aldeidi / chetoni ⇒ Tutti gli alcoli (primari, secondari o terz.)



RIDUZIONI → AD ALCOL / AD ALCANO

RIDUZIONI AD ALCOL



① IDROGENAZIONE CATALITICA H_2 / Ni ΔT ΔP

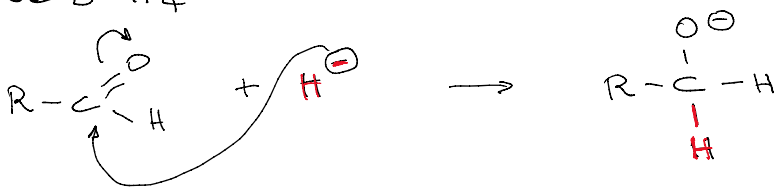
② RIDUCENTI SPECIFICI PER IL GR. CARBONILICO

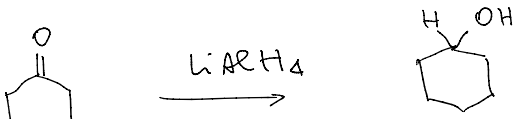
i: AlH_4 Litio Alluminio idruro (etere)

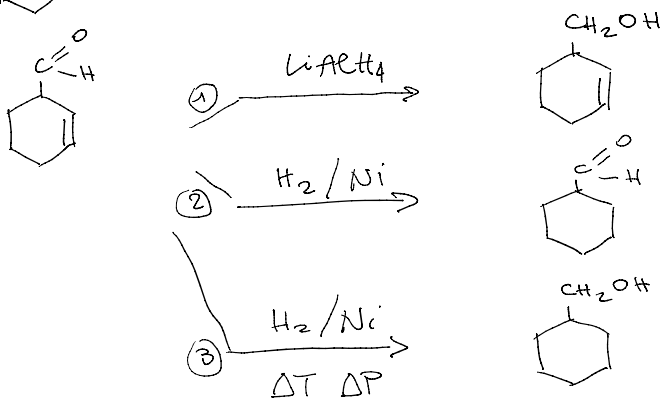
② RIDUCENTI SPECIFICI PER

$LiAlH_4$ Litio Alluminio idruro (Etere)

$NaBH_4$ Sodio Boro idruro (Acool)







RIDUZIONE AD ALCANO

① CLEMMENSEN HCl Zn (Hg) solo per CHETONI

② WOLFF-KISHNER NH_2-NH_2 KOH sia per ALDEIDI che per CHETONI

OSSIDAZIONE

Si possono utilizzare ossidanti blandi come Ag^+ (Ag_2O in NH_3)