



KENYATTA UNIVERSITY

UNIVERSITY EXAMINATIONS 2011/2012

FIRST SEMESTER EXAMINATION FOR THE DEGREE OF MASTER OF SCIENCE

SCH 504: MODERN SYNTHETIC ORGANIC CHEMISTRY

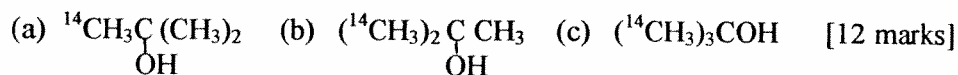
DATE: Monday 5th December, 2011

TIME: 9.00 a.m. – 12.00 p.m.

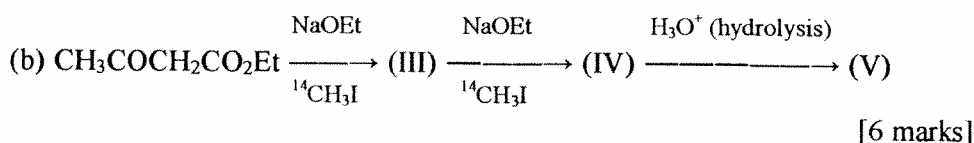
INSTRUCTION:

Answer **ALL** questions

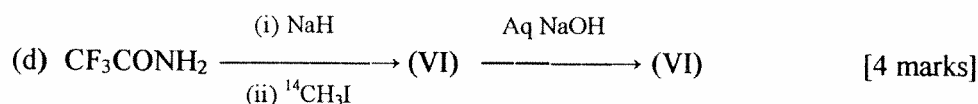
Q1. (i) Propose synthetic routes to the following labelled compounds from Grignard or related organometallic reactions with $^{14}\text{CH}_3\text{MgBr}$ (or iodide) as the source of ^{14}C label and any other starting material:



(ii) What final ^{14}C -labelled products are likely to be formed in the following reaction sequences? **Outline the mechanism of each step of the reactions.**



(c) What product would you expect to get if (IV) above is treated with sodium hydroxide under mild condition (to initiate retro-Claisen reaction)? Explain the difference in the course of the reaction. [5 marks]



[Total marks for Q1:32]

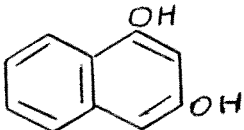
Q2. Put down the products formed in the following reaction sequences, **outlining** the **mechanism** of **each** reaction step. (Where more than one stereo-products are possible, e.g. in (b), put down the structures of both and suggest which is likely to dominate and why).

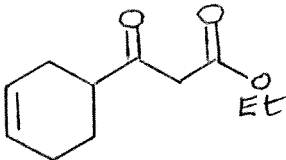
- (a) $\text{Ph}_3\text{P}^+\text{CH}_2\text{OCH}_3 \text{ Br}^- \xrightarrow{\text{NaH}} ? \xrightarrow{\text{PhCHO}} ? \xrightarrow{\text{H}_3\text{O}^+} ?$ [6 marks]
- (b) $[(\text{CH}_3)_3\text{S=O}]^+ \Gamma^- \xrightarrow{\text{NaH}} ? \xrightarrow{4\text{-Methylcyclohexanone}} ?$ [8 marks]
- (c) $\text{CH}_3\text{COCH=CH}_2 + \text{Cyclohexanone} \xrightarrow{\text{NaOEt}} ? \xrightarrow{\text{NaOEt}} ?$ [7 marks]
- (d) $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COCH}_3 \xrightarrow{\text{Mg}^0(\text{Hg})} ? \xrightarrow{\text{H}_3\text{O}^+} ?$ [6 marks]
- (e) $\text{PhNH}_2 + \text{CH}_2=\text{CHCHO} \xrightarrow{\text{H}_3\text{O}^+} ? \xrightarrow{\text{[O]}} ?$ [7 marks]
(cyclisation; $-\text{H}_2\text{O}$)

[Total marks for Q2:34]

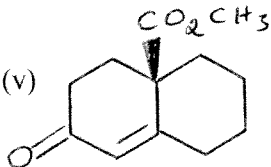
Q3. Using retrosynthetic analyses where appropriate, propose synthetic routes to the following compounds (from given compound as one of the starting materials and/or reaction method(s) given). **Outline the mechanism of each reaction step.**

- (i) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{COOH}$ from $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Br}$ [6 marks]

- (ii)  from PhCH_2COCl [7 marks]

- (iii)  from butadiene by cycloaddition and Claisen reactions [7 marks]

- (iv) $(\text{CH}_3)_2\text{CHCH}(\text{NH}_2)\text{CO}_2\text{H}$ using any suitable synthetic route for an amino acid [7 marks]

- (v)  from cyclohexenone and using Michael addition and aldol condensation reactions [7 marks]

[Total marks for Q3: 34]