CORK INSTITUTE OF TECHNOLOGY

INSTITIÚID TEICNEOLAÍOCHTA CHORCAÍ

Continuous Assessment 1
Semester 1 Examinations 2018/2019

Module Title:	**Topics in Organic Chemistry**

Module Code:	CHEO7003
School:	Science & Informatics
Programme Title:	Bachelor of Science in Analytical and Pharmaceutical Chemistry — Year 3 Bachelor of Science in Analytical Chemistry with Quality Assurance — Year 3
Programme Code:	SCHEM_7_Y3 SCHQA_8_Y3
External Examiner(s):	
Internal Examiner(s):	Dr. W. Doherty
Instructions:	Answer any 3 questions. All questions are worth 25 marks. Total marks available is 75 marks.
Duration:	1 hour
Sitting:	11/10/2018
Requirements for this examination:	

Note to Candidates:

Please check the Programme Title and the Module Title to ensure that you have received the correct examination paper. If in doubt please contact an Invigilator.

Q 1.

(a) Draw 3-methylpentan-1-one. (4 Marks)

(b) Draw the keto-enol tautomerism for 3-methylpentan-1-one. (5 Marks)

(c) Draw both enolates that can be formed from 3-methylpentan-1-one and label which one is the thermodynamic enolate anion and which one is the kinetic enolate anion. (8 Marks)

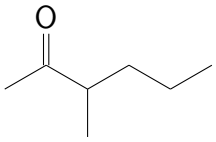
(d) Which of the enolates (thermodynamic or kinetic) requires equilibrium conditions? Why? (8 Marks)

Total for Question 1: 25 Marks

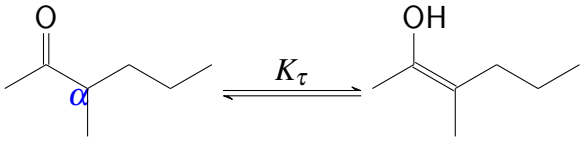
Solution:

Error in paper should have been 3-methylpentan-2-one not 3-methylpentan-1-one so will accept your answers based on its merits bearing in mind this error.

(a)

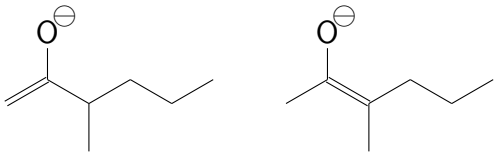


(b)



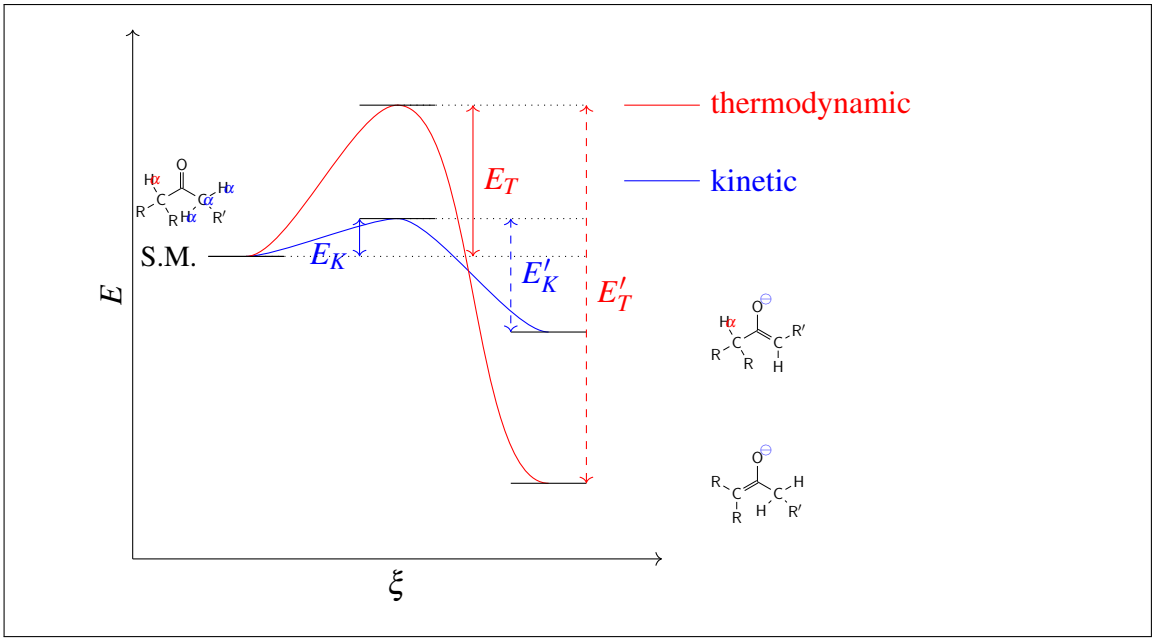
keto enol

(c)



kinetic thermodynamic

(d) The thermodynamic enolate requires equilibrium conditions. As can be seen in the diagram below, while the kinetic product may be formed first under equilibrium conditions the kinetic product can revert to the starting material whereby it can go the kinetic route OR the thermodynamic route. Once it enters the thermodynamic product it cannot go back. Therefore over time under equilibrium conditions the thermodynamic product will be formed.

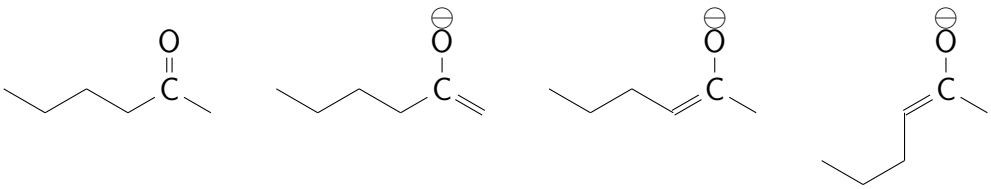
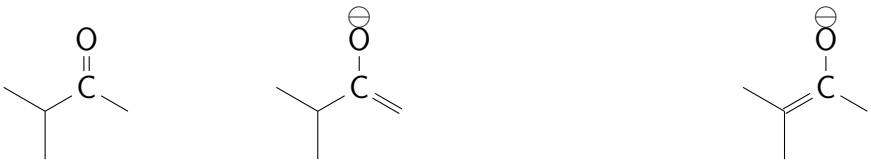


Q 2.

(a) List the conditions that generate the kinetic enolate. (7 Marks)

(b) For each of these conditions explain why they lead to the formation of the kinetic enolate and not the thermodynamic enolate. (7 Marks)

(c) Under thermodynamic conditions the amounts of kinetic and thermodynamic products for hexan-2-one and 3-methylbutan-1-one are given below:

Ketone	Kinetic Enolate	Thermodynamic Enolate
		
Thermo, KH,20 °C	42%	58% in total
		
Thermo KH, 20 °C	88%	12%

Explain why the amount thermodynamic product for 3-methylbutan-1-one is so low

compared to that of hexan-2-one. (11 Marks)

Total for Question 2: 25 Marks

Solution:

(a)

Kinetic Product
Low Temp
Excess Base
Bulky Base
Strong Base
Aprotic Solvent
Low alkyl substitution
Short Reaction Times

(b) Low temp – prevents equilibrium being set up, not enough thermal energy to overcome the activation energy for the thermodynamic product so therefore favours kinetic product.

Excess base – ensures all carbonyl forms enolate and no possibility of equilibrium being set-up. If not enough base will have an equilibrium situation

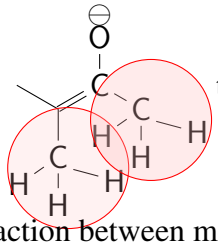
Strong base – ensures rapid deprotonation (so no equilibrium)

Aprotic solvent – prevents reprotonation of enolate which would establish equilibrium

Low alkyl substitution – less destabilisation so formation of kinetic form more likely

Short reaction Times – Long reaction times enable equilibrium to be setup so keep reaction times short

(c) Steric reason prevent a higher percentage of the thermodynamic product being formed

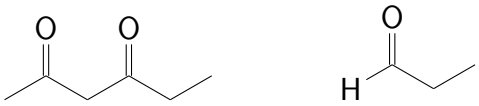
would expect  to predominate but branching interferes and causes steric interaction between methyl groups leading to a lower percentage

Q 3.

(a) For the following molecules

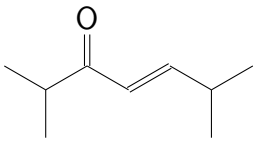
(i) Name the two starting materials. (4 Marks)

(ii) Draw ALL possible aldol products. (8 Marks)



(iii) **Giving reasons**, which one of the four products would you think would be produced in greatest amount? (7 Marks)

(b) Determine the two carbonyl compounds that could be used to produce the following enone in an aldol condensation reaction.

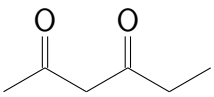


(6 Marks)

Total for Question 3: 25 Marks

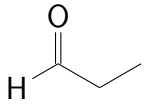
Solution:

(a) (i)



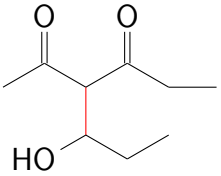
2,4-hexandione

OR hexan-2,4-dione

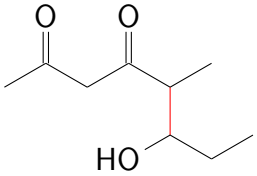


propanal

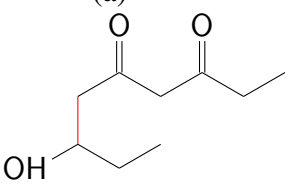
(ii)



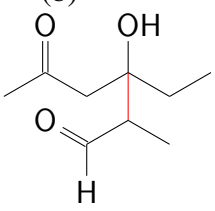
(a)



(b)



(c)

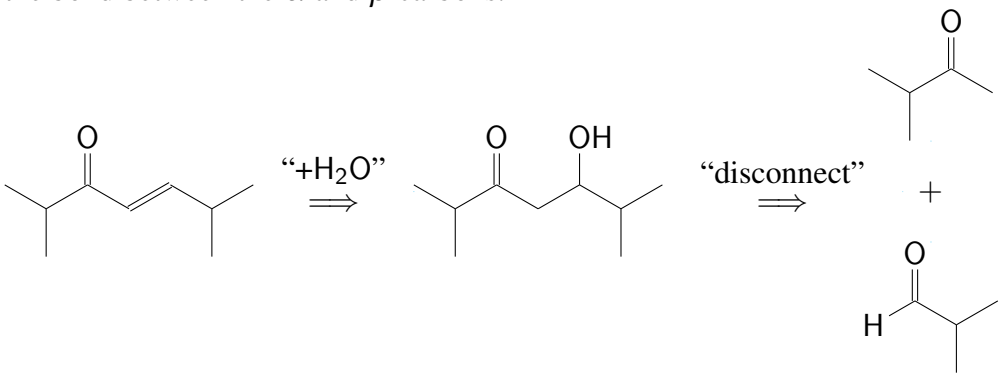


(d)

I will accept the condensation product ie conjugated double bond after elimination of water if/where it exists. The question stated aldo product not aldol condensation product hence the hydroxyketones drawn.

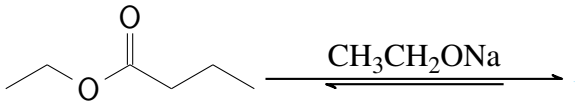
(iii) The most likely product is (a) above. The aldehyde is more electrophilic than the diketone so will be the electrophile. The diketone has an activated methylene group (between the carbonyls so C3 will be the nucleophilic carbon. Hence we get a new carbon-carbon bond from the C3 of the diketone to C1 of the aldehyde.

(b) We can do a reverse aldol on this and form the β-hydroxyketone and then break the bond between the α and β carbons.



Q 4.

(a) For the following Claisen condensation reaction, show clearly the mechanism and draw the Claisen product A.



A (13 Marks)

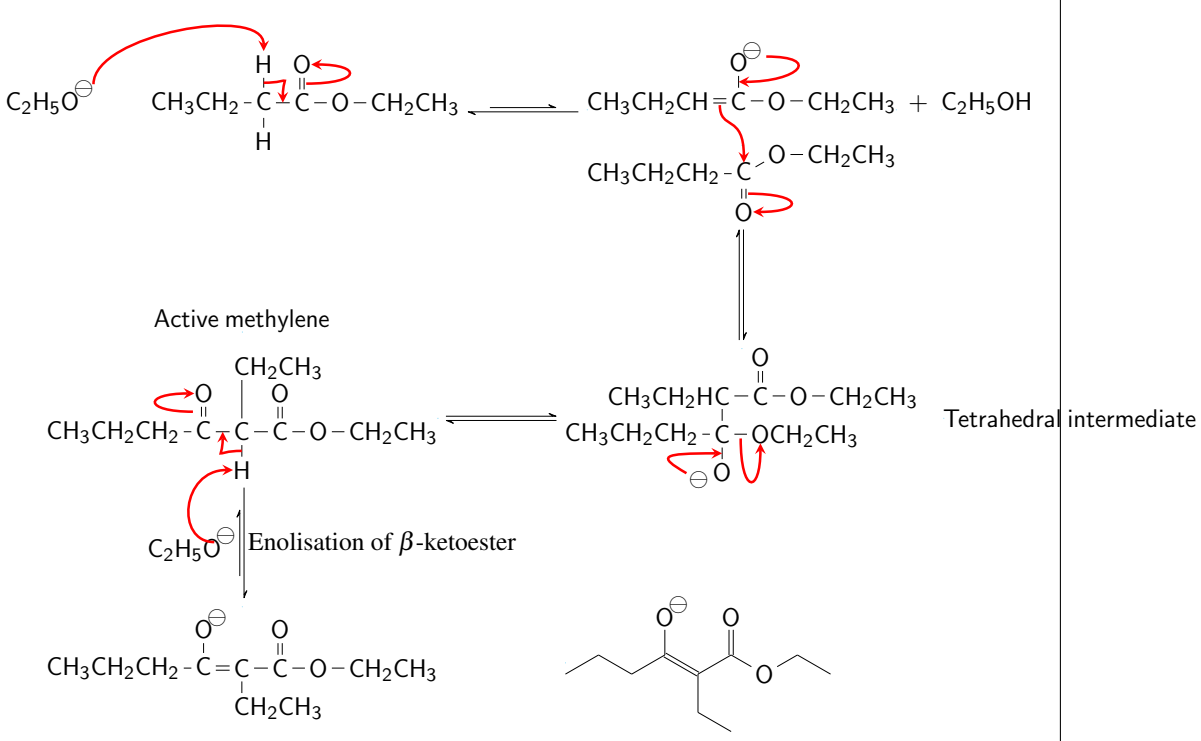
(b) Why is the formation of the enolate of the β-keto ester necessary? (7 Marks)

(c) What is meant by 'acid work-up' and how would you carry it out? (5 Marks)

Total for Question 4: 25 Marks

Solution:

(a)



(b) If the enolate of the β-keto ester is not formed the active metylene containing form is in equilibrium with the tetrahedral form which is in equilibrium...which is in equilibrium with the starting material. So unless the enolate is formed we will not have a huge yield of the β-keto ester.

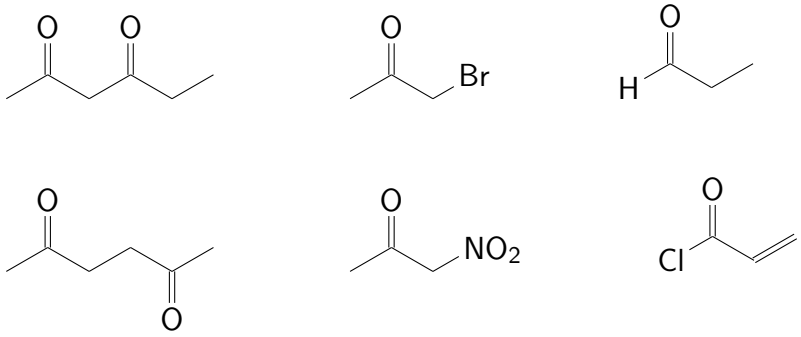
(c) Acid-work up is the process of addind a strong (mineral) acid to a salt of your product. As the salt is formed from a weak acid and a base, the addition of a strong acid will reprotonate the weak acid. In such systems the strong acid will deprotonate and the weak acid will be reprotonated. The equilibrium always lies to the side of the weaker acid.

Once the salt of the β-keto ester has been formed (the last step above), it is separated from the mixture by precipitation or otherwise. Then a strong acid as added to the salt, this will reprotonate the β-keto ester (the weaker acid) forming the claisen product.

Q 5.

(a) What is meant by the term "active methylene group"? (5 Marks)

(b) For the following molecules identify the active methylene groups. **Marks will be lost if non-active methylene groups are selected**. *Redraw the molecules in your answer book and circle the active methylene groups.* (10 Marks)



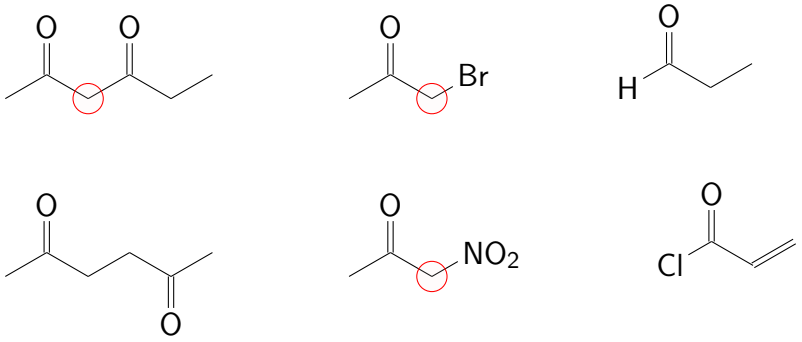
(c) For any two of the above molecules with active methylene groups draw resonance structures to show why the α-H is so acidic. (10 Marks)

Total for Question 5: 25 Marks

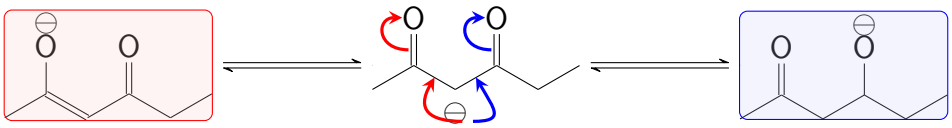
Solution:

(a) A methylene group ($-CH_2-$) that is α- to two carbonyl groups is called an ACTIVE METHYLENE GROUP . It can also be any electronwithdrawing group that will stabilise the anion formed.

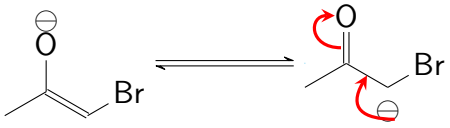
(b)



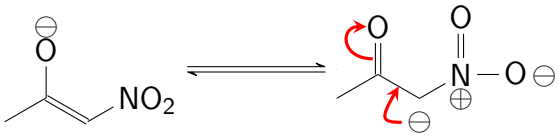
(c)



The anion formed is readily stabilised, hence making the formation of the anion more favourable, ie making the compound more acidic.



Can see negative charge next to Br which is very electronegative and will stabilise the anion, eading to more likely formation of anion and H+...ie more acidic.



Can see negative charge next to positive N which is will stabilise the anion, leading to more likely formation of anion and H+...ie more acidic.

Q 6.

(a) Draw the following molecules:

3-methylpentan-2-ol 2-methylpentan-2-ol 2,2-diethylbutan-1-ol
3-methylpentan-3-ol (8 Marks)

(i) Label each alcohol above as primary, secondary or tertiary. (2 Marks)

(ii) Which, if any, of the above alcohols (as you have drawn them) will give a positive iodoform test? (7 Marks)

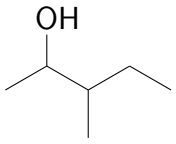
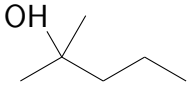
(b) What are the reagents used in the iodoform test? (4 Marks)

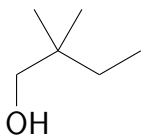
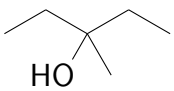
(c) Why is the formation of iodoform used as a characteristic test rather than the formation of chloroform ($CHCl_3$) or bromoform ($CHBr_3$) (4 Marks)

Total for Question 6: 25 Marks

Solution:

(a) Typo in question, 2,2-diethylbutan-1-ol should have been 2,2-di**methyl**butan-1-ol but will examine each drawing on its own merits.

		
	3-methylpentan-2-ol	2-methylpentan-2-ol
Alcohol Type	2°	3°
Iodoform Test	YES	NO

		
Alcohol Type	1°	3°
Iodoform Test	NO	NO

(b) The reagents are iodine and sodium hydroxide, I_2,NaOH

(c) Iodoform, CI_3 is yellow solid precipitate and is easily identifiable. Chloroform (CCl_3) and bromoform (CBr_3) are both colourless liquids and not so easily identifiable.