UNIVERSITI SAINS MALAYSIA

Second Semester Examination
Academic Session 2008/2009

April/May 2009

KOT 323 – Organic Chemistry III
[Kimia Organik III]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of **SIXTEEN** printed pages before you begin the examination.

Instructions:-

Answer **FIVE** (5) questions.

Answer each question on a new page.

You may answer either in Bahasa Malaysia or in English.

If a candidate answers more than five questions, only the answers to the first five questions in the answer sheet will be graded.

1. (a) Give the structures (including configurations where pertinent) of compounds **A** through **K**.

(i) urea (H_2NCONH_2) + hot dilute NaOH → **A** + NH_3

(ii) phosgene ($COCl_2$) + 1 mol C_2H_5OH, then + NH_3 → **B** ($C_3H_7O_2N$)

(iii) bromobenzene + Mg, ether → **C** (C_6H_5MgBr)

C + ethylene oxide, followed by H^+ → **D** ($C_8H_{10}O$)

D + PBr_3 → **E** (C_8H_9Br)

E + NaCN → **F** (C_9H_9N)

F + H_2SO_4, H_2O, heat → **G** ($C_9H_{10}O_2$)

G + $SOCl_2$ → **H**(C_9H_9OCl)

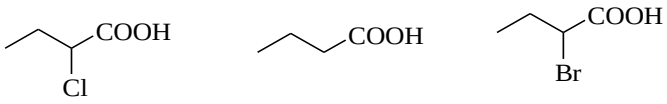
H + anhydrous HF → **I** (C_9H_8O)

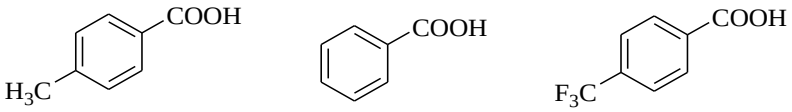
I + H_2, catalyst → **J** ($C_9H_{10}O$)

J + H_2SO_4, warm → **K**(C_9H_8)

(14 marks)

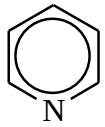
(b) Rank the following compounds in each group in order of increasing acidity. Justify your answer.

(i) 

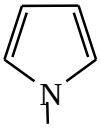
(ii) 

(6 marks)

2 (a) Complete the following proposed acid base reactions and predict whether reactants or products are favoured giving an explanation.

(i)  + CH_3COOH ⟶

pyridine acetic acid

(ii)  + CH_3COOH ⟶

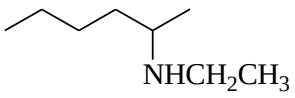
pyrrole acetic acid

(8 marks)

(b) Show how you would synthesize *N*-benzylaniline from aniline by acylation reduction.

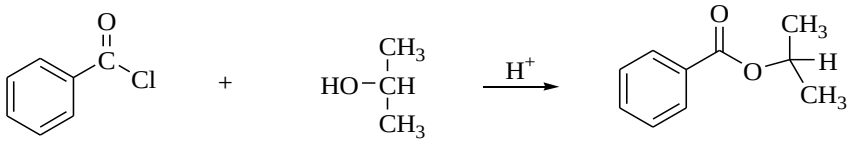
(6 marks)

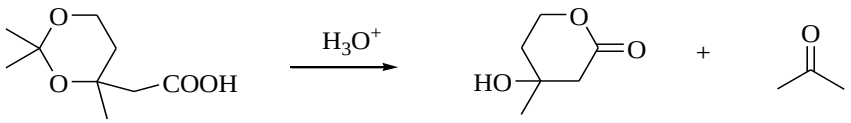
(c) Show the three (3) possible products formed when the following amine is reacted with excess iodomethane then followed by heating with silver oxide (Hofmann elimination). Predict the major product.

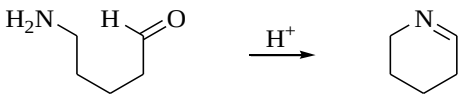


(6 marks)

3 (a) Draw a stepwise mechanism for each of the following reactions.

(i) 

(ii) 

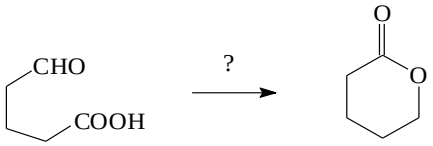
(iii) 

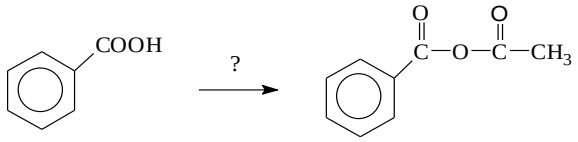
(15 marks)

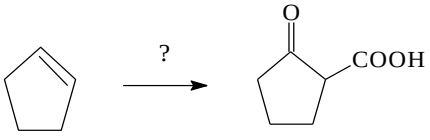
(b) Propose a mechanism for the reaction of benzoyl chloride (PhCOCl) with acetic acid, and show the structure of the resulting acid anhydride.

(5 marks)

4 (a) Show how you would accomplish the following synthesis in good yields.

(i) 

(ii) 

(iii) 

(6 marks)

(b) State the similarities and differences of the major IR absorption characteristics between carboxylic acids and amides.

(4 marks)

(c) The tertiary structure of a protein can be maintained through the formation of salt bridges which is an ionic interaction between the positive ammonium group and the negative acid group. Explain how changes in pH can disrupt the tertiary structure of a protein.

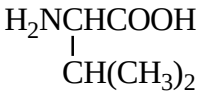
(5 marks)

(d) A decapeptide undergoes partial hydrolysis to give peptides whose amino acids are shown below. Reaction of the decapeptide with Edman's reagent releases PTH-Leu. What is the sequence of the decapeptide?

(i)	Pro, Ser	(v)	Glu, Ser, Val, Pro
(ii)	Gly, Gly	(vi)	Glu, Pro, Gly
(ii)	Met, Ala, Leu	(vii)	Met, Leu
(iv)	Gly, Ala	(viii)	His, Val

(5 marks)

5 (a) In the laboratory, an α-amino acid can be prepared from a carboxylic acid. Show the two possible methods that you would use to synthesise valine, starting with the appropriate carboxylic acids.



valine

(10 marks)

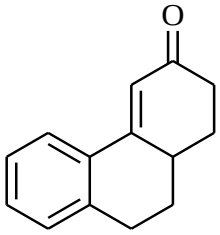
(b) What stereochemistry would you expect in the synthesis product from (a)? Draw the possible structure(s) in Fischer projection.

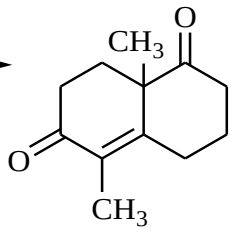
(4 marks)

(c) Show how you would separate the L-valine and D-valine by enzymatic resolution.

(6 marks)

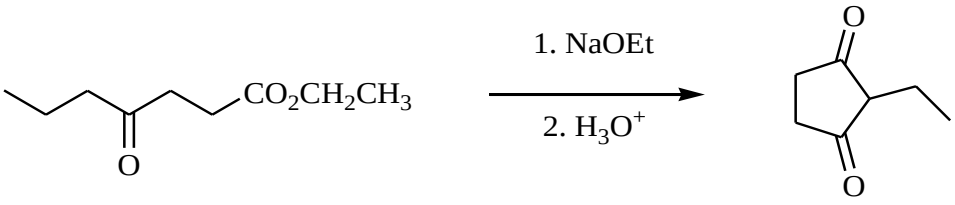
6. (a) Michael reaction and intramolecular aldol addition are the stages of a Robinson annulation. Predict the starting materials necessary for the following Robinson annulation.

(i) **L** + **M** ⟶ 

(ii) **Q** + **R** ⟶ 

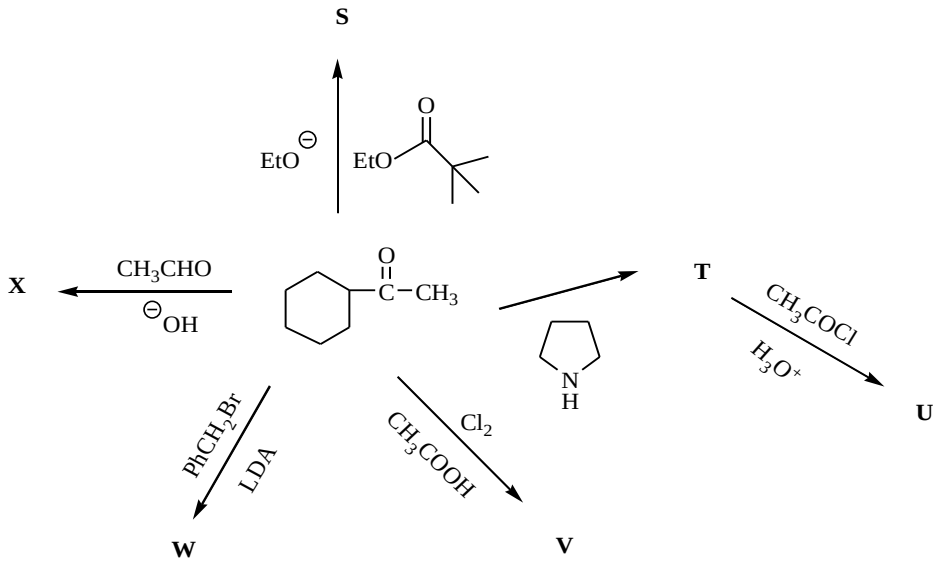
(8 marks)

(b) Show the detailed, stepwise mechanism for the transformation below;



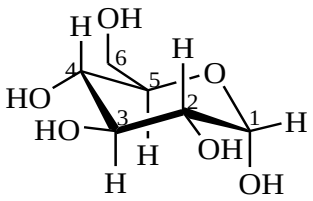
(6 marks)

(c) Give the structures of **S**-**X** in the reactions below;



(6 marks)

7 (a) The structure of cyclic hemiacetal form of D-glucose as chair conformation is shown below;



(i) Which is the anomeric carbon of this structure.

(ii) Draw β-glucosidic linkage of the disaccharide structure from the reaction of two molecules of D-glucose.

(iii) What is the name of this reaction?

(5 marks)

(b) Glucose actually exists as a pyranose (six-membered ring) but not as furanose (five-membered ring).

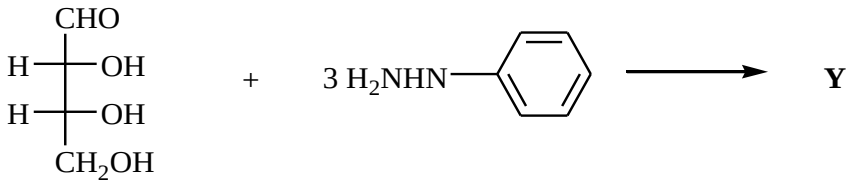
(i) How can you determine whether the methyl-β-D-glucoside has a five- or a six-membered ring?

(ii) What are the products obtained from this determination?

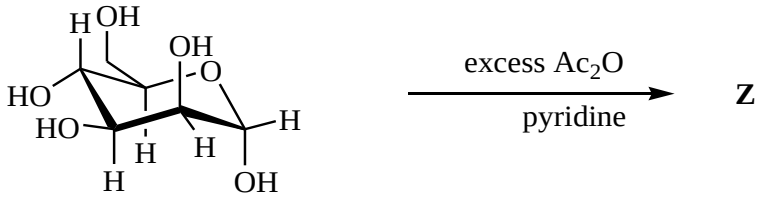
(5 marks)

(c) Draw the structure of **Y** and **Z**.

(i)



(ii)



(4 marks)

(d) Aldose **AA** is optically active. Treatment with sodium borohydride converts it to an optically active alditol. Ruff degradation of **AA** gives optically active **BB** and Ruff degradation of **BB** gives optically active D-glyceraldehyde. Give the structures and names of **AA**, **BB** and their alditols.

(6 marks)

TERJEMAHAN

Arahan:-

Jawab **LIMA** (5) soalan.

Jawab setiap soalan pada muka surat yang baru.

Anda boleh menjawab sama ada dalam Bahasa Malaysia atau Bahasa Inggeris.

Jika calon menjawab lebih daripada lima soalan, hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

1. (a) Beri struktur (termasuk konfigurasi jika relevan) kepada sebatian **A** hingga **K**.

(i) urea (H_2NCONH_2) + NaOH panas, cair → **A** + NH_3

(ii) phosgene ($COCl_2$) + 1 mol C_2H_5OH, kemudian + NH_3 → **B** ($C_3H_7O_2N$)

(iii) bromobenzene + Mg, ether → **C** (C_6H_5MgBr)

C + ethylene oxide, diikuti H^+ → **D** ($C_8H_{10}O$)

D + PBr_3 → **E** (C_8H_9Br)

E + NaCN → **F** (C_9H_9N)

F + H_2SO_4, H_2O, panaskan → **G** ($C_9H_{10}O_2$)

G + $SOCl_2$ → **H** (C_9H_9OCl)

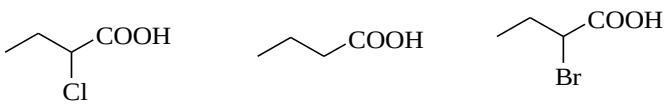
H + HF kontang → **I** (C_9H_8O)

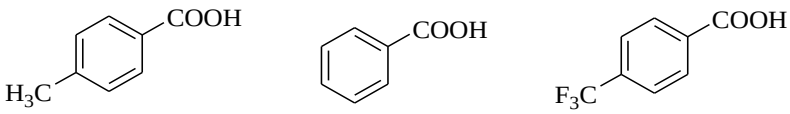
I + H_2, mangkin → **J** ($C_9H_{10}O$)

J + H_2SO_4, dipananakan → **K** (C_9H_8)

(14 markah)

(b) Susun sebatian berikut di dalam setiap kumpulan mengikut keasidan yang meningkat. Beri penjelasan tentang jawapan anda.

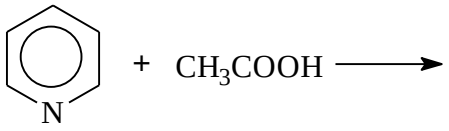
(i) 

(ii) 

(6 markah)

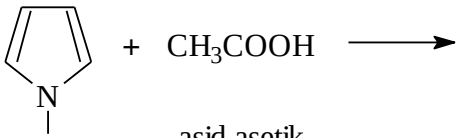
2. (a) Lengkapkan tindak balas asid-bes yang diberikan dan tentukan sama ada bahan tindak balas atau hasil tindak balas yang lebih utama. Terangkan mengapa.

(i)



piridina asid asetik

(ii)



asid asetik

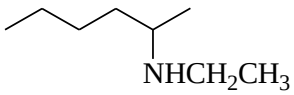
pirol

(8 markah)

(b) Tunjukkan bagaimana N-benzilanilin disintesiskan daripada anilin melalui pengasilan-penurunan.

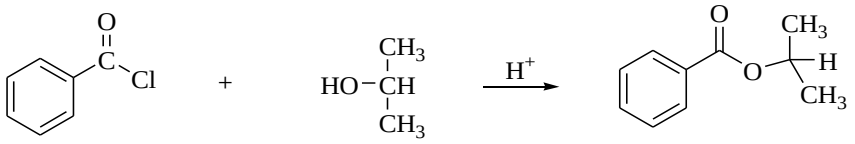
(6 markah)

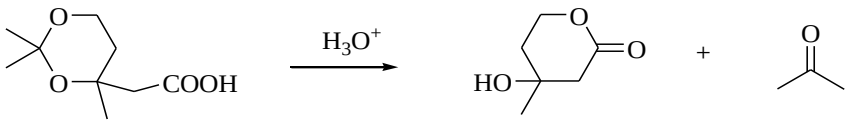
(c) Berikan tiga (3) hasil yang diperoleh apabila amina ditindakbalaskan dengan lebihan iodometana serta disusuli dengan pemanasan menggunakan oksida perak (Penyingkiran Hoffmann). Tentukan hasil utama.

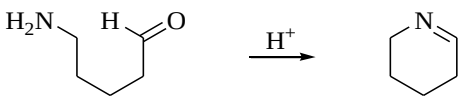


(6 markah)

3 (a) Lukis suatu mechanism langkah demi langkah bagi setiap tindak balas berikut.

(i) 

(ii) 

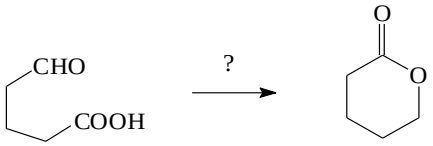
(iii) 

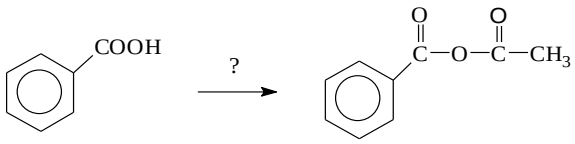
(15 markah)

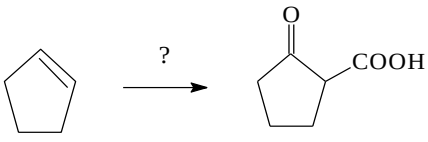
(b) Cadangkan mekanisma bagi tindak balas benzoil klorida (PhCOCl) dengan asid asetik dan tunjukkan struktur anhidrida yang dihasilkan.

(5 markah)

4. (a) Tunjukkan bagaimana anda menyelesaikan sintesis-sintesis berikut dengan penghasilan yang baik.

(i) 

(ii) 

(iii) 

(6 markah)

(b) Nyatakan kesamaan dan perbezaan pada penyerapan IR utama yang mencirikan kumpulan asid karboksilik dan amida.

(4 markah)

(c) Struktur tertier protein dapat dikekalkan melalui pembentukan titian garam yang merupakan interaksi ionik di antara kumpulan positif ammonium dan kumpulan negatif asid. Terangkan bagaimana perubahan pH boleh menjejaskan struktur tertier protein.

(5 markah)

(d) Suatu dekapeptida melalui hidrolisis separa dan menghasilkan beberapa peptida dengan asid amino tertentu seperti yang ditunjukkan di bawah. Tindak balas dekapeptida ini dengan reagen Edman membebaskan PTH-Leu. Apakah turutan untuk dekapeptida ini?

(i)	Pro, Ser	(v)	Glu, Ser, Val, Pro
(ii)	Gly, Gly	(vi)	Glu, Pro, Gly
(ii)	Met, Ala, Leu	(vii)	Met, Leu
(iv)	Gly, Ala	(viii)	His, Val

(5 markah)

5. (a) Dalam makmal, asid α-amino boleh disediakan daripada asid karboksilik. Dengan menggunakan asid karboksilik yang sesuai, tunjukkan dua cara yang boleh digunakan untuk menyediakan valina.

valina

(10 markah)

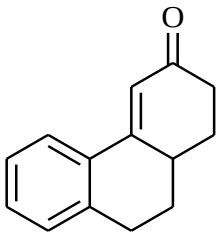
(b) Apakah stereokimia yang dijangkakan untuk hasil sintesis daripada (a)? Lukiskan struktur yang mungkin dalam unjuran Fischer.

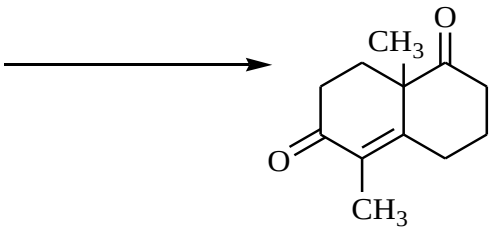
(4 markah)

(c) Tunjukkan bagaimana anda memisahkan L-valina dan D-valina melalui resolusi enzim.

(6 markah)

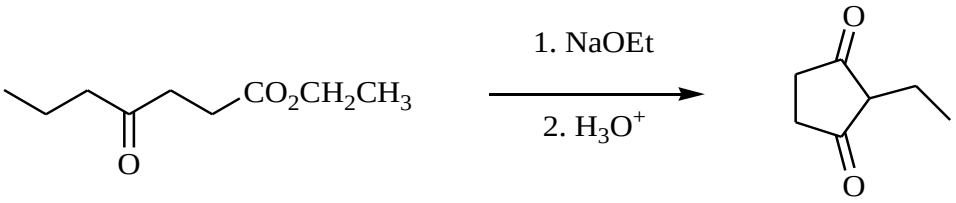
6. (a) Tindak balas Michael dan penambahan aldol intramolekul adalah peringkat dalam penggelangan Robinson. Ramalkan bahan permulaan yang perlu untuk penggelangan Robinson.

(i) **L** + **M** 

(ii) **Q** + **R** 

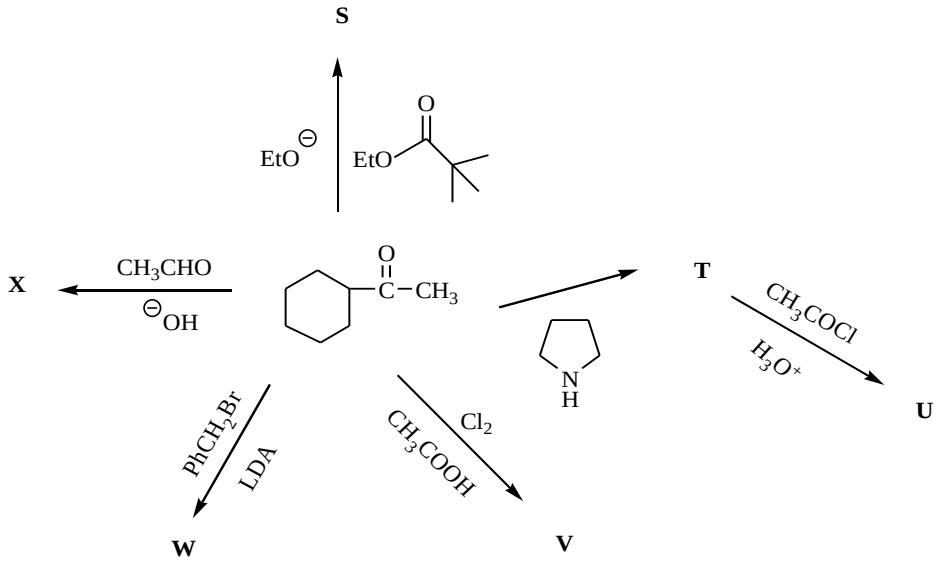
(8 markah)

(b) Tunjukkan dengan terperinci, langkah mekanisma untuk transformasi di bawah;



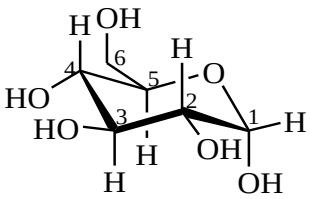
(6 markah)

(c) Berikan struktur **S**-**X** dalam tindak balas di bawah;



(6 markah)

7 (a) Struktur bentuk hemiasetal siklik D-glukosa sebagai konformasi kerusi ditunjukkan di bawah;



(i) Tunjukkan karbon anomerik bagi struktur ini.

(ii) Lukis ikatan β-glukosidik struktur disakarida daripada tindak balas dua molekul D-glukosa.

(iii) Apakah nama tindak balas ini?

(5 markah)

(b) Glukosa sebenarnya wujud sebagai piranosa (enam-gelangan) tetapi bukan sebagai furanosa (lima-gelangan).

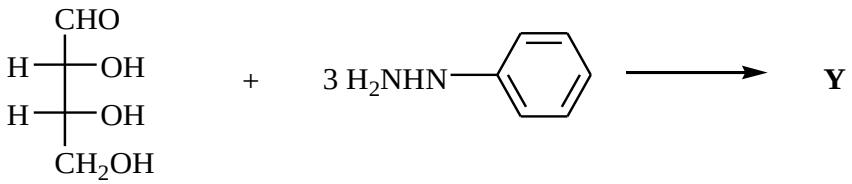
(i) Bagaimana anda boleh menentukan samada metil-β-D-glukosida mempunyai lima- atau enam gelangan?

(ii) Apakah hasil yang didapati daripada penentuan ini?

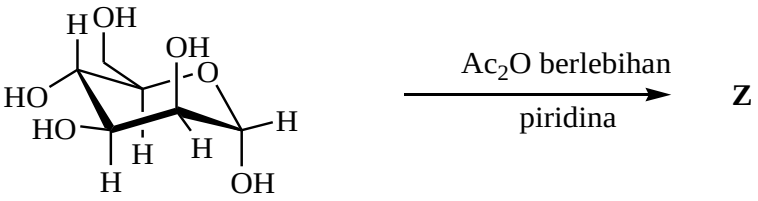
(5 markah)

(c) Lukis struktur **Y** dan **Z**.

(i)



(ii)



(4 markah)

(d) Aldosa **AA** adalah aktif optis. Pengolahan dengan natrium borohidrida menukarkannya kepada aktif optis alditol. Degradasi Ruff pada **AA** memberikan aktif optis **BB** dan degradasi Ruff pada **BB** memberikan aktif optis D-gliseraldehid. Beri struktur dan nama **AA**, **BB** dan alditolnya.

(6 markah)

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