A/K IV

More Addition Rxns w/

- N – species
- C – species
- "hydrides"
- "organometallics"

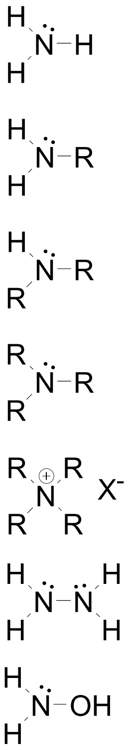
Spectroscopy

Ref 16: 8 - 9 ; (12: 3 - 8)

Prob HMWK # 07

Adv Rdg 18: 1 - 2I

Amine Terminology



ammonia

1° amine

2° amine

3° amine

quaternary
ammonium salt

hydrazine, H_2NNH_2

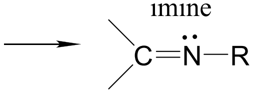
hydroxylamine

"Amine" Additions

"amine" = good Nu,
b/c lone pair e⁻'s

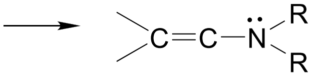
1° amine
(incl. hydrazine, hydroxylamines)

imine



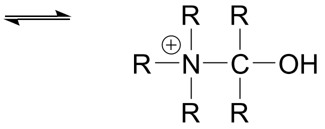
2° amine

enamine



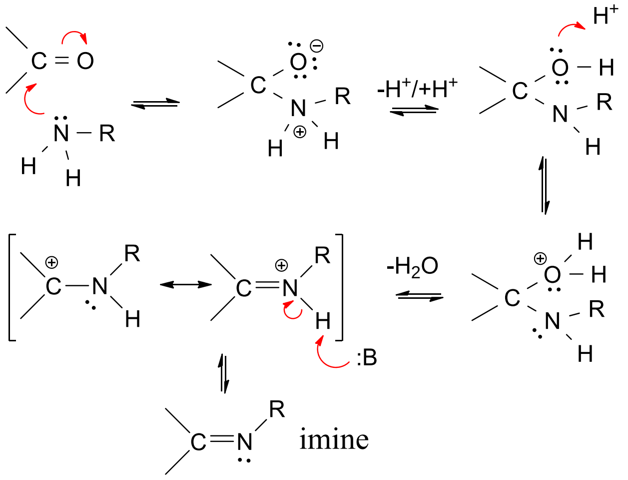
3° amine

"reversible complex"
(no apparent product)



optimum rxn conditions:slightly acidic (pH 4 – 6), providing a "neutral mech."

Mech. for Imine Form^n



Notes:

- works w/ 1° amines, hydrazines, hydroxylamines, ...
- can be reduced to amines w/ Na^+ H_3BCN^-

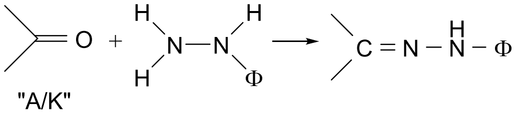
Applications

1.) Prep. of A/K derivatives for analytical purposes

(for details, see lab)

- add^n products are prepared
  w/ substituted phenylhydrazines, $\Phi NHNH_2$

- products are insoluble; m.p. can be used for ID



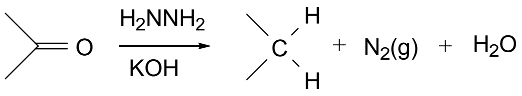
- by imine like mech.

- b/c products insoluble, equil. shifted to the right

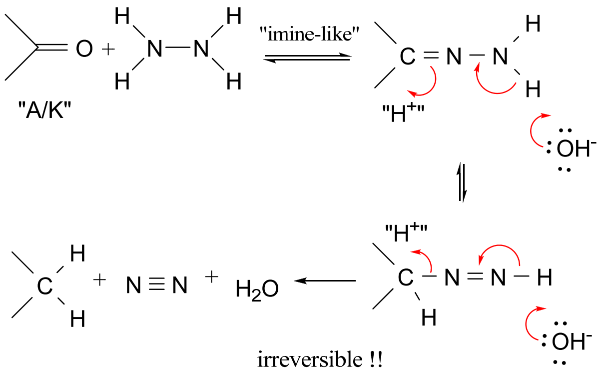
∴ derivatives can be isolated easily

2.) Wolff – Kishner Reduction

Overall



Mech.



Wolff – Kishner ....

Comments:

- applies to all A/K's (aromatic & aliphatic)

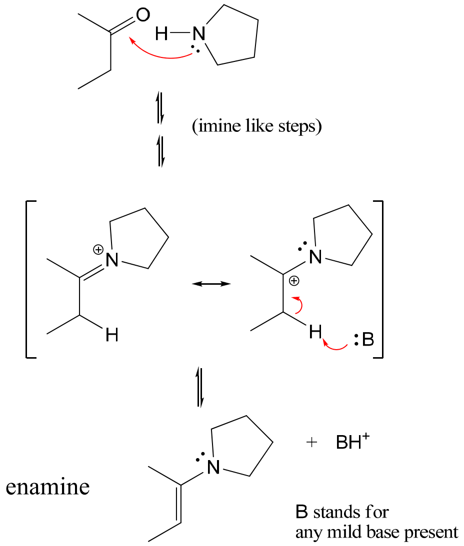
- Clemmensen (Zn(Hg)/HCl) reduction or mild
  hydrogenation will not touch aliphatic ketones

- in particular, applies to arylketones
  available from Friedel-Crafts acylation

Enamine Form^n

- important for 2° amines (they can't form imines)
- most commonly used: pyrrolidine

typical mech.

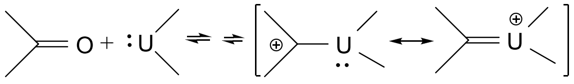


Note: 1° amines can also form enamines;
but they are less stable than imines

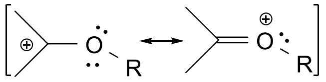
Generalization for Add^n of Alcohols/Amines

Key intermediate: resonance stabilised cation

U = nucleophilic center (O or N):

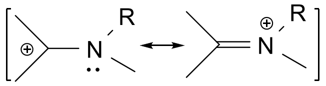


for acetals



"oxonium ion"

for amine derivatives



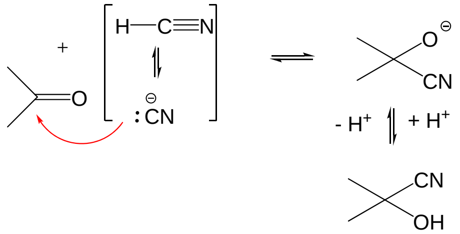
"imonium ion"

These react further to form the ultimate products.

Add^n of "C species"

1.) HCN under slightly basic conditions

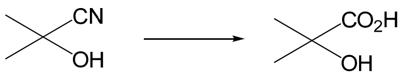
(products useful for further synthesis)



"cyanohydrine"

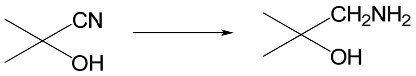
Further transformations:

acid hydrolysis:



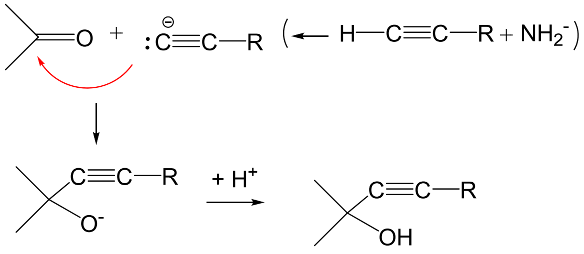
α-hydroycarboxylic acids

hydride reduction:



1,2-aminoalcohols

2.) Alkynide Addition



Note: C,C – Bond Formation

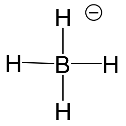
Useful for further synthsis

Hydride Reduction of A/K's

A/K's → Alcohols

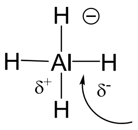
common reagents

$NaBH_4$



"mild"

$LiAlH_4$



"strong"

"σ bond acts as nucleophile"

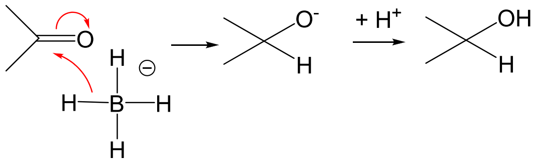
due to Δ E/N's

recall E/N's: H, 2.1; B, 2.0; Al, 1.5

hydride reduction

NaBH$_4$ strong enough for A/K's

Simple Mech.



aldehyde → 1° alcohol;

ketone → 2° alcohol

Note: H:$^-$ from NaH does not work,

b/c orbitals don't match

Cannizzaro Rxn

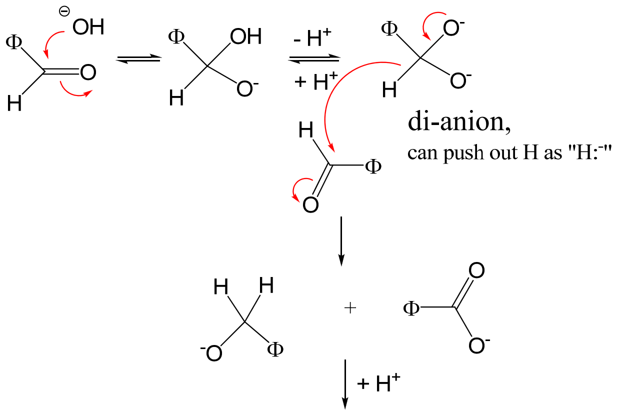
applicable to aldeydes w/t α H, e.g., benzaldehyde

strong base and high temp, are required

disproportonation rxn:

$$2\,RCHO \rightarrow RCH_2OH + RCO_2H$$

alcohol acid

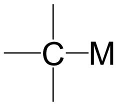


di-anion,
can push out H as "H:$^-$"

$$\Phi CH_2OH + \Phi CO_2H$$

Organometallics

Recall:

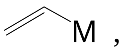
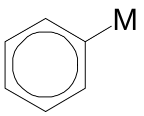


where M = metal, esp. Mg, Li

prepare from haloalkane:

$$RX \xrightarrow{2\,Li} R{-}Li + LiX$$

$$RX \xrightarrow{Mg} R{-}Mg{-}X$$

R can be 1°, 2°, 3°; also  , 

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organometallics

C – M bond highly polarized

has much ionic character

acts as nuclephile in add^n rxn

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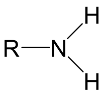
organometallics react w/ any "acidic" molecule (*usually, undesirable side rxn*)

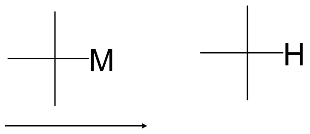


$R{-}C{\equiv}C{-}H$

$R{-}O{-}H$

$R{-}CO_2H$

H_2O



+

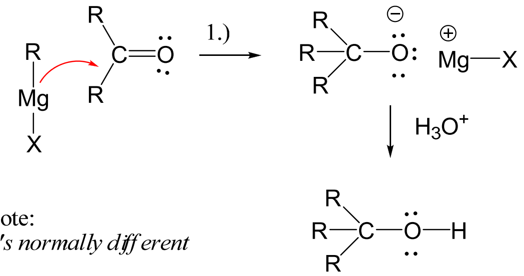
corresponding anion

acid organometallic "hydrocarbon"

A/K + "Grignard"

(Li cmpds react similarly)

Mech.:

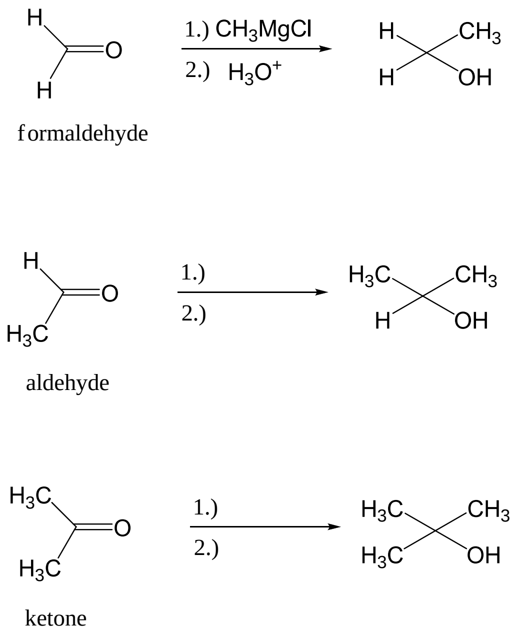


Note:
R's normally different

∴ "A/K's" → alcohol

new C–C bond formed !!

Examples

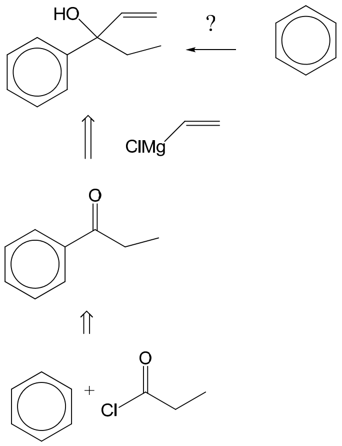


1° ROH

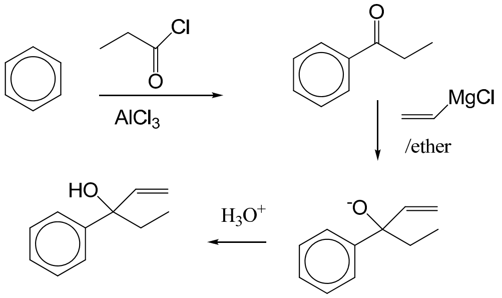
2° ROH

3° ROH

Practice: Retrosynthetic Analysis

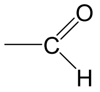


Synthetic Steps:

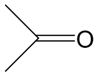


Spectroscopy

1.) IR



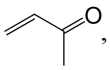
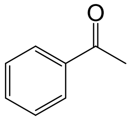
C - H stretch: 2700 - 2900 cm^{-1}
(lower than normal sp^3 C-H)



carbonyl C=O stretch

sat^d aldehyde: ~ 1730 cm^{-1}

sat^d ketone : ~ 1715 cm^{-1}

unsat^d A/K : e.g., , 

~ 1685 -1705 cm^{-1}

Explanation:

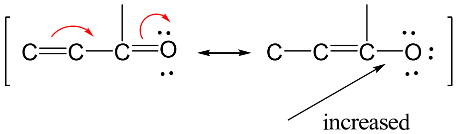
- double bonds stronger, stiffer than single bonds,
- wavenumber ↑ w/ increasing bond strength
- acc. to Hooke's Law; $\tilde{\nu} \propto \sqrt{\frac{f}{\mu}}$
- C=O absorbs at larger $\tilde{\nu}$ than C–O

IR

- conjugation & "hyperconjugation"

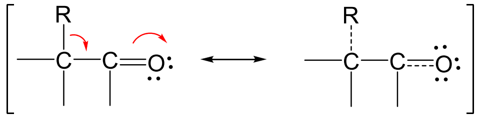
  reduce double bond character of C=O

conjugation effect



increased
single bond character

hyperconjugation effect for ketones:



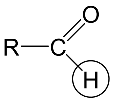
∴ bond order ↓ ,

bond strength ↓.,

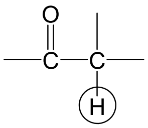
f ↓ , $\boxed{\tilde{\nu}\downarrow}$

2.) NMR

chemical shifts, δ

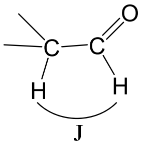


aldehyde H: δ = 9 - 10 ppm

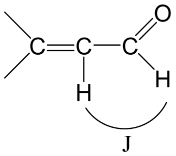


"α H" : δ ~ 2.5 ppm

coupling constants, J (vicinal)



J = 1 - 3 Hz; avg ~ 3 Hz



J = 5 - 8 Hz; avg ~ 6 Hz