Carboxylic Acids II

Prep

Rxns

Spectroscopy

Ref 18: 2J - 4

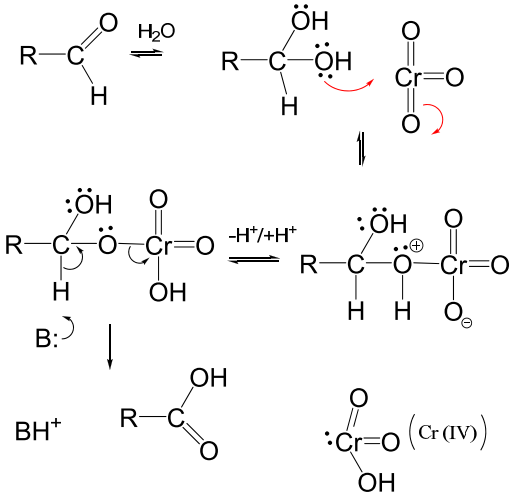
Prob 18: 6 - 8, 21 - 23

Adv Rdg 18: 4 - 6

Prep.

1.) Oxid^n of 1° ROH or Aldehyde
w/ Cr(VI) in aqueous medium
(recall:oxid^n of 1° ROH w/ PCC/(anhydrous) → aldehyde)

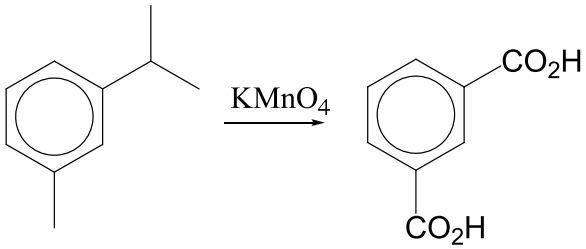
In presence of H_2O, hydrate of aldehyde forms & mech. of oxidation repeats



2.) Benzylic Oxid^n

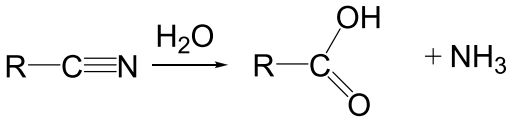
(seen earlier, under "Aromatics")

Ex.

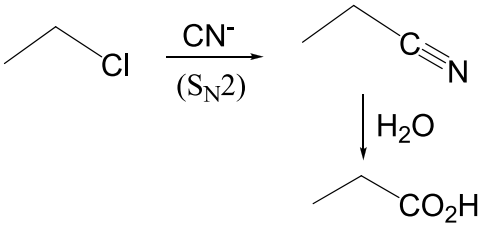


3.) Hydrolysis of Cyanides (Nitriles)

(in base or acid)



Ex.:



N.B. • chain length ↑

• hydrolysis rxn applies to cyanohydrins , available from A/K's

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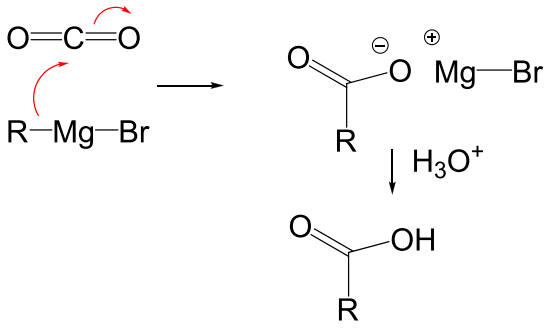
3a.) Hydolysis of Other Acid Derivatives (see later)

4.) Grignard Rxn

~~(see also Lab #6~~, obsolete)

Overall: "Grignard" + CO_2 → 'acid"

Mech.



Rxns

1.) Reduction to 1° Alcohols

use $LiAlH_4$ or, even better, BH_3

(mech. later)

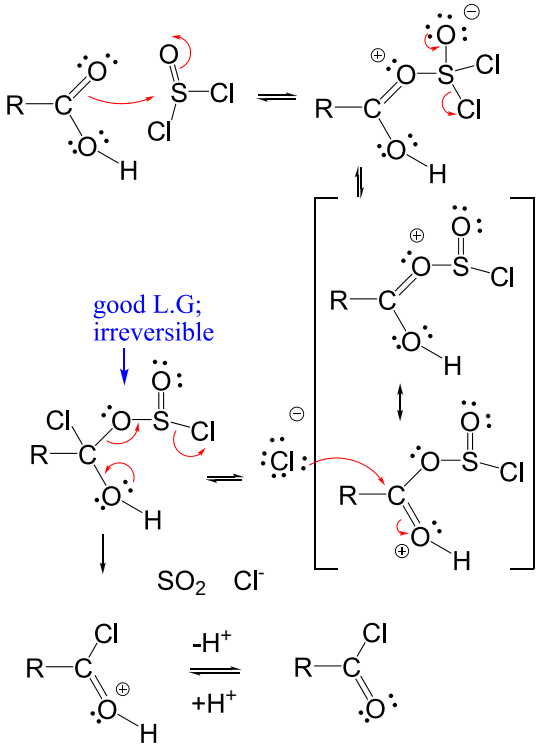
2.) Rxn w/ organometallics,
esp., Li-R

⇒ ketones

(mech. later)

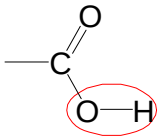
3.) Acyl Chloride Form^n
w/ Thionyl Chloride ($SOCl_2$)

Mech.

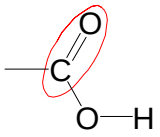


Spectroscopy

IR

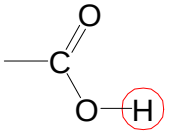


O–H stretch , 2500 – 3300 cm^{-1}
very broad due to H-bonding

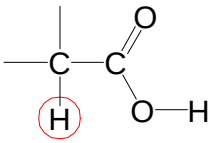


carbonyl stretch:
1760 cm^{-1}, if free (no H-bonding)
1710 cm^{-1}, if H-bonded (normal)

NMR

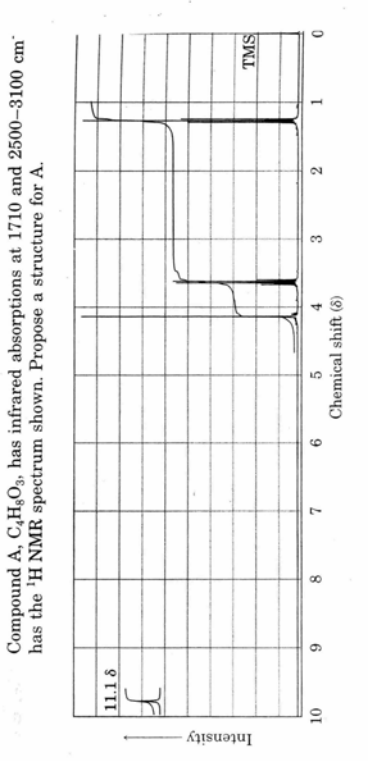


δ ≈ 12 ppm, variable,
often "broad singlet",
subject to D_2O exchange



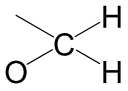
δ ≈ 2.5 ppm,
similar to other α H's of carbonyls

Spectroscopy Practice



Solution

$C_4H_8O_3 \Rightarrow$ D of U = 1

δ (ppm)	# of H's	multi-plicity	part structure
11.1	1	s	$-CO_2H$
4.2	2	s	
3.7	2	q	$-CH_2CH_3$
1.2	3	t	on O

Ans.