

Carboxylic Acids II

Prep

Rxns

Spectroscopy

Ref 18: 2J - 4

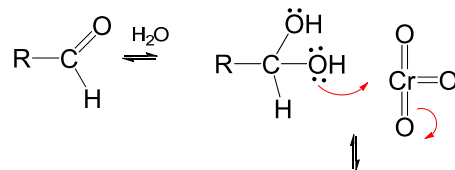
Prob 18: 6 - 8, 21 - 23

Adv Rdg 18: 4 - 6

Prep.

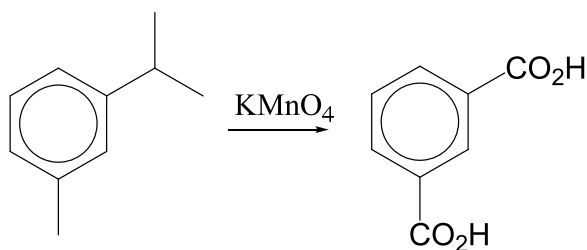
1.) Oxidⁿ of 1° ROH or Aldehyde
w/ Cr(VI) in aqueous medium
(recall: oxidⁿ of 1° ROH w/ PCC/(anhydrous) → aldehyde)

In presence of H₂O, hydrate of aldehyde forms
& mech. of oxidation repeats

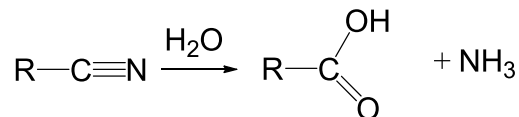


2.) Benzylic Oxidⁿ
(seen earlier, under “Aromatics”)

Ex.



3.) Hydrolysis of Cyanides (Nitriles)
(in base or acid)



N.B. • chain length ↑
• hydrolysis rxn applies to
cyanohydrins, available from A/K's

3a.) Hydrolysis of other Acid Derivatives (see later)

4.) Grignard Rxn

(see also Lab #6)

Overall: "Grignard" + $\text{CO}_2 \rightarrow$ 'acid'

Mech.

Rxns

1.) Reduction to 1° Alcohols

use LiAlH_4 or, even better, BH_3

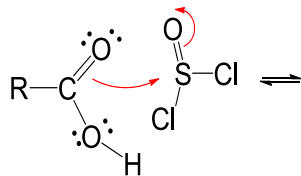
(mech. later)

2.) Rxn w/ organometallics,
esp., Li-R $\Rightarrow$ ketones

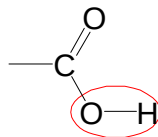
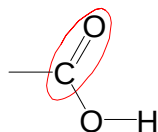
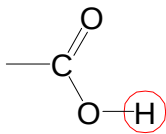
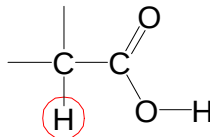
(mech. later)

3.) Acyl Chloride Formⁿ
w/ Thionyl Chloride (SOCl_2)

Mech.

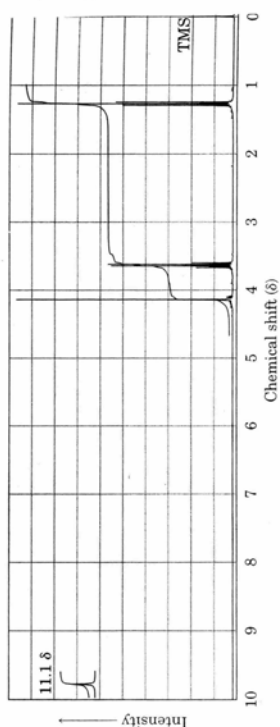


Spectroscopy

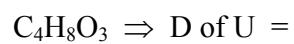
IRO-H stretch, $2500 - 3300 \text{ cm}^{-1}$
very broad due to H-bondingcarbonyl stretch:
 1760 cm^{-1} , if free (no H-bonding)
 1710 cm^{-1} , if H-bonded (normal)NMR $\delta \approx 12 \text{ ppm}$, variable,
often "broad singlet",
subject to D_2O exchange $\delta \approx 2.5 \text{ ppm}$,
similar to other α H's of
carbonyls

Spectroscopy Practice

Compound A, $C_4H_8O_3$, has infrared absorptions at 1710 and 2500–3100 cm^{-1} has the 1H NMR spectrum shown. Propose a structure for A.



Solution



δ (ppm)	# of H's	multi- plicity	part structure
11.1			
4.2			
3.7			
1.2			

Ans.