

Organic Chemistry – Exercise 6

Distribution: November 6, 2025

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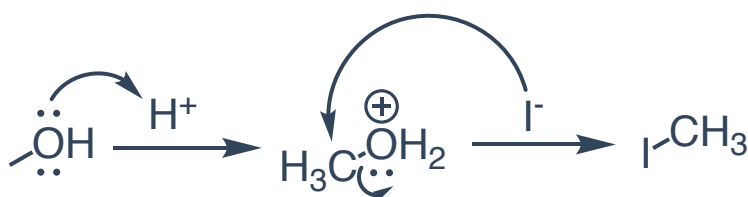
1. Acetic acid is an organic acid responsible for the taste and the smell of the vinegar. It is used in food production as a preservative and flavoring, as a cleaning agent and as a reactant or catalyst in production of chemicals, plastic materials and pharmaceuticals. It is industrially synthesized from methanol via Monsanto process. The first step of this process is the reaction of methanol with hydrogen iodide.

- a. Write the equation of the reaction between methanol and hydrogen iodide. Give the name of the main product.



The main product of this reaction is iodomethane (methyl iodide).

- b. Show the detailed mechanism of this reaction! Precisely, what type of reaction is this? Explain your answer.



This is S_N2 reaction. As methyl cation is very unstable, it cannot be formed, which is why the reaction proceeds via S_N2 mechanism.

- c. What is the role of hydrogen iodide in this reaction? Could potassium iodide be used instead?

The hydrogen iodide provides iodide ions which are acting as nucleophiles in the system and also protonates methanol. By protonation, it converts hydroxyl group into a better leaving group – water. Potassium iodide could be used instead, but the rate of reaction would be slower as the worse leaving group would be present.

- d. Does an increase in the concentration of hydrogen iodide affect the rate of this reaction? Explain your answer.

As this is a S_N2 reaction, the rate is dependent on the concentrations of both reactive species – $r = k[\text{CH}_3\text{OH}][\text{HI}]$, so the rate will be dependent on the concentration of both hydrogen iodide and methanol. The increase in concentration of hydrogen iodide will increase the reaction rate.

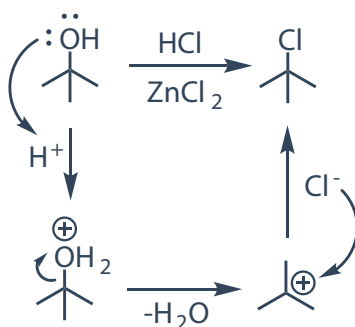
2. The Lucas test is a qualitative test for alcohols. It is used to differentiate between primary, secondary and tertiary alcohols. The Lucas reagent is a solution of zinc chloride in concentrated hydrochloric acid.

- a. What type of reaction happens between alcohols and Lucas reagent?

Nucleophilic substitution.

Primary, secondary, and tertiary alcohols react differently with the Lucas reagent. Tertiary alcohols react immediately with the reagent at room temperature and the resulting halide is observed as a phase not miscible with aqueous phase. Secondary alcohols react after a few minutes of heating the reaction mixture, while primary alcohols practically do not react with this reagent. However, the test is usually used only for detection of tertiary alcohols.

- b. Show the mechanism of the reaction that happens when *tert*-butanol (2-methylpropan-2-ol) reacts with the Lucas reagent. What is the name of this mechanistic pathway (be precise!)?



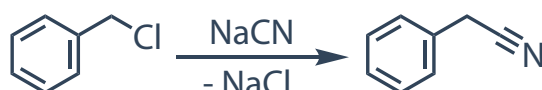
This reaction is happening via S_N1 mechanism. There is a good leaving group in the system, the formed tertiary carbocation is stable and the weakly basic nucleophile is used – all suggesting that the mechanism is S_N1.

- c. Based on the mechanism of the reaction, explain in detail the difference in reactivity between primary, secondary and tertiary alcohols.

As the reaction is occurring through S_N1 mechanism, it is important to take into account the stability of the carbocation that is formed and the quality of the leaving group. As the leaving group is the same in all cases (protonated hydroxyl group leaves as water), the main difference in reactivity comes from stability of the formed cations. Tertiary cations are stable (because of the three-fold +I effect that can be explained by hyperconjugation) and they can be readily formed, so tertiary alcohols react immediately. Secondary carbocations are less stable, which is why the system needs additional energy (heating) in order for the reaction to proceed. Primary cations are usually unstable, so they are not formed in the case of primary alcohols, which is why the reaction does not happen in this case.

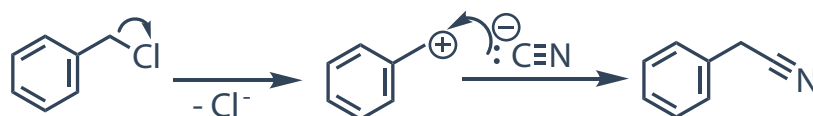
3. Phenylacetic acid is a catabolite of phenylalanine, one of the essential amino acids. Phenylacetic acid can be synthesized through a two-step process, where the first step is the reaction of substituted benzyl halide and cyanide ion, and the second step is hydrolysis of the formed nitrile.

- a. Write the equation (using structural formulae) for the reaction of benzyl chloride with sodium cyanide.



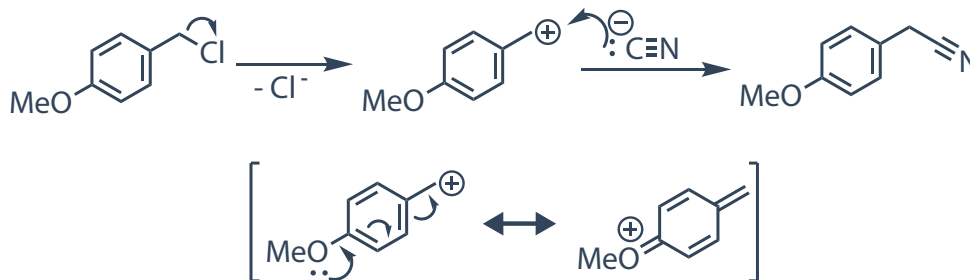
The product is phenylethane nitrile (phenylacetone nitrile).

- b. Name the mechanism of this reaction (precisely)? Show its mechanism.



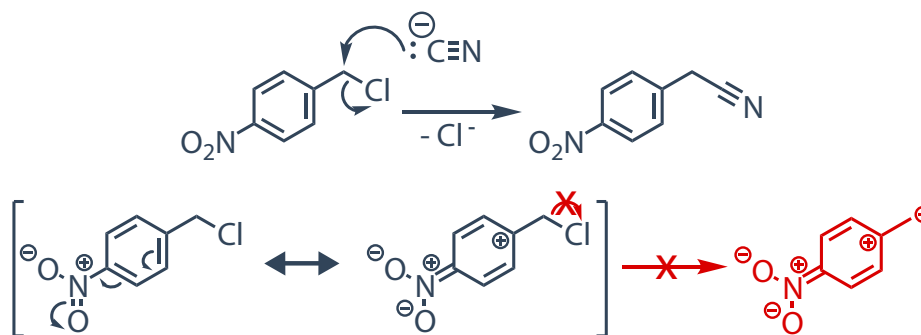
This is monomolecular nucleophilic substitution $\text{S}_{\text{N}}1$. Note: carbocation stabilized by resonance favors $\text{S}_{\text{N}}1$.

- c. Comment on whether the mechanism of the reaction would differ if *p*-methoxybenzyl chloride was used in this reaction. Would this reaction be faster or slower than the one in a)? Explain your answers by showing the mechanism and resonance structures of the intermediate (if one is formed).



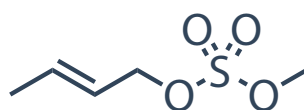
In this case, the formed carbocation is more stable than in the previous case, since methoxy group has +M effect. As the formed carbocation is additionally stabilized by resonance, its formation is favored, so the mechanism will again be $\text{S}_{\text{N}}1$. The reaction will be faster than in a) (more stable intermediate).

- d. Comment whether the mechanism of the reaction would differ if *p*-nitrobenzyl chloride was used in this reaction. Explain your answers by showing the mechanism and resonance structures of the intermediate (if one is formed).



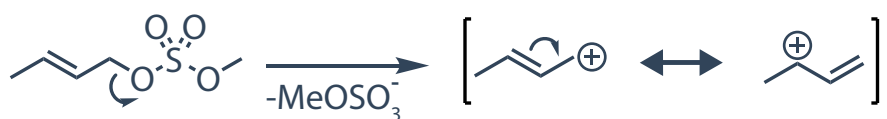
In this case, nitro group has -M effect and it significantly decreases the electron density in the neighborhood of the potential carbocation, which is why its formation is not favored in this case. Due to this, carbocation formation is not possible in this case, which is why the reaction proceeds via $\text{S}_{\text{N}}2$ mechanism.

4. Consider the following compound.



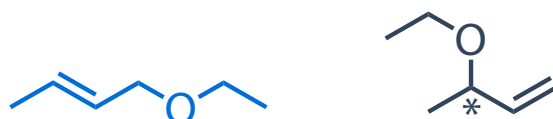
It can react with ethanol in a monomolecular nucleophilic substitution reaction to give **two different products**.

- a. Show the formation of the intermediate. Show the resonance structures of this intermediate and comment on its stability.



The formed cation is allylic cation, which is stabilized by resonance.

- b. Propose the structures of the potential two products after the reaction with ethanol. Are these products chiral and, if they are, are they enantio-pure? Explain your answers.



There are two possible products. The name of the product in blue is 1-ethoxybut-2-ene and the name of the product in black is 3-ethoxybut-1-ene. The product in black has one stereocenter (marked with asterisk), but the product is obtained in the form of racemic mixture, as the cation can be attacked from both sides with equal probability.

- c. What is the potential side reaction that can occur in this system? Show its mechanism, give the reaction type (precisely) and give the name of the product. How could you favor the main reaction over the side reaction by varying the reaction conditions?



Monomolecular elimination E1 can compete with S_N1 reaction. The product formed in this case is 1,3-butadiene. The S_N1 reaction can be favored by performing the reaction at low temperature (to prevent elimination).

5. Give the structures of the major products formed in the following reactions (include stereochemical details where relevant)! Give the acronyms for the reaction mechanisms by which those products are obtained!

