CHM2123 ANSWERS TO LAB QUESTIONS

LAB 1

1. Ethyl Acetate and water are immiscible compounds, meaning they do not mix together since they have different chemical properties. Water is far more polar and the substances rearrange in layers when mixed together. Therefore, this mixture could not be used for recrystallization. Also,the recrystallization process will not occur if the solute is very soluble in the solvent; a more desired solvent would be ethanol since the caffeine dissolved, but still has a chance to recrystallize.

2. NaCl is an ionic compound that is capable of removing emulsions from an extraction funnel by [increasing the ionic strength of the aqueous phase], which results in the breaking up of emulsions. [3] The NaCl disperses the emulsions, which causes them to break apart.

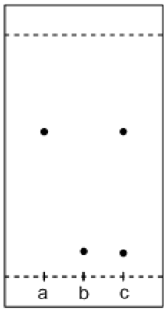
3. The tea was boiled in order to extract the caffeine since the solubility of this compound is higher in water at higher temperature; it has a solubility of approximately 16 mg/ml at room temperature, 200 mg/ml at 80°C, or 666 mg/ml in boiling water (Sigma-Aldrich). The tea was then chilled so that the caffeine becomes less soluble in the water and is transferred more easily to the dichloromethane during the extraction.

4. If a drop of brewed tea was spotted on a TLC plate and developed, the caffeine would have a high Rf value than the catechin. The catechin contains multiple polar hydroxyl groups that can interact strongly with the polar silica gel, making it migrate more slowly across the plate. Caffeine does not contain any hydroxyl groups, will interact less strongly with the polar silica gel and will migrate at a greater rate.

5. Sand was added to the Erlenmeyer flask to help break apart the tough cell walls of the plant cells and release the contents of the cytoplasm.

6.

Compound	Rf Value
A	0.6
B	0.1
2:1 A:B	0.6, 0.1



Just because spot C is a 2:1 mixture of A:B, it does not mean that the Rf value will be a weighted average of the two compounds. It simply means that the two compounds will separate and travel to their respective Rf value.

8. a. Cyclohexane; cyclohexanol

Cyclohexanol would have a smaller Rf since it is a more polar compound than cyclohexane, meaning it will form more bonds with the eluent, thus moving lower on the TLC plate (and having a smaller Rf value).

b. 1-octanol; 3-octanol

1-octanol would have a smaller Rf due to the polarity of the –OH group on carbon 1. It is less sterically hindered than the 3-octanol, which has the –OH group on the third carbon. This allows more bonding to occur with the eluent, causing a smaller Rf value.

c. The compound with R-NH2 will be a more polar compound than the R-N(CH3)2, since the primary amine group is exposed and not sterically hindered. This allows the functional group to make bonds with the eluent, thus having a smaller Rf value. The R-N(CH3)2 has a tertiary nitrogen, which is difficult to make bonds with the eluent, causing it to be less polar and moving higher up the TLC plate, with a higher Rf value.

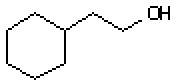
d. The compound R-COOH, a carboxylic acid, will have a smaller Rf value because carboxylic acids are known to be the most polar with eluents, thus having the smallest Rf's. The compound with R-COOCH3 has the methyl group hindering the potentially bonds with the eluent, therefore it will travel higher up the TLC plate.

The 4:1 hexane:ethyl acetate is a less polar eluent than 1:4 hexane:ethyl acetate, therefore the Rf values will all be smaller, but still have the same order between two compounds. The more polar eluent will allow for larger Rf values, but for non-polar compounds they will be much smaller since the less polar eluent is less capable of competing with the compound in terms of adhering to the silica gel.

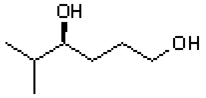
9. The polyphenols (catechin) would be separated into the aqueous phase when extracted with sodium carbonate and DCM and instead of extracting, I would extract the aqueous phase (containing the polyphonic anions) and protonate the polypheonoic anoins to convert the salts back to their acidic form. I would then continue the reaction and using the methods of extraction with DCM, obtaining the catechin in the organic layer and then use the methods of filtration and evaporation and finally recrystallization to get my final product – pure catechin.

LAB 2

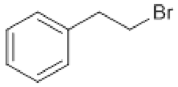
1.

a.  + Na^+ + Br^-

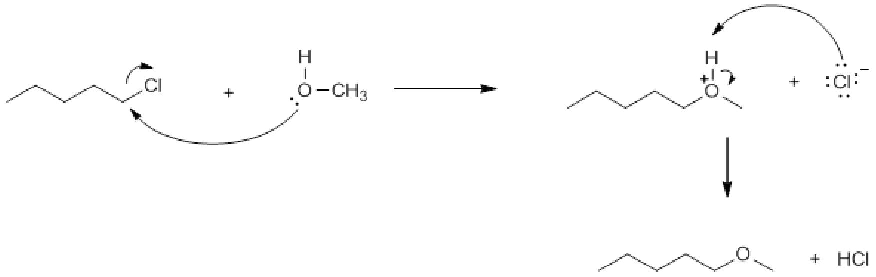
b.  + Na^+ + Cl^-

c.  + Na^+ + Cl^-

 + Na^+ + Cl^-

2.  will have the fastest rate of reaction with NaOH in an SN2 reaction because the leaving group, which is Br is located on a primary carbon. The fastest reactions for SN2 happen at a primary carbocation. The other compounds have their leaving groups on either tertiary, or secondary carbons. This is true due to the steric hinderance seen in secondary and tertiary carbocations; the nucleophile will have a harder time attacking the carbon-leaving group bond, causing a more difficult reaction to perform, which is ultimately unfavoured.

3.a)



b) Two ways to increase the overall yield of the reaction is:

i. Increasing the substrate concentration increases the chances of collisions in order to produce the product. The more collisions, the more products that will be formed.

ii. Using an aprotic solvent, like DMF or DMSO will increase the overall yield. An aprotic solvent will not bind to the nucleophile, allowing it more freedom to react.

4. In this reaction, the nucleophile is ionic; therefore, a very polar solvent is required to dissolve it. Also, it is an SN2 reaction, these reaction usually prefer aprotic solvents so as to allow the nucleophile to react more easily. However, in this case the nucleophile is the conjugate base of the solvent. Therefore, even if it does interact with the solvent, it will still produce the same nucleophile and not affect the rate of the reaction.

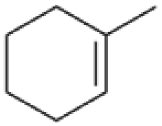
5. To determine which type of reaction is occurring, the experiment would be performed and the rate of the reaction could be measured by taking samples, titrating and measuring the concentration of NaOH over time. The graphs for the ln[NaOH] versus time and 1/[NaOH] versus time could be plotted. If the graph of the natural logarithm is a straight line, the reaction is first order, and therefore an SN1 reaction. If this graph is not a straight line but the graph of the inverse of the concentration is, the reaction is second order and therefore, an SN2 reaction. To verify the above, the initial concentration of the nucleophile could be increased. Since SN1 reaction rates are only affected by the electrophile concentrations, this should not affect the rate if it is indeed SN1. However, this would increase the rate of an SN2 reaction since both reagents are involved in the rate of these reactions.

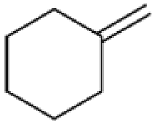
LAB 3

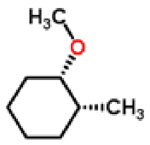
1. A) To turn 2-bromobutane into 1-butene, using a hindered base such as KOtBu, will produce the desired product. This is the Hoffman product. This is because the hindered base will remove the most sterically accessible hydrogen.

B) To turn 2-bromobutane into 2-butene, using a small base such as OH- will produce the desired product. This is the Zaistev product. Small bases produce the more stable alkene because they are able to access the sterically hindered hydrogens.

3. a) 1-methylcyclohex-1-ene **b)** methylenecyclohexane **c)**1-methoxy, 2-methylcyclohexane







4. Bromoethane will undergo mostly an SN2 reaction and 1-bromo-2-methylpropane will undergo mostly an E2 reaction. This is because =1-bromo-2-methylpropane is a hindered molecule, and hence the large nucleophile will not access the carbon as easily, therefore favouring an elimination reaction. The bromoethane is not hindered, and will allow for an SN2 reaction.

5. a) This will be an elimination reaction because of the tertiary carbon and the presence of a small base (hydroxide ion). When a strong base is present with a tertiary C and a strong base (-OH), elimination predominates.
b) This will be a substitution reaction because with a primary carbon and a small base that's not hindering elimination will not take place.
c) This will be a substitution reaction because with methyl groups attached to a halide, only substitution takes place.

d) This will be a substitution reaction because there is no anti-periplanar H for elimination to occur.

6. Increasing the temperature of the reaction will favour the production of 1-pentene over 1-pentanol because of heating favours elimination. Increasing the temperature allows more number of molecules able to reach the activation energy barrier and hence elimination occurs. Also, having a large hindered base KOtBu will result in E2 reaction because the base is too sterically hindered to act as a good nucleophile.

LAB 4

Part A

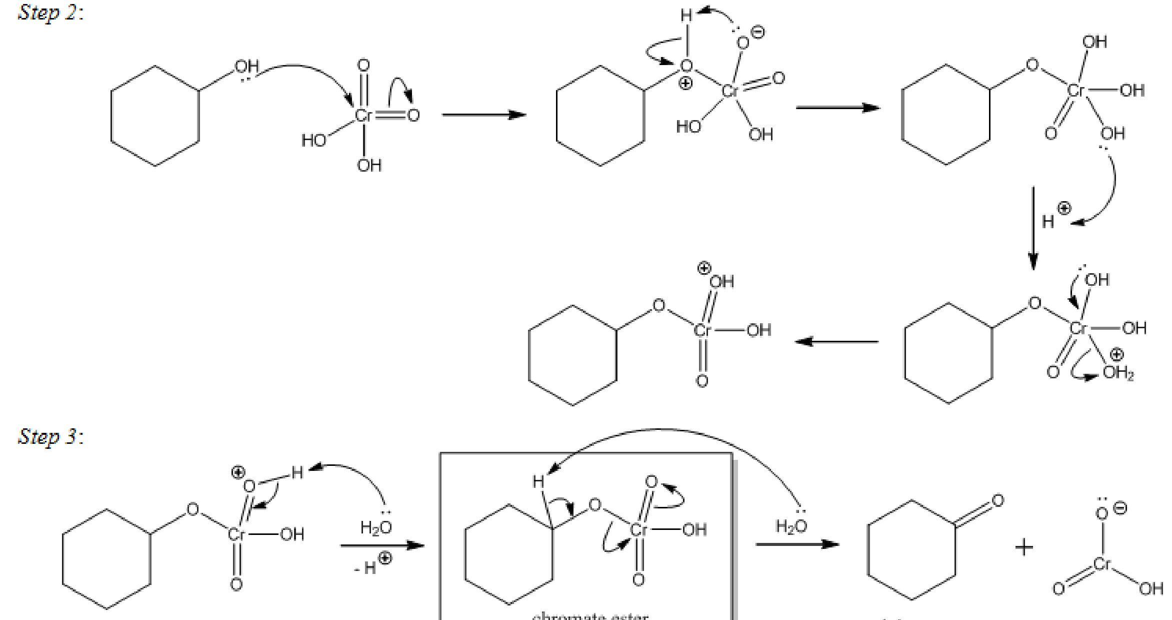
1. 4-nitrobenzyl alcohol is more polar than 4-nitrobenzaldehyde. This is because of the hydrogen bonding capabilities due to the presence of OH groups. Since aldehydes lack OH groups, they are incapable of intermolecular hydrogen bonding. More polar compounds interact more strongly with the polar silica gel and therefore migrate more slowly than less polar compounds, and so they have a smaller Rf value.

2.

2. *Step 1:* $Na_2Cr_2O_7 + H_2O \rightleftharpoons 2\ HCrO_4^-\ Na^+$

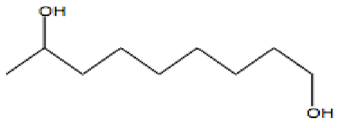
$HCrO_4^-\ Na^+ + H_2SO_4 \rightleftharpoons NaHSO_4 + H_2CrO_4$ (chromic acid)

Step 2:

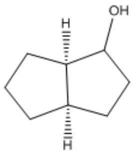


Part B

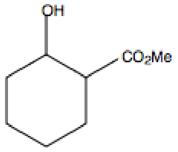
1. a)



b)

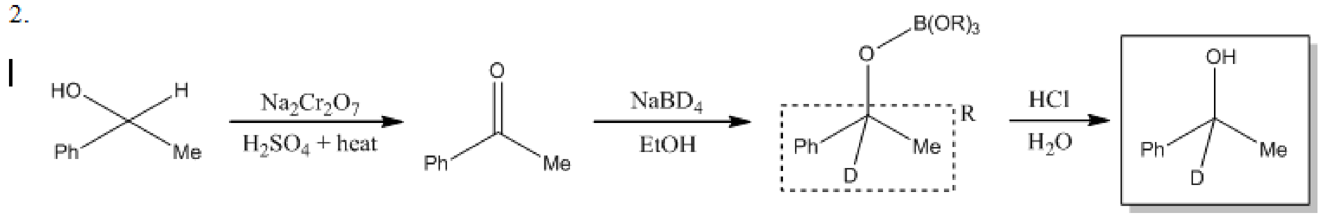


c)



d) No reaction, sodium borohydride cannot reduce carboxylic acids. The NaBH4 can act as a base, albeit a weaker one than NaH and LiAlH4. It would react with the carboxylic acid to produce hydrogen gas and a carboxylate anion. That is why we add acid and water at the end of the lab; to get rid of the excess NaBH4.

2.

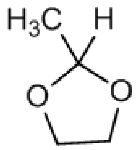


LAB 5

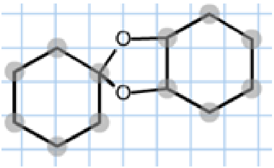
1. a) The spectrum of the product in 18 has two different methyl groups because of the chiral centre that permits stereochemistry among the two methyl groups. Furthermore, cyclic compounds are most stable when they are arranged in an envelope conformation, similar to chairs for cyclohexanes, but the fact that the ring is in an envelope conformation is what causes the peaks to occur separately, as opposed to 1 single peak.

b) Only two signals are expected in the H NMR spectrum of 2,2-dimethoxypropane. Based on the information provided in the chemical formula, the degree of unsaturation of the compound was zero, indicating that there are no double bonds, nor ring structures. A plane of symmetry was easily identified when drawing out the compound, and as a result only two signals are possible for this H NMR. The first signal will occur around 3 to 4 ppm, as it is a CH3 group, beside oxygen that acts as an electron withdrawing group. This signal will be a singlet based upon multiplicity, which states that the amount of peaks per signal is based on n+1, where n is the number of hydrogens on the adjacent carbon, which in this case is zero. This multiplicity is also true for the second signal, meaning that it too will be a singlet. This signal is from the CH3 group on the compound, but unlike the previous one, it is not near an electron withdrawing group, thus its chemical shift is not increased, and it will occur, like normal, in the range of 1 to 2 ppm.

2.a)



b)



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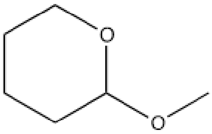
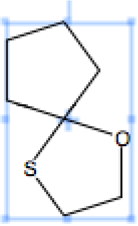


d)



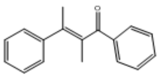
4. (second #3)

The reaction of β-D-glucose produces the same ratio of diastereomers as α-D-glucose because the step where the protonated hydroxyl group leaves forms an achiral product. This achiral product is identical for both β-D-glucose and α-D-glucose, so the same ration of products is formed. The carbon that is double bonded to the oxygen in a resonance structure has planar hybridization, so the methanol can attack either above or below the carbon and produce one of two diastereomers.

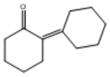
<u>LAB 6</u>

1.

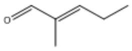
A)



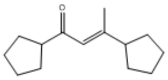
B)



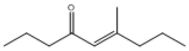
C)



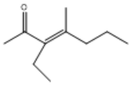
D)



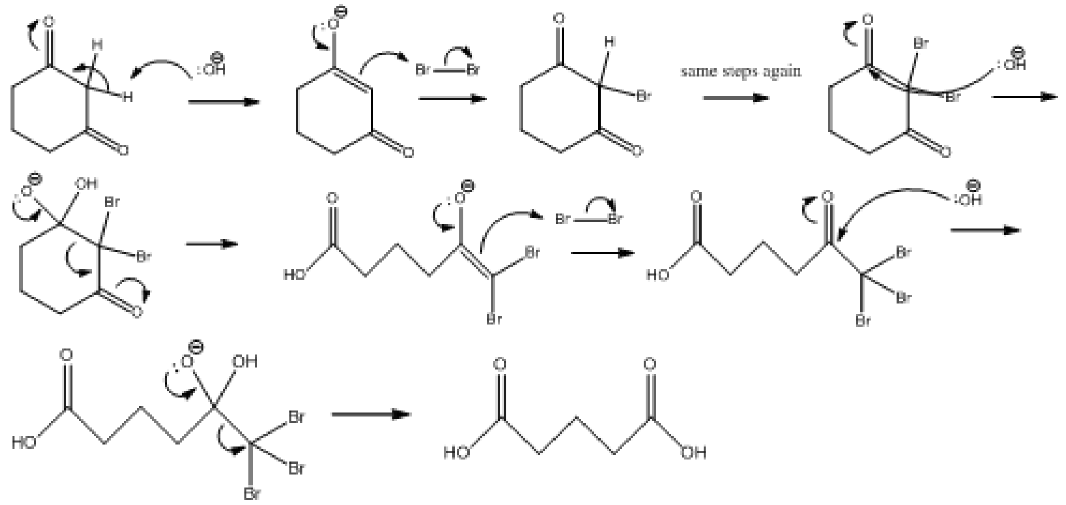
E)

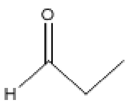


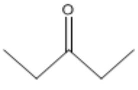
and



4. Firstly, bromination will occur with the help of the base which will deprotonate the alpha carbon and allow a bromine to replace both of the hydrogens. The hydroxyl will then attack the carbon of one of the carbonyl groups and cause the ring to open. This results in a 5 carbon chain with a carboxylic acid at one end. The other end of the open ring is stabilized by resonance. A third bromination will occur at this end, resulting in good leaving group (the alpha carbon with three bromine atoms). A hydroxyl group can then attack the carbonyl and form another carboxylic acid. The final product is then 1,5-pentanedioic acid.



5.  First HNMR graph, C3H6O: Propanal produce 3 separate signals in an HNMR: the CH3, CH2 and CH groups. The integration 1:2:3 indicate the presence of the above mentioned group, but not in what order. The CH group is seen at eh 9.7 – 9.9 ppm range, this means there must be an atom that is causing the downfield shift: an oxygen. The chemical equation indicates the presence of one unsaturation, which leads to the finding that a carbonyl group is present, on the carbon that has a single hydrogen and is downshifted. The triplet component of the HC=O group indicates that the adjacent carbon has 2H's. The CH2 group is located around the 2.4 – 2.5 ppm range. The quintet splitting indicates the presence of 4 surrounding hydrogens, one of which we know is on the HC=O group attached. Therefore, the final group in the molecule – CH3 can be observed at the 1.1 – 1.2 ppm range. It has a triplet splitting, indicating the presence of only 2H's on the adjacent carbon.

6.  Second HNMR graph, C5H10O: Pentan-3-one is a symmetrical molecule, meaning there will be equivalent CHx groups. In the molecule, there are two sets of equivalent protons: the two CH2 groups produce one signal, and the two CH3 groups produce a signal. The CH2 groups are seen at around 3.4 – 3.5 ppm: the quartet is due to the 3H's on the adjacent carbons, and the downfield shift is due to the carbonyl group. The chemical equation indicates the presence of one unsaturation, which lead to the finding that a carbonyl group is present. The CH3 groups are seen at around 1.0 – 1.2 ppm: the triplet is due to the 2H's on the adjacent carbons. The integration ratio can confirm the structure, due to the equivalent signals and CHx groups that are possible.

LAB 7

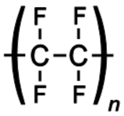
1. The carbonyl functional group on the acetylated product acts as an electron-withdrawing group and withdraws electron density (draws out the negative charge) from the N atom, which makes it a lot less reactive/nucleophilic. Whereas, the amine product has H groups on it that make it more nucleophilic. ALSO - My TA made a correction - “Resonance with lone pair”

2. Since pyrrolidine is a secondary amine (not a primary as in our lab), the first intermediate produced is an enamine. This species is a very reactive nucleophile and needs to be reduced immediately to an amine in order to prevent it from attacking another 2-butanone molecule. This is done by adding NaBH4 at the same time as the starting material. In other words, secondary Amines form Iminiums which can’t be isolated and so the reaction has to take place in one pot.

3. The product after step 8 is a secondary amine. The glacial acetic acid was added during that step and some of the secondary amine may be protonated. The resulting equilibrium protonation and deprotonation may cause streaking up the TLC plate. To remove the streaking triethyl amine is added to the mixture to ensure complete deprotonation and prevent the streaking.

LAB 8

1.Teflon’s chemical formula is –(CF2CF2)-

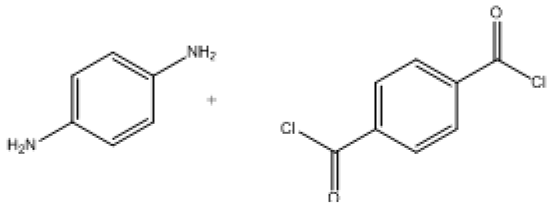


$$\left(-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}- \right)_n$$

Telfon is chemically stable because the carbon-fluorine bonds are very high in strength. Specifically, they have London dispersion forces due to the high electronegativity of fluorine. Also, Teflon is made up of single bonds, alkanes, and they are the most stable kind of bonds.

3.

a)



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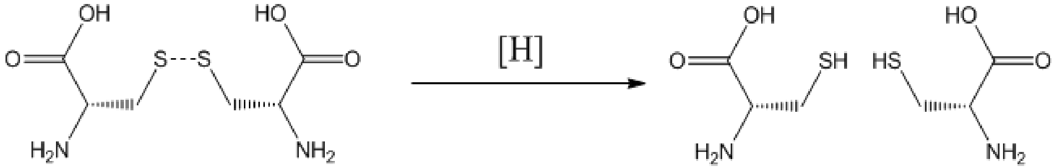
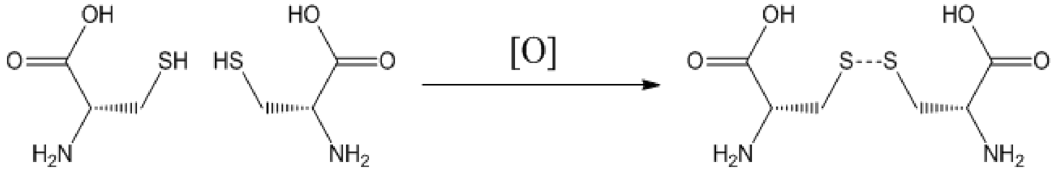
b) The strength of Kevlar is due to hydrogen bond interactions between two strands of the polymer. The hydrogen on the nitrogen and the oxygen of the carbonyl interact strongly.

4. Disulphide bridges are a common example of cross-linking that occurs between thiols. For instance, disulphide bridges form between cysteine residues in the protein keratin. These linkages cause kinks in the overall structure of keratin, causing hair to be curly or wavy. This curliness can be reduced and straightened via a chemical perm or relaxer.

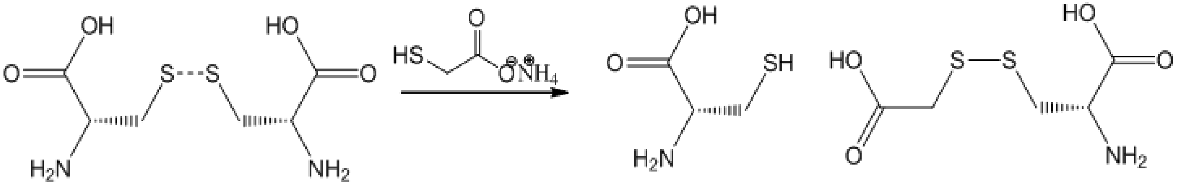
Most chemical perms use reducing agents. Normally, disulphide bridges are formed from thiol R-SH groups that are oxidized to become disulphide bridges R-S-S-R. The reducing agents in chemical perms thus break the disulphide S-S bond to yield the thiol groups RSH and HSR, as per the following equation (shown with the amino acid cysteine):



Once the hair has been straightened, it is then made "permanently" straight by re-forming the disulphide bridges in the new "straightened" positions. This is done by adding an oxidizing agent, which regenerates the disulphide bridges as shown:

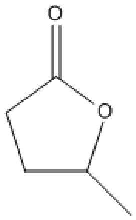


A similar effect as the perm can be achieved with a chemical relaxer. Relaxing agents like ammonium thioglycolate break the disulphide bridge by removing a sulfur atom from the linkage, forming a lanthionine group and a cysteine molecule:

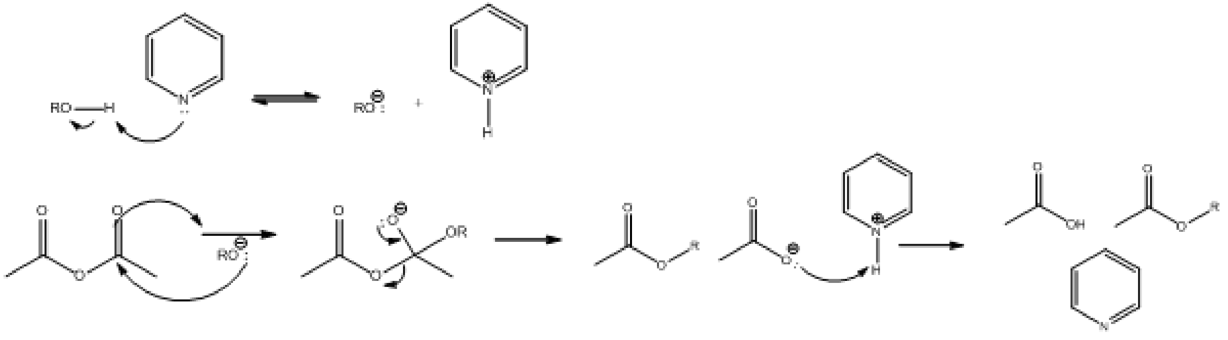


This process, called lanthionization, involves irreversible breakage of the disulphide bridge. Because the linkage cannot be reformed, the resultant change in hair style (reducing in curliness/waviness) is permanent.

7. *gamma*-valerolactone:



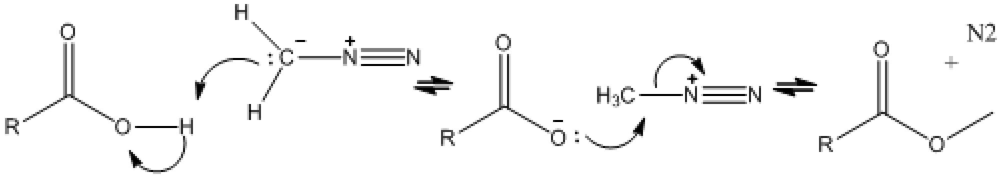
8.



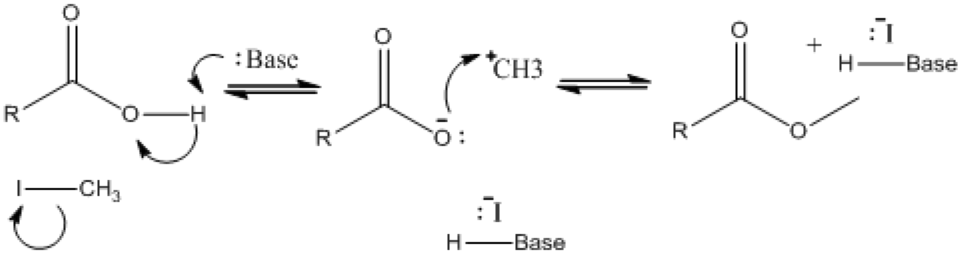
10. These two reactions would not work because t-BuOH and t-BuBr are too hindered to allow those reactions to occur. In the first reaction, t-BuOH is a good base but it is too hindered to be nucleophilic and it cannot attack the carbonyl carbon and add to form the ester. t-BuBr will not react with the deprotonated oxygen because the carbocation formed when the bromine leaves is too hindered to allow the oxygen to bind.

11.

a) $RCO_2H + CH_2N_2$ → RCO_2CH_3



b) $RCO_2H + CH_3I$ →(base) RCO_2CH_3

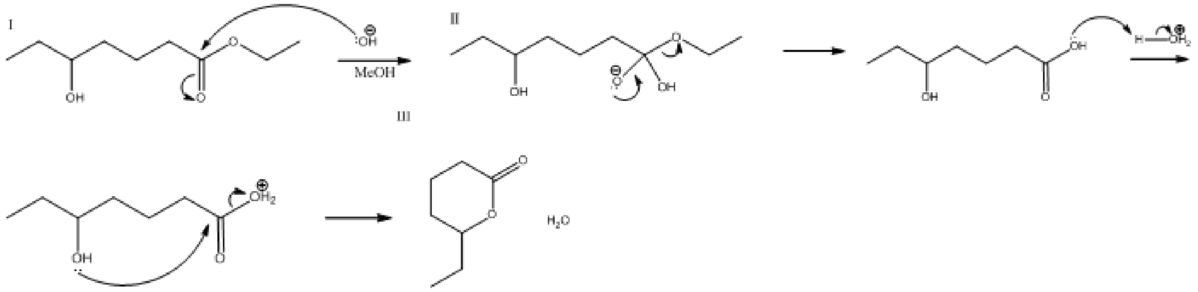


LAB 9

2. A micelle, as referenced in Part B Introduction, is the physical phenomenon of amphipathic molecules being placed in a water based environment. Micelles are formed from molecules that have a polar head (i.e. Soap salts) and non-polar tail (like a chain of saturated hydrocarbons).

When placed in this environment, naturally the tails want to do whatever possible to make themselves isolated from the water molecules. To accomplish this, many tails will group towards each-other, leaving the polar heads facing out. These heads will interact with the water, but keep it from reaching the non-polar tails. These self-assembling structures of hydrocarbons can be observed in a wide variety molecules as long as they exhibit the amphipathic properties described above.

3.



5.

6.