Stratingh Institute for Chemistry

Problem Set
02. December 2021

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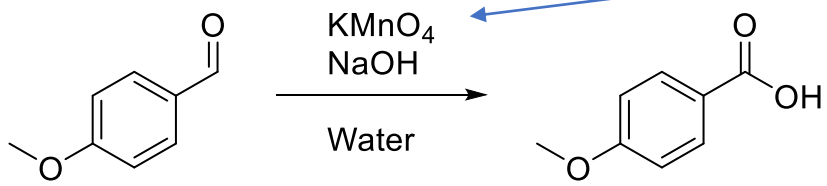
Goal

Discuss chemistry!

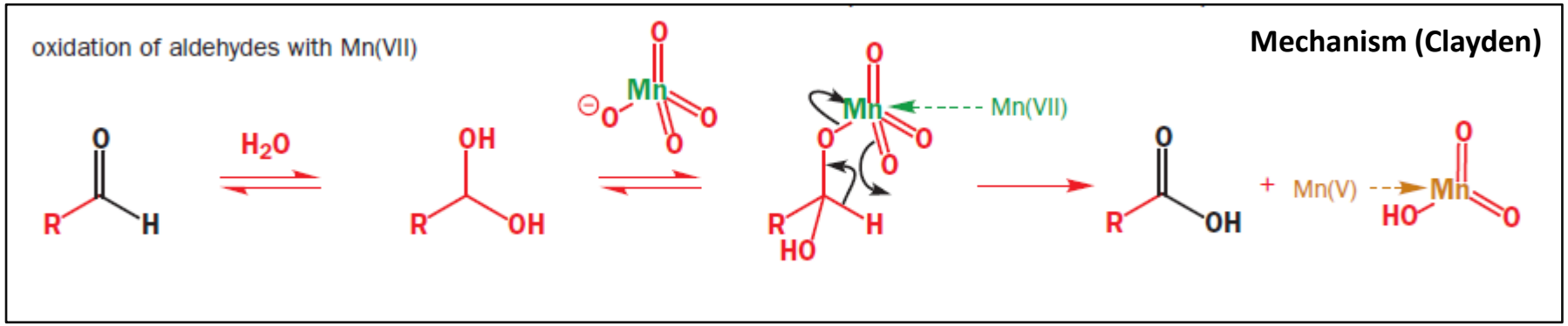
Ideas / Experiences / Concepts

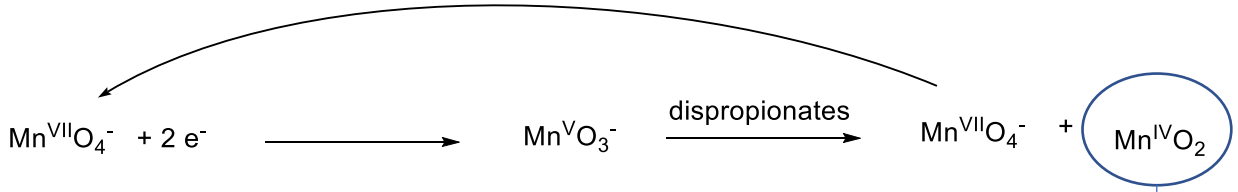
For your project you need p-Anisidine. Unfortunately, there are delivery problems. Luckily Steven has some Anisaldehyde (see below) and tells you can easily convert this to your starting material. To sweeten the deal, he even as a nice oxidation procedure for you:

How many equivalents necessary?



Anisaldehyde Anisic acid

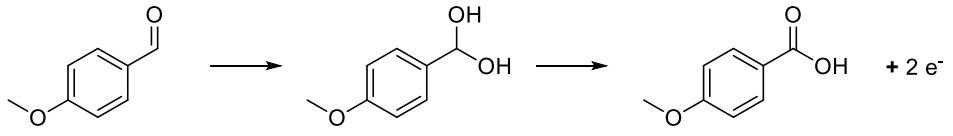




Permanganate is ultimately reduced to manganese dioxide

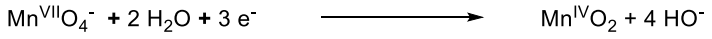
a. Write the redox equation of this reaction

Oxidation:

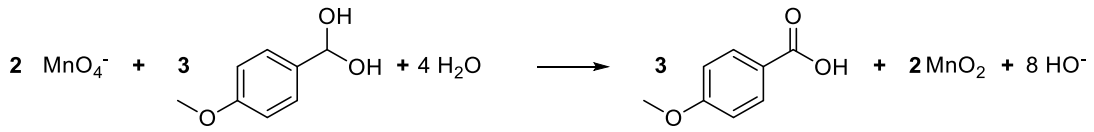


Oxidation states
Aldehyde: +1
Carboxylic acid: +3

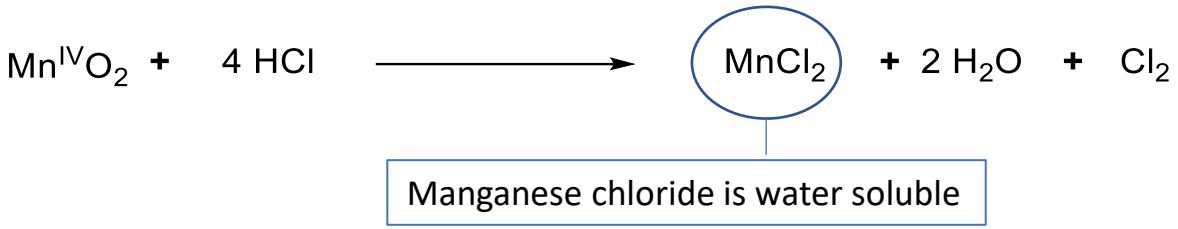
Reduction:



Redox:



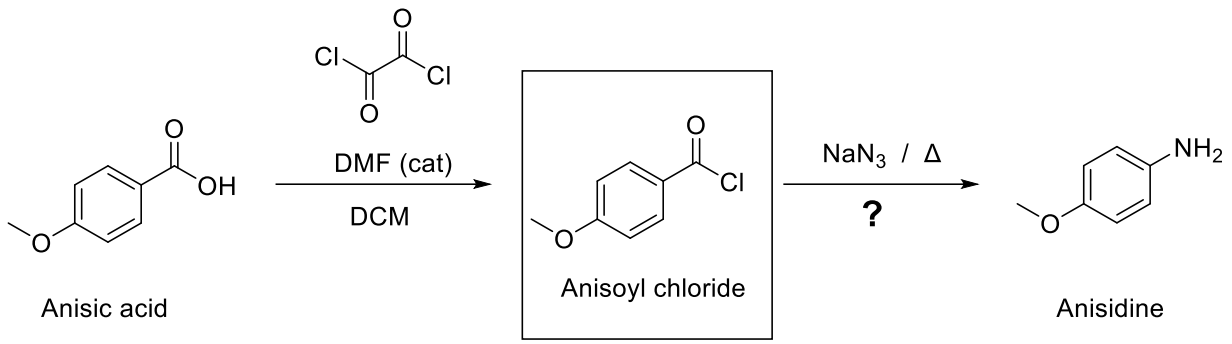
b. The reaction is complete, and it is time to clean up. At that moment you notice all your glassware has brown stains! What is this and how can you clean your glassware?



c. For future projects you want to avoid this cleaning up. Name <u>three</u> alternative oxidation conditions that can be used for this substrate. Which one would you pick next time? (personal choice)

1. Jones oxidation (CrO_3 / H_2SO_4)
2. Pinnick ($NaClO_2$ / NaH_2PO_4)
3. TEMPO / NaOCl
4. $AgNO_3$ / H_2O_2
5. H_2O_2 / ZnO
6. Ag_2O (Tollens)

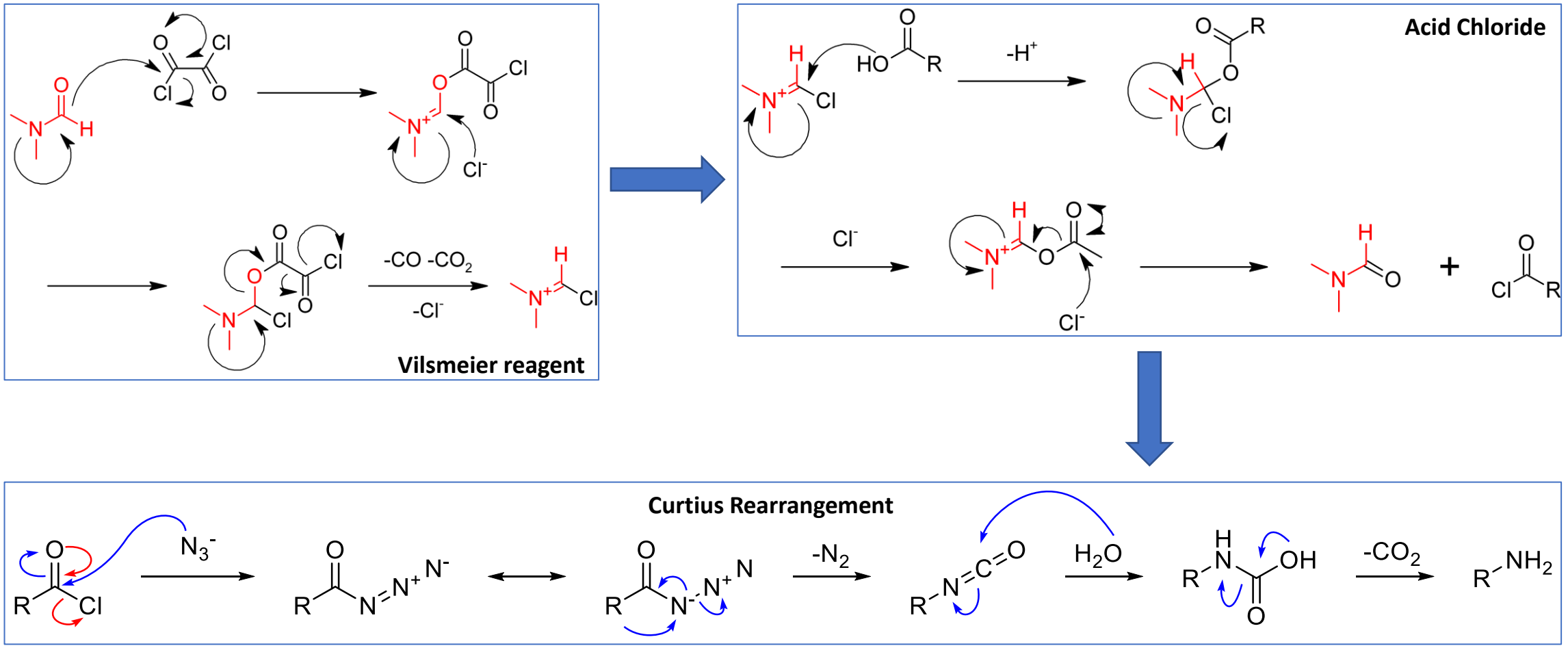
The next step is a rearrangement, but Steven forgot to tell you the details:



a. What is the name of this reaction?

Curtius rearrangement

b. Write down the mechanism of the formation of A and the subsequent rearrangement.

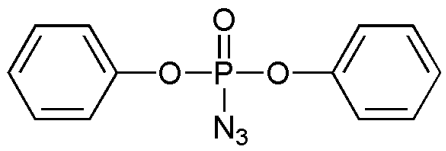


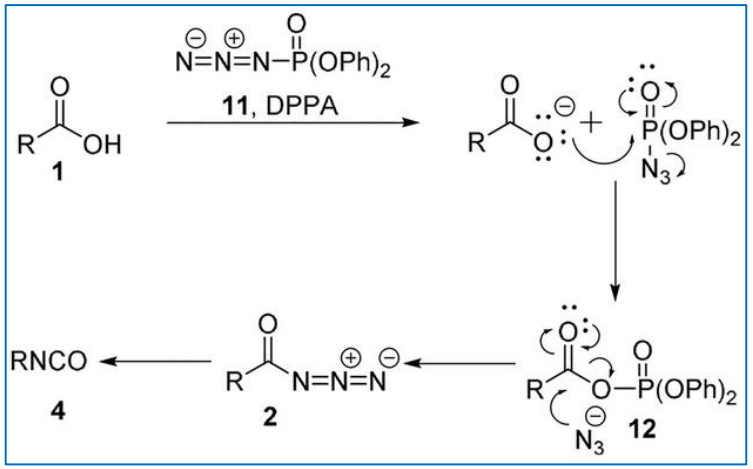
c. What solvent is used in the second step?

In the presence of water or in t-BuOH with acidic quench.

d. Which reagent can be used to perform both steps in one pot? What practical considerations should be considered when working with this chemical?

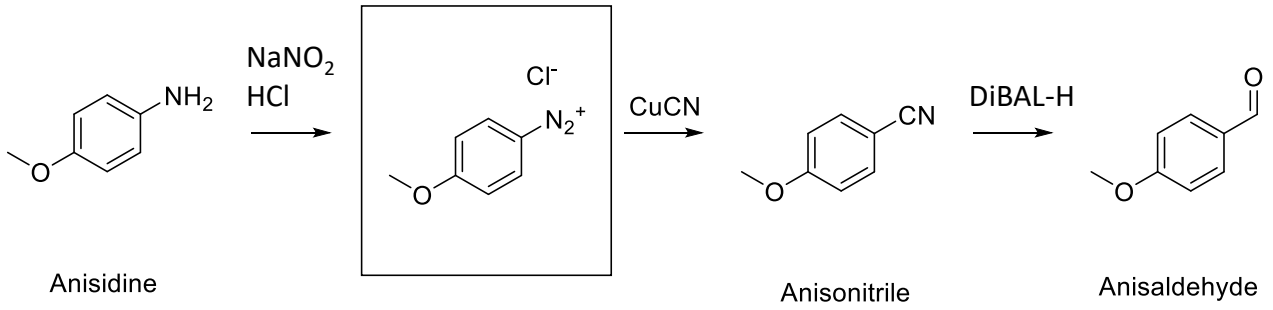
Diphenylphosphoryl azide (DPPA)





When DPPA is stored at room temperature for a long time, it might be slowly and partially hydrolyzed with moisture in air to produce diphenyl phosphate and toxic explosive hydrazoic acid.

Disaster! The Anisaldehyde that you used was from Jeffrey! Quick, before Jeffrey notices it is gone convert Anisidine back to Anisaldehyde! Fortunately, Sebastian knows a way convert the amine back into an aldehyde:



Anisidine | Anisonitrile | Anisaldehyde

a. Provide the name of this reaction (first two steps) and fill in the blanks of the equation.

Sandmeyer Rearangement (reaction of the week: Problem Session 4)

b. Unfortunately, because of the time pressure you did not have time to wait for the reactions to run to completion. As a result, your Anisaldehyde is contaminated with Anisic acid and Anisidine. Propose a purification method and provide details on the required equipment and chemicals (types & volumes, etc).

Acid-base separation:

Solvent: TBME

Acid wash: Dilute HCl (0.1 M)

Basic wash: $NaHCO_3$ (aq.)

Feedback

- What are your thoughts on the problem-set of this week?