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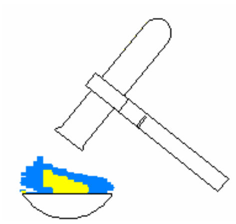
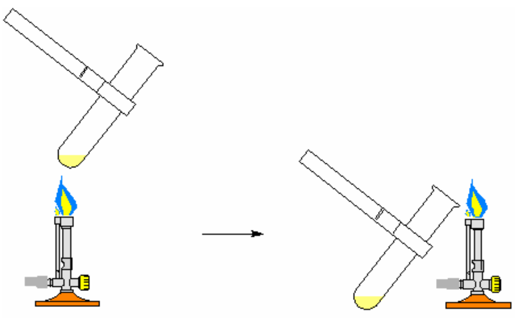
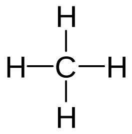
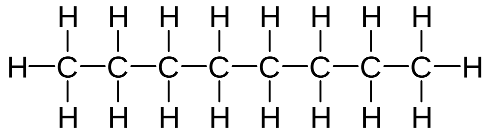
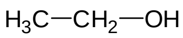
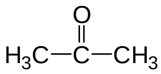
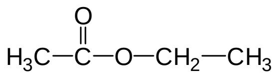
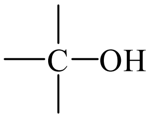
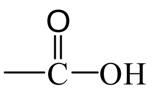
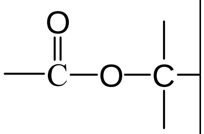
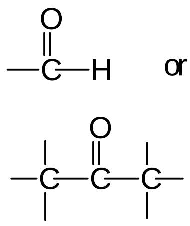
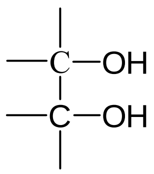
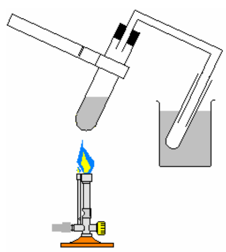
PD Dr. R. Heimann

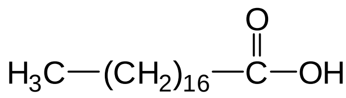
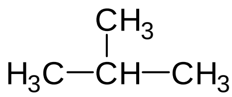
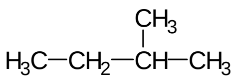
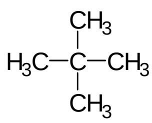
Experiments for an Introduction to Organic Chemistry

1. Combustion of organic compounds	E69 Ignite 1 ml of some organic compounds (e.g. ethanol, ethyl acetate, acetone, fuel) in a porcelain dish. Hold a large test tube with its open end above the flame to collect gaseous combustion products. Pay attention! The test tube gets hot! Fill in 5 ml calcium hydroxide solution, close the test tube with a stopper and shake. A white chalking is observed. Carbon dioxide is identified as a combustion product. 	ethanol, ethyl acetate, acetone, fuel, calcium hydroxide solution, porcelain dish, large test tube
	E70 Take a large test tube and fill in 5 ml ethanol and a boiling stone. Heat until the liquid is boiling. Then hold the open end of the test tube to the flame and ignite the ethanol vapours. 	ethanol, large test tube, boiling stone
	E71 Repeat E70 with ethanol-water-mixtures. Prepare a mixture of 50 Vol% of ethanol and a mixture of 20 Vol% of ethanol. Try to ignite the vapours. In both cases you can ignite the vapours, but in case of the lower concentrated solution the vapours burn only a short time. Now fill 1 ml of the 20 Vol% solution in a porcelain dish and try to ignite it. You will see that this is not possible.	ethanol, large test tube, porcelain dish

Models for combustion reactions	E72 Build molecular models of the organic compounds being involved in E69 - 71. Simulate the combustion reactions with models and derive the stoichiometric equations. Include methane with the simplest organic molecules. Use the following formulas:  methane  octane (fuel)  ethanol  acetone  ethyl acetate	model kit

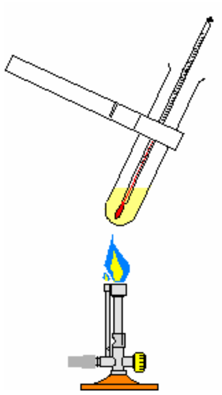
2. Analytical standard tests	Introductory remark: The following experiments are useful for detecting functional groups in molecules. You will need them also later on, e.g. for discovering the products of chemical reactions. Therefore prepare stock solutions. They are stable for years.	
Cerium test for alcohol groups 	E73 Cerium nitrate test (group test for alcohols): Prepare a stock solution by dissolving 40 g ceric ammonium nitrate in 100 ml 2 M nitric acid. Dilute 1 ml reagent with 2 ml water. Add 5 drops of the unknown sample and shake. If it contains an alcohol, the colour will change from yellow to orange/red. Make blank tests with positive reacting compounds (ethanol and other alcohols) and with negative reacting compounds (e.g. hydrocarbons, carbonic acids, esters, ketones).	ceric ammonium nitrate, nitric acid, ethanol, acetic acid, ethyl acetate, acetone, fuel
BTB test for carboxylic groups 	E74 Bromothymol blue test (group test for acids): Prepare a stock solution by dissolving 0.02 g bromothymol blue (BTB) and 0.6 g sodium hydroxide in 100 ml ethanol. To 1 ml BTB reagent add 1 ml of the unknown sample. If it contains an acid, the colour will change from blue to yellow/orange. Run blank tests with positive reacting compounds (carbonic acids or inorganic acids) and with negative examples (e.g. hydrocarbons, alcohols, esters, ketones). Note that the BTB test is only a proof for carbonic acids if inorganic acids can be excluded.	bromothymol blue, sodium hydroxide, acetic acid, sulphuric acid, fuel, ethanol, ethyl acetate, acetone
PHT test for ester groups 	E75 Phenolphthalein test (group test for esters): Prepare stock solutions of 0.1 g phenolphthalein (PHT) in 100 ml ethanol; and of 3 M NaOH in water (12 g sodium hydroxide in 100 ml solution). To 1 ml ethanol (it is necessary as a solution aid) add 1 ml of the unknown sample and 3 drops of phenolphthalein solution. Then add drop by drop NaOH solution until the pink indicator colour just appears. (Shake thoroughly after any drop, and avoid strictly to add more NaOH solution than is absolutely necessary.) Put the reaction vessel into a warm water bath (40 °C) and shake every minute. If the sample contains an ester, the pink solution becomes colourless within some minutes. Run blank tests with positive reacting compounds (esters) and with negative examples (e.g. hydrocarbons, alcohols, carbonic acids, ketones). Note that for carbonic acids much NaOH solution is necessary because of neutralization.	phenolphthalein, ethanol, sodium hydroxide ethyl acetate, fuel, acetic acid, acetone

DNPH test for aldehyde or ketone groups 	E76 Dinitrophenylhydrazine test (group test for a carbonyl compound, i.e. aldehydes or ketones): Prepare a stock solution by dissolving 1 g dinitrophenylhydrazine (DNPH) in 168 ml water and 33 ml hydrochloric acid (37 %). Stir well for 15 minutes, and then filtrate to get a clear yellow reagent solution. To 1 ml DNPH reagent add 1 drop of the sample and shake. If it contains a carbonyl compound, a yellow precipitate or turbid is observed. Run blank tests with positive reacting compounds (aldehydes, ketones) and with negative reacting compounds (e.g. hydrocarbons, alcohols, carbonic acids, esters). Note that ethanol can be denaturated with ketones and then also gives a positive test.	2,4-dinitrophenyl-hydrazine, hydrochloric acid (37%), acetone, fuel, ethanol, acetic acid, ethyl acetate
Copper test for diol groups 	E77 Copper sulphate test (group test for alcohols with two or more neighbouring alcohol groups): Prepare stock solutions of 0.1 M copper sulphate in water (2.5 g $CuSO_4 \cdot 5 H_2O$ in 100 ml solution); and of 3 M sodium hydroxide in water (12 g NaOH in 100 ml solution). To 1 ml 0.1 M $CuSO_4$ add 1 ml of the sample. Shake well. Add 3 M NaOH solution drop by drop until a clear dark blue colour (indicating a diol) is observed. If a light blue precipitate (copper hydroxide) is formed, add maximum 5 drops NaOH solution extra. Run blank tests with positive reacting compounds (e.g. glycerol, sugar, tartrate) and with negative examples (e.g. ethanol, ethyl acetate, acetone). Make a solution of the solid substances first (half a spatula dissolved in 5 ml of water).	Copper sulphate, sodium hydroxide, glycerol, ethanol, ethyl acetate, acetone, sugar, sodium potassium tartrate
Testing kitchen compounds	E78 Apply the standard tests (E73 - 76) to liquid kitchen substances (e.g. vinegar, brandy, lemon juice, sugar water, salt water, cooking oil). If the test solution is coloured (e.g. dark vinegar) fill 20 ml of it into a large test tube, distil some millilitres and test the colourless distillate. Run blank tests, if necessary. Note that cooking oil is not solvable in ethanol. Perform the PHT test (E75) with 1-propanol as solution aid (instead of ethanol). 	1-propanol, distillation apparatus

Testing everyday products	E79 Apply the standard tests (E73 - 76) to other everyday products (e.g. acetic cleanser, nail polish dissolver, denaturated alcohol, perfume, liquid glue, spot remover). Run blank tests, if necessary.	
Testing candles	E80 Scrape with a knife some wax from a paraffin and a stearin candle. Put one spatula of wax into a test tube, add 2 ml BTB reagent (E74) and heat for a minute: Positive test result (yellow) with the stearin candle, negative result (blue) with the paraffin candle. Make a blank test with pure stearic acid: yellow. Explain the results by means of formulas. $H_3C—(CH_2)_{16}—CH_3$ octadecan (paraffin candle)  stearic acid (stearin candle)	paraffin candle, stearin candle, stearic acid, standard tests
3. Homologous series and isomerism	E81 Build molecular models of some homologous and isomeric hydrocarbons and discuss their boiling temperatures in terms of intermolecular interactions. Use the following formulas: CH_4 methane, b.p. - 169 °C $H_3C—CH_3$ ethane, - 89 °C $H_3C—CH_2—CH_3$ propane, - 42 °C $H_3C—CH_2—CH_2—CH_3$ butane, b.p. - 1 °C  isobutane, - 10 °C $H_3C—CH_2—CH_2—CH_2—CH_3$ pentane, b.p. + 36 °C  isopentane, + 28 °C  neopentane, + 10 °C Compare the *melting* temperatures of pentane (m.p. = - 130 °C) and neopentane (m.p. = - 17 °C): Explain the differences in terms of sphere packings. Use the model kit to predict the number of isomeric hexanes C_6H_{14}. Which of the hexanes have the highest and the lowest boiling temperature?	model kit

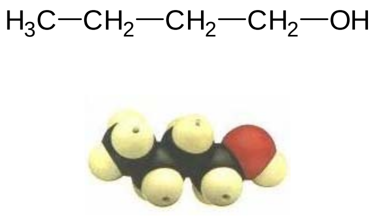
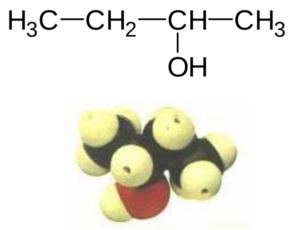
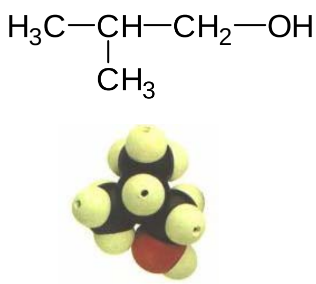
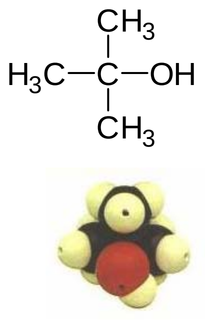
<table>
<tr>
<td>Homologous alcohols</td>
<td>
E82 Inquire the properties of some homologous alcohols (ethanol, 1-propanol, 1-butanol):

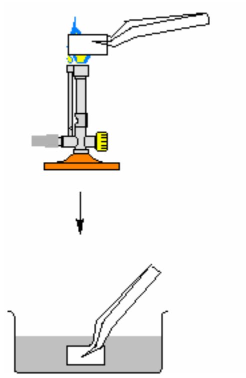
Run the cerium test (E73).
Test the solubility in water and in salt water (3 M NaCl solution): Shake 2 ml alcohol and 2 ml solvent in a test tube and observe complete or incomplete solubility.
Boiling temperature: Give 5 ml alcohol, a boiling stone and a thermometer in a large test tube and heat until the liquid is boiling. Take the test tube out of the flame and measure the temperature. Repeat the procedure (heating and measuring) five times. The last measured temperature is the boiling point. Note: The alcohol vapours

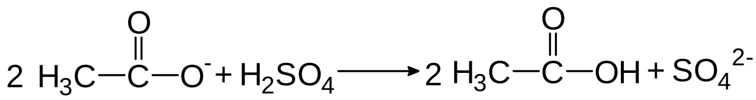
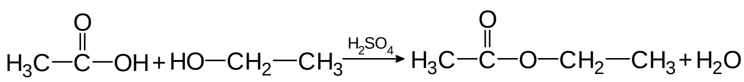


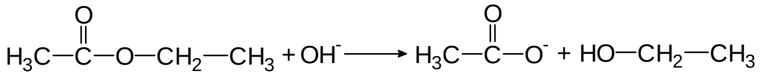
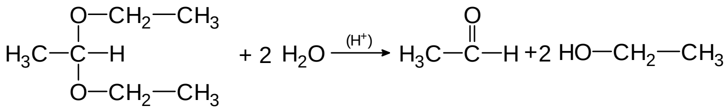
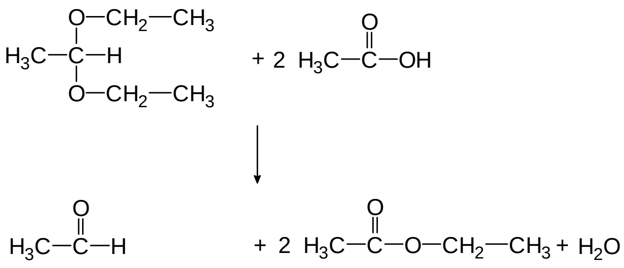
might ignite during heating (see E70).
Discuss the results in terms of intermolecular interactions:

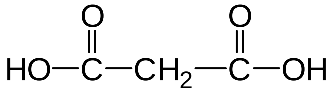
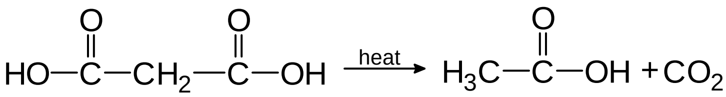
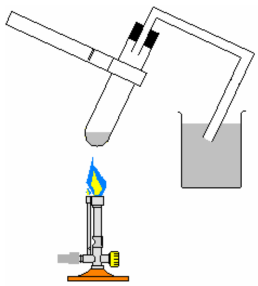
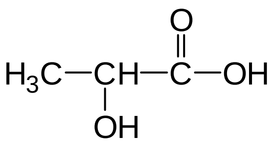
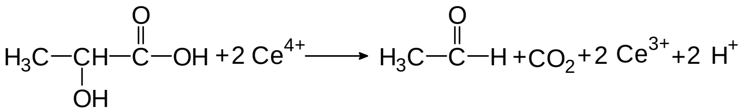
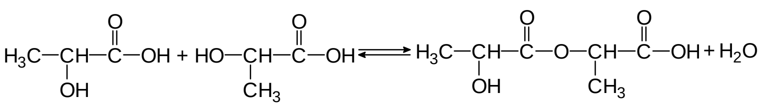
<table>
<tr><th></th><th>ethanol</th><th>1-propanol</th><th>1-butanol</th></tr>
<tr><td>cerium test</td><td>red</td><td>red</td><td>red</td></tr>
<tr><td>water</td><td>soluble</td><td>soluble</td><td>not soluble</td></tr>
<tr><td>salt water</td><td>soluble</td><td>not soluble</td><td>not soluble</td></tr>
<tr><td>b.p. (°C)</td><td>78</td><td>97</td><td>118</td></tr>
</table>
</td>
<td>ethanol,
1-propanol,
1-butanol,
3 M NaCl solution,
standard tests,
thermometer,
boiling stone,
large test tube</td>
</tr>
<tr>
<td>Isomeric butanols</td>
<td>
E83 Inquire the properties of some isomeric alcohols (1-butanol, 2 -butanol, tertiary butanol):
Run the cerium test (E73).
Determine the boiling temperatures (see E82).
Test the solubility in water:
Put 1 ml alcohol into the test tube and add water in portions of 1 ml until it dissolves completely. Shake well after each 1 ml portion.
Discuss the results in terms of intermolecular interactions.
<table>
<tr><th></th><th>1-butanol</th><th>2-butanol</th><th>tert. butanol</th></tr>
<tr><td>cerium test</td><td>red</td><td>red</td><td>red</td></tr>
<tr><td>soluble in x ml water</td><td>11 ml</td><td>4 ml</td><td>1 ml</td></tr>
<tr><td>b.p. (°C)</td><td>118</td><td>99</td><td>83</td></tr>
</table>
</td>
<td>1-butanol,
2-butanol,
tert. butanol,
standard tests,
thermometer,
boiling stone,
large test tube</td>
</tr>
</table>

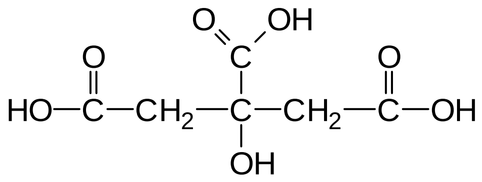
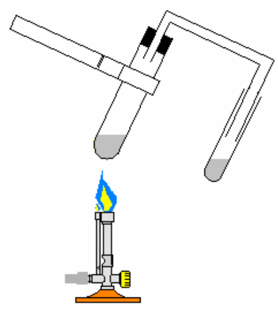
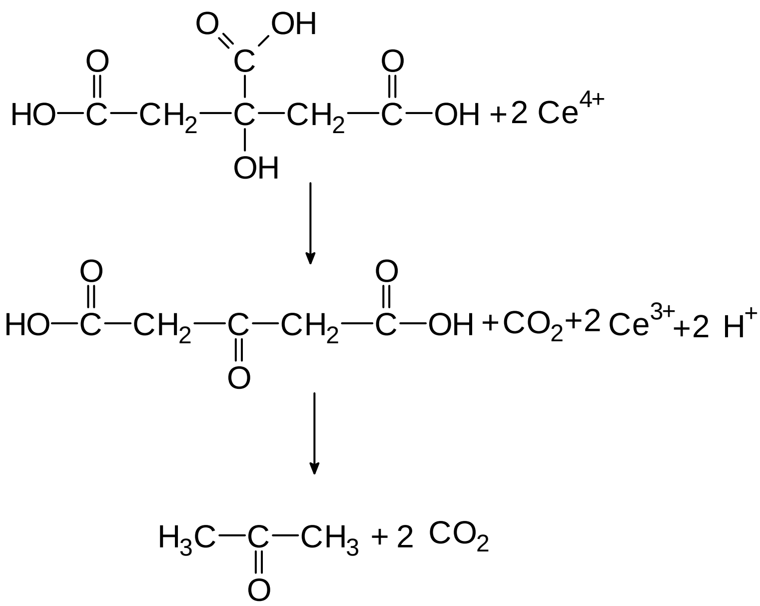
Models	E84 Build molecular models of all isomeric butanols and verify that a fourth constitutional isomer exists (isobutanol). Which properties do you expect? Note that in the case of 2-butanol mirror-inverted molecular structures (enantiomers) are possible. Which properties do you expect for them? Note that only tertiary butanol is a solid at room temperature (m.p. = 25 °C). Explain this in terms of sphere packings. Use the following formulas:  1-butanol  2-butanol  isobutanol  tertiary butanol	model kit

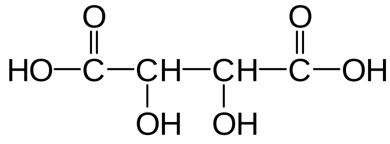
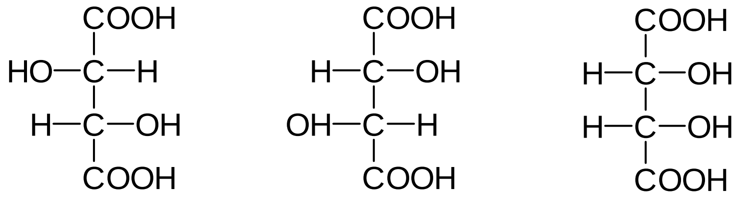
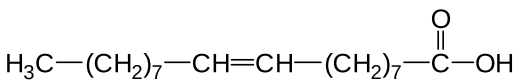
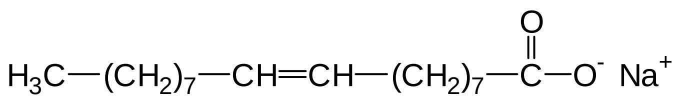
4. Basic organic reactions	E85 Heat a copper foil (2 cm x 2 cm). Dip the hot foil into 5 ml 2-propanol in a porcelain dish. Repeat this procedure nine times: Each time black CuO is produced in the flame and reduced to red copper by 2-propanol which is oxidized to acetone.  $H_3C-CH(OH)-CH_3 + CuO \longrightarrow H_3C-C(=O)-CH_3 + Cu + H_2O$ Perform the DNPH test (E76) to confirm the presence of acetone. Use 6-10 drops of the liquid in the porcelain dish for the test (instead of one drop). Repeat this experiment with other alcohols (e.g. ethanol p.a.; with denaturated alcohol itself the DNPH test is often positive because it contains ketones). $H_3C-CH_2-OH + CuO \longrightarrow H_3C-C(=O)-H + Cu + H_2O$	copper foil, 2-propanol, ethanol, standard tests, porcelain dish
Oxidation of alcohols with cerium nitrate	E86 Perform the cerium test (E73) in a large test tube with 4 ml reagent, 8 ml water and 20 drops of 2-propanol. Heat until the colour is light yellow. Stop heating and wait until the liquid is colourless. Distil some millilitres and test the colourless distillate (see E78). Avoid delayed boiling! $H_3C-CH(OH)-CH_3 + 2\,Ce^{4+} \longrightarrow H_3C-C(=O)-CH_3 + 2\,Ce^{3+} + 2\,H^+$ The DNPH test is positive, the cerium test slightly positive (there is still some alcohol). If you do not want to do the distillation, you can test the liquid directly. In this case you need 2-5 drops of the liquid to get a positive DNPH test. Repeat this experiment with ethanol p.a.. You can detect the smell of acetaldehyde and the DNPH test is positive. Distillation is not necessary.	ethanol, 2-propanol, standard tests, large test tube, distillation apparatus

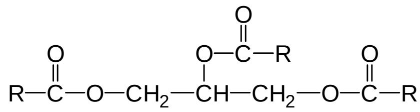
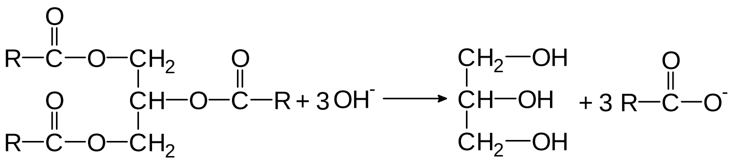
Acetic acid synthesis	E87 In a large test tube put half a spatula of sodium acetate, and add 2 ml 1.5 M H_2SO_4 and a boiling stone. Heat gently; avoid delayed boiling. Into the vapours put a wet indicator paper: It turns orange or red (acid). Smell cautiously: Pungent smell of acetic acid.  Make a blank test by heating 1.5 M H_2SO_4: The indicator paper proves that only water steam is produced. Sulphuric acid is not volatile.	sodium acetate, 1.5 M H_2SO_4, boiling stone, large test tube, indicator paper
Ferric chloride test for acetate	E88 Prepare a stock solution by dissolving 8 g ferric chloride ($FeCl_3$ * 8 H_2O) in 100 ml of water. Put ten drops of the unknown sample into a test tube. Add two drops of PHT (E75). If the colour is perceptible pink, add 1.5 M H_2SO_4 until the pink colour disappears. Then add two drops of the ferric chloride solution and shake. An orange or red colour is typical for acetate. If you want to do the test with a solid, e.g. sodium acetate, dissolve a third of a spatula full of the solid in 5 ml of water first and then take ten drops for the test.	ferric chloride solution, PHT, 1.5 M H_2SO_4, sodium acetate
Ester synthesis	E89 Put into a test tube 2 ml alcohol (ethanol, 1-propanol, 1-butanol), 2 ml acetic acid and 0,5 ml sulphuric acid and shake well. Let the test tubes stand for 5 minutes. Then add 5 ml 1 M Na_2CO_3 in small portions: Carbon dioxide evolves and a liquid phase separates: Typical ester smell. Do not shake! Perform with the ester phase the PHT test (E75) in a larger scale (3 ml ethanol + 2 ml ester phase + 6 drops phenolphthalein + 3 M NaOH drop by drop until the pink colour just remains). Decolourization at 40 °C within several minutes confirms the formation of esters in all three experiments (Shaking the test tubes every minute during the PHT test is absolutely necessary!), e.g.  Note that the formation of tertiary butyl acetate cannot be achieved in this way because the tertiary butyl group is too bulky. Reconstruct the steric hindrance by means of the model kit.	ethanol, 1-propanol, 1-butanol, acetic acid, conc. H_2SO_4, 1 M Na_2CO_3, PHT test, model kit

Ester hydrolysis	E90 Into a 50 ml screw cap bottle put 5 ml ethyl acetate and 20 ml 3 M NaOH. Screw up and shake well for 2 minutes: The ester phase and smell disappear. The ester has been hydrolysed to acetate and ethanol.  Distil some millilitres (see E78). To this purpose put the reaction mixture into a large test tube and add 2 boiling stones (!). Perform the standard tests with the distillate. Confirm that the distillate contains alcohol. Perform the ferric chloride test with the residue. Acetate can be detected.	ethyl acetate, 3 M NaOH, standard tests, ferric chloride solution, boiling stones, screw cap bottle, distillation apparatus
Acetal hydrolysis	E91 Put in a test tube 2 ml diethyl acetal and 2 ml 1.5 M H_2SO_4 (by no means conc. H_2SO_4!). Stopper it with a cork and shake well for 1 minute: The acetal phase disappears; typical aldehyde smell.  Repeat this experiment with 2 ml acetal + 2 ml 3 M NaOH: No reaction. Acetal is hydrolysed only in an acid medium (H^+ is needed as catalyst).	diethyl acetal, 1.5 M H_2SO_4, 3 M NaOH
	E92 Predict the test results of acetal with the standard tests (E73 - 76). Verify your hypotheses by performing the tests: Surprising results! Explain them by paying attention to the pH of the reaction medium. Test the pH value of the cerium nitrate reagent (E73) and of the DNPH reagent (E76) by means of indicator paper: It turns red. Note: the PHT test (E75) is performed in an alkaline medium, in contrast to the cerium test (E73) and the DNPH test (E76).	diethyl acetal, standard tests, indicator paper
Acetal reaction	E93 Put into a 50 ml screw cap bottle 5 ml diethyl acetal + 8 ml acetic acid + 3 drops sulphuric acid. Shake well after every drop H_2SO_4. Let stand for one day (or a week). Then test the reaction mixture with the standard tests (E73 - 76). Explain the results in terms of the following reaction:  Note: It can be concluded from the negative result of the cerium test (E73) that the acetal has been converted completely. Therefore it cannot be responsible for any other positive test result. Simulate the reaction above by means of the model kit.	diethyl acetal, acetic acid, conc. H_2SO_4, standard tests, model kit

Malonic acid	E94 Malonic acid:  Confirm the presence of carboxylic groups by means of the BTB test (E74). Use 1 ml of a solution of half a spatula of malonic acid in 5 ml water for the test. Then heat half a spatula of malonic acid gently in a large test tube until it decomposes. Put a wet indicator paper into the vapours: orange or red colour. Smell very cautiously: Pungent smell of acetic acid.  	malonic acid, BTB test, indicator paper, large test tube
	E95 Put half a spatula of malonic acid into a large test tube. Heat and lead the gas into a beaker with 20 ml of calcium hydroxide solution. A milky precipitation can be observed; so carbon dioxide is detected. Note: Take the beaker away before you stop heating! 	malonic acid, calcium hydroxide solution, large test tube, distillation apparatus
Lactic acid	E96 Lactic acid:  Perform the standard tests (E73 - 76) with lactic acid. With the cerium test (E73) an anomaly is observed: First red (alcohol group), then gas bubbles (CO_2), typical aldehyde smell, and decolourization ($Ce^{4+} \rightarrow Ce^{3+}$). The DNPH test with the reaction mixture shows a positive result.  The positive test result with the PHT test (E75) is also surprising. Lactic acid contains small amounts of dimeric ester molecules:  Note: Monomeric lactic acid molecules exist in enantiomeric forms. Build mirror-inverted forms with the model kit.	Lactic acid, standard tests, model kit

Citric acid	E97 Citric acid:  Perform the standard tests (E73 - 76) with citric acid. Use a solution of half a spatula full of citric acid in 5 ml of water. Note: With the cerium test (E73) citric acid shows similar behaviour as lactic acid (E96) but no aldehyde smell. Repeat the cerium test in a large test tube. Mix 4 ml reagent, 8 ml water, a boiling stone and a spatula full of citric acid. Let the developed gas pour into 2 ml of calcium hydroxide solution. Heat the large test tube to this purpose. A milky precipitation indicates carbon dioxide.  Perform a distillation with the same reaction mixture (see E78) and test the distillate with the BTB test and the DNPH test. The BTB test is negative, the DNPH test is positive when you use 2 drops of the distillate. Citric acid is first transformed to acetonedicarboxylic acid and then to acetone and other decomposition products: 	citric acid, standard tests, calcium hydroxide solution, large test tube, distillation apparatus, boiling stone

Tartaric acid	E98 Tartaric acid:  Perform the standard tests (E73 -76) and the copper test (E77): Detect the carboxylic groups with the BTB test and the diol group with the copper test. Use a solution of half a spatula full of tartaric acid in 5 ml of water for the tests. Note: The copper test is only positive after neutralization of tartaric acid to tartrate. Make a blank test with sodium potassium tartrate. Inquire by means of the model kit that tartaric acid molecules can exist in three stereoisomeric forms. Fischer projection:  D(-)form L(+)form meso form m.p. 170 °C 170 °C 140 °C Discuss the properties of the isomers in terms of their stereochemical relations.	tartaric acid, sodium potassium tartrate, standard tests, copper test, model kit
Oleic acid	E99 Oleic acid:  Test the solubility of 2 ml oleic acid in 2 ml water, 2 ml ethanol and 2 ml fuel: It is not solvable in water. Explain this in terms of intermolecular interactions. Confirm the carboxylic group by means of the BTB test (E74). Neutralize 2 ml oleic aid with 2 ml 3 M NaOH in a large test tube. Add 20 ml water, stopper it with a cork and shake well: Soap lather is observed.  sodium oleat (soap) Note: Oleic acid is a liquid (m.p. = 13 °C); stearic acid (E80) is a solid (m.p. = 70 °C). Explain this in terms of reduced flexibility of the hydrocarbon chain at the double bond. Use the model kit to demonstrate the rigidity of the double bond. Confirm also the possibility of cis-trans-isomerism. (Natural oleic acid has cis configuration.)	oleic acid, stearic acid, ethanol, fuel, BTB test, 3 M NaOH, large test tube, model kit

Cooking oil	E100 Cooking oil:  R = long chain Perform the PHT test (E75) with cooking oil. Use 1-propanol instead of ethanol as a solution aid. Heat with a flame instead of a water bath. Decolourization can be observed in 1-2 minutes. Put into a large test tube 4 ml cooking oil, 4 ml 1-propanol (solution aid), 8 ml 3 M NaOH and 3 boiling stones. Shake well and heat the mixture. Clear monophase solution. Perform the standard tests (E73 - 76) and the copper test (E77) with the reaction mixture. Put 0.5 ml of the reaction mixture into a test tube, add 10 ml water, stopper it and shake well: Soap lather (sodium oleat, sodium stearat). The copper test is positive: Clear, dark blue solution (glycerol). Perform a blank test with glycerol. The PHT test (with 1-propanol as solution aid) is negative: Cooking oil (an ester) has been completely hydrolysed:  cooking oil glycerol oleat/stearat (soap)	cooking oil, 1-propanol, 3 M NaOH, standard tests, glycerol, boiling stones, large test tube