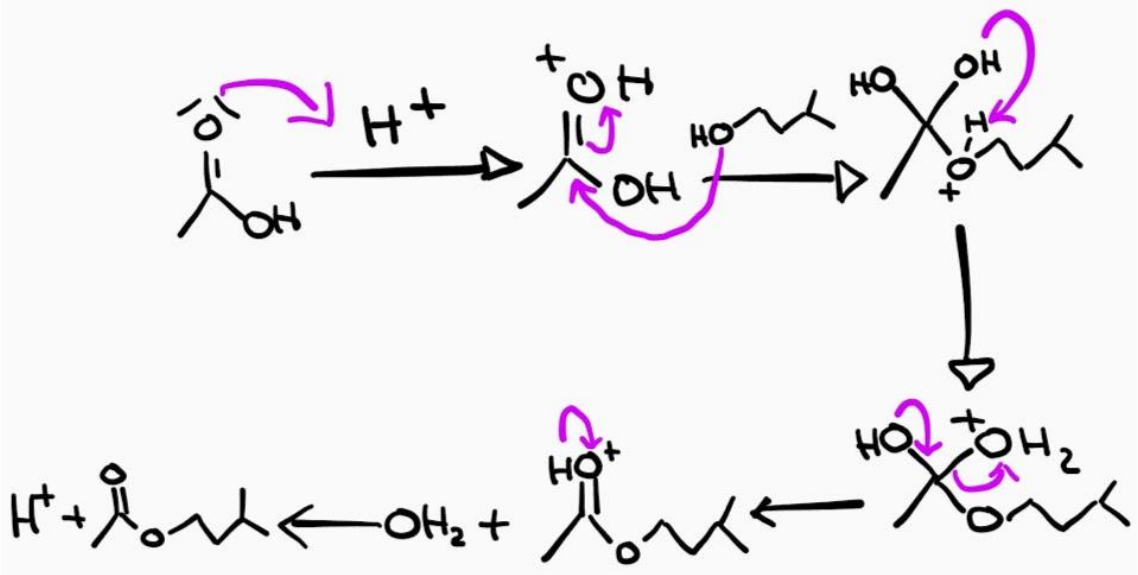
Ioritz Arburua Leonis, 30-04-2020

EXPERIMENTATION IN ORGANIC CHEMISTRY:
5th Practice: Esterification

A. Main Features of the practice:

1. Main objective of the practice:
   - Perform a Fischer esterification reaction. One of the first methods to synthetize esters.
2. Mechanism of the reaction:



As we can observe, H^+ is catalytic because it is observed in the fist step but released in the last one. So, we can add it in catalytic amount to the reaction.

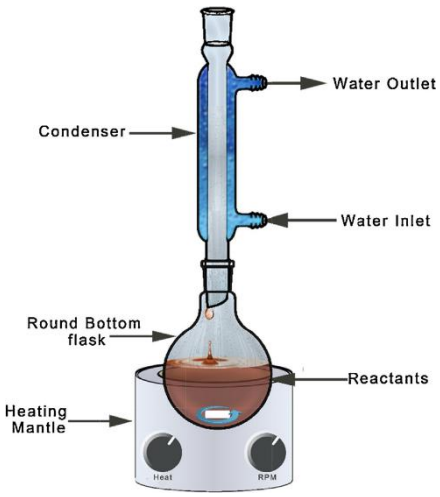
3. Dangerous reagents, preventive measures; H and P phrases

Dangerous Reagents	Preventive Measures; H and P phrases
Acetic Acid	H226: Flammable liquid and vapor. H314: Causes severe skin burns and eye damage. P210: Keep away from heat/sparks/open flames/hot surfaces. No smoking. P260: Do not breathe dust /fume /gas /mist /vapours /spray. P264: Wash hands thoroughly after handling. P280: Wear protective gloves / protective clothing/ eye protection / face protection. P301+P330+P331: If swallowed: Rinse mouth. Do not induce vomiting. P303+P361+P353: If on skin (or hair): Remove/take off immediately all contaminated clothing. Rinse skin with water/shower. P304+P340: If inhaled: Remove victim to fresh air and keep at rest in a position comfortable for breathing. P305+P351+P338: If in eyes: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. P310: Immediately call a POISON CENTER or doctor/doctor. P363: Wash contaminated clothing before reuse.

Dangerous Reagents	Preventive Measures; H and P phrases
Sulphuric Acid	H314: Causes severe skin burns and eye damage. P260: Do not breathe mist, vapours, spray. P264: Wash exposed skin thoroughly aften handling. P280: Wear protective gloves, protective clothing, eye protection, face protection. P301+P330+P331: If swallowed: Rinse mouth. Do NOT induce vomiting. P303+P361+P353: If on skin (or hair): Take off immediately all contaminated clothing. Rinse skin with water/shower. P304+P340: In inhaled. Remove person to fresh air and keep comfortable for breathing. P305+P351+P338: If in eyes: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. P310: Immediately call a POISON CENTER/doctor. P363: Wash contaminated clothing before reuse. P405: Store locked up. P501: Dispose of contents/container to comply with local, state and federal regulations.
Isoamyl alcohol	H226: Flammable liquid and vapour. H315: Causes skin irritation. H318: Causes serious eye damage. H332: Harmful if inhaled. H335: May cause respiratory irritation. P210: Keep away from heat/sparks/open flames/hot surfaces. No smoking. P302+P352: In on skin: wash with plenty of soap and water. P305+P351+P338: If in eyes: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. P370+P378: In case of fire: Use sand, carbon dioxide or powder extinguisher for extinction. P403+P233: Store in a well-ventilated place. Keep container tightly closed. P403+P235: Store in a well-ventilated place. Keep cool.
Sodium Bicarbonate	H320: Causes eye irritation. P264: Wash exposed skin thoroughly after handling. P305+P351+P338: If in eyes: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. P337+P313: If eye irritation persists: Get medical advice/attention.
Sodium Sulphate Anhydrous	H412: Harmful to aquatic life with long lasting effects. P273: Avoid release to the environment. P501: Dispose of contents/container to an approved waste disposal plaint.

4. <u>Experimental Procedure and Observations:</u>

- Pour 12,5 mL of acetic acid and 10 mL of isoamyl alcohol into a 50 mL round bottomed flask.
- Add a stirring bar and mix it until the solution is homogeneous.
- Add slowly and carefully 2,5 mL of sulphuric acid.
- Connect the reflux condenser and activate the water flow (see the image).
- Heat the solution for 1 hour.
- After that time, let the solution cool down before moving it to a separation funnel.
- Add 15 mL water and shake vigorously. Let the phases divide.
- Get rid of the bottom phase (aqueous phase) and redo it with other 15 mL of water.
- Wash the organic phase 3 times with 15 mL of $NaHCO_3$ in order to eliminate all the excess of acetic acid.



- If pH is still not basic proceed again with two more portions of 15 mL $NaHCO_3$.
- Clean the organic phase two more times with 5mL of saturated NaCl solution.
- Use Na_2SO_4 in order to dry the organic phase and filter it to get rid of the water remaining. Collect the filtrate in an Erlenmeyer.
- Weigh the product.

B. Results:

1.

Molecular formula	MW (g/mol)	Density (g/cm^3)	State	Colour
C_2H_3OOH	60,052	1,05	Liquid	Colourless
$C_5H_{11}OH$	88,148	0,810	Liquid	Colourless
$C_7H_{14}O_2$	160,19	0,876	Liquid	Colourless

Calculations of n:

- Acetic acid

$$12{,}5\ \text{mL} \times \frac{1{,}05\ \text{g}}{1\ \text{mL}} \times \frac{1\ \text{mol}}{60{,}052\ \text{g}} = 0{,}2186\ \text{mol}$$

- Isoamyl alcohol

$$10\ \text{mL} \times \frac{0{,}810\ \text{g}}{1\ \text{mL}} \times \frac{1\ \text{mol}}{88{,}148\ \text{g}} = 0{,}0919\ \text{mol}$$

→ Isoamyl alcohol is the limiting reagent.

- Theoretical weight or volume of final product:

$$0{,}0919\ \text{mol} \times \frac{160{,}19\ \text{g}}{1\ \text{mol}} = 14{,}72\ \text{g} = 16{,}80\ \text{mL}$$

Theoretical Melting or Boiling point (°C):

$C_7H_{14}O_2$ → $T_{boiling}$ = 142°C

2. <u>Yield. Analysis of the results:</u>

$$\text{Yield} = \%\ 70 = \frac{\text{m}_{\text{practical.}}}{14{,}72} \rightarrow \text{m}_{\text{practical.}} = 10{,}304\ \text{g}$$

3. Spectroscopic Data:

H-NMR of isoamyl acetate:

We can see that there is a symmetry element between the two metiles in the isoamyl group, so their signals will only appear once. Looking at the molecular formula, we expect to find 5 signals:

- 3.97 ppm: This signal corresponds to the H_2 next to the esther. This Hs are the most decoupled ones due to their proximity to electron density withdrawing groups. In addition, the multiplicity and integration correspond to this position.
- 1.91 ppm: This signal is created by the CH_3 at the left of the esther. It is near the carbonyl group so it will be pretty much decoupled. Moreover, the multiplicity suggests that any other H are near.
- 1.62-1.52: This signal belongs to the CH. as it is a tertiary carbon, it is more decoupled than usual carbon chain hydrogens. Moreover, the multiplicity (9 peaks) matches this suggestion.
- 1.40: This signal corresponds to CH_2 next to the isoamyl group. As it is further from the ester group its effect will be reduced. Additionally, the multiplicity and the integration agree with this position.
- 0.80 ppm: This signal suits for the CH_3-s of the isoamyl and the integration suits as well. Additionally, they are very far away from electron subtracting groups so their chemical shift has to be low.

C-NMR of isoamyl acetate:

As the isoamyl group has two metiles that are symmetric, there will be only one signal of them. The rest of the molecule is not symmetric so the number of signals expected are 6:

- 170.9 ppm: This signal corresponds to the carbonyl C. It has a very characteristic chemical shift.
- 62.9 ppm: This signal is created by the C next to the esther. It is very close to the ester so it will have a big chemical shift.
- 37.2 ppm: This signal corresponds to the C attached to the isoamyl group. It is a bit further from the ester group but its effect is still noticeable.
- 24.9 ppm: This signal belongs to the CH of the isoamyl. As it is a tertiary C it is pretty decoupled.
- 22.3 ppm: This signal corresponds to the CH_3-s of the isoamyl. This C is pretty coupled and has a small chemical shift value.
- 20.8 ppm: This signal belongs to the CH_3 at the left of the esther. It is in the opposite part of the ester and this makes this C very coupled.

IR spectra of isoamyl acetate

Approximately at 1750 cm^{-1} there is a big peak that corresponds to the Carbonyl group of the ester. Moreover, at 3000 cm^{-1} the peak means that the system is not saturated.

4. Conclusions:

Even though we didn't have the chance to access the lab and proceed with the practices ourselves, we have been able to see some of the concepts we have learnt in Kimika Organikoa I put into practice which can be very beneficial for our comprehension in the matter.