UNIVERSITI SAINS MALAYSIA

Final Examination
2016/2017 Academic Session

May/June 2017

JIK 419 – Advanced Organic Chemistry
[Kimia Organik Lanjutan]

Duration : 3 hours
[Masa : 3 jam]

Please ensure that this examination paper contains **TEN** printed pages before you begin the examination.

Answer **FIVE** questions. You may answer **either** in Bahasa Malaysia or in English, but not a mix of both languages.

All answers must be written in the answer booklet provided.

Each question is worth 20 marks and the mark for each sub question is given at the end of that question.

In the event of any discrepancies in the exam questions, the English version shall be used.

*Sila pastikan bahawa kertas peperiksaan ini mengandungi **SEPULUH** muka surat yang bercetak sebelum anda memulakan peperiksaan ini.*

*Jawab **LIMA** soalan. Anda dibenarkan menjawab soalan **sama ada** dalam Bahasa Malaysia atau Bahasa Inggeris, tetapi campuran antara kedua-dua bahasa ini tidak dibenarkan.*

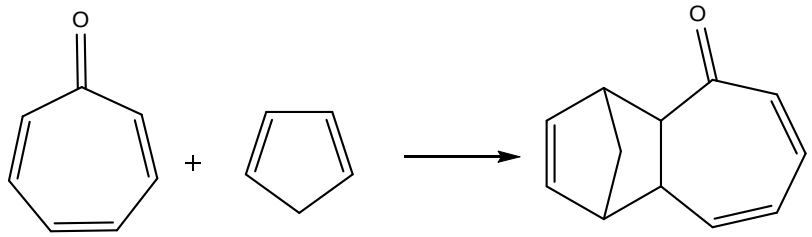
Setiap jawapan mesti dijawab di dalam buku jawapan yang disediakan.

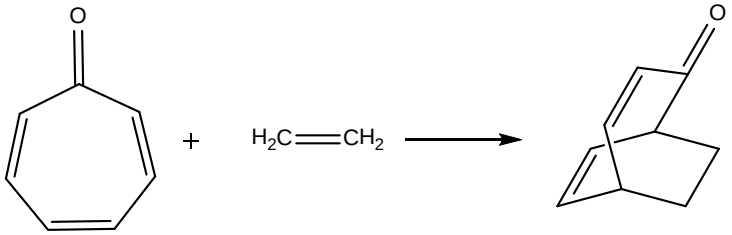
Setiap soalan bernilai 20 markah dan markah subsoalan diperlihatkan di penghujung subsoalan itu.

Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah diguna pakai.

1. (a) Compare the reaction of 2,4,6-cycloheptatrienone with cyclopentadiene to that with ethene.

Bandingkan tindak balas 2,4,6-sikloheptatrienon dengan siklopentadiena dan etena.





(i) Which pericyclic reaction is involved?

Apakah tindak balas perisiklik yang terlibat?

(ii) Why does 2,4,6-cycloheptatrienone use two π electrons in one reaction and four π electrons in the other?

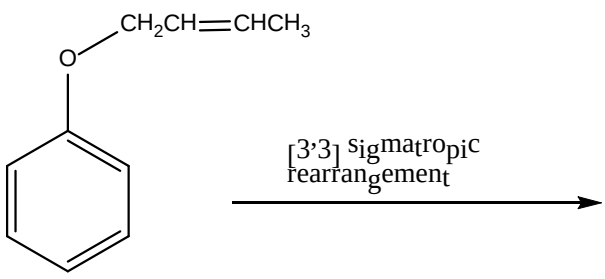
Mengapakah 2,4,6-sikloheptatrienon menggunakan dua π elektron dalam satu tindak balas dan empat π elektron dalam yang lain?

(6 marks/*markah*)

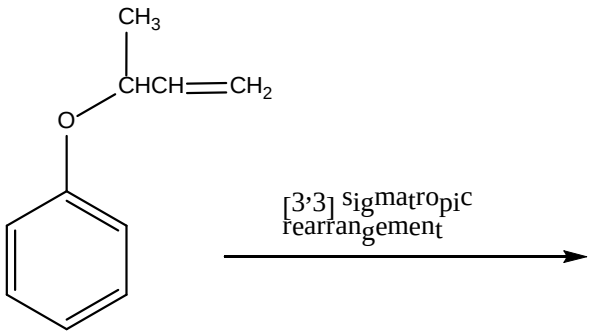
(b) Give the structure of the product of each of the following sigmatropic rearrangements:

Berikan struktur hasil untuk setiap penyusunan semula sigmatropik berikut:

(i)

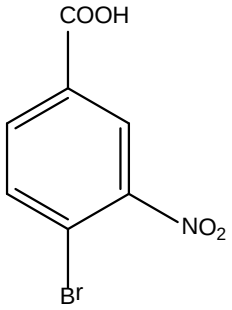


(ii)



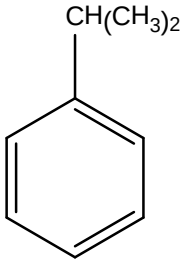
(6 marks/*markah*)

(c) Show how the following compound could be prepared from benzene:
Tunjukkan bagaimana sebatian berikut dapat disediakan daripada benzena:



(8 marks/*markah*)

2. (a) Give the structure of the major product(s) formed when isopropylbenzene reacts with the following reagents:
Berikan struktur hasil/hasil-hasil utama apabila isopropilbenzena bertindak balas dengan reagen-reagen berikut:



Isopropylbenzene

(i) $Br_2/FeBr_3$

(ii) SO_3/H_2SO_4

(iii) $CH_3COCl/AlCl_3$

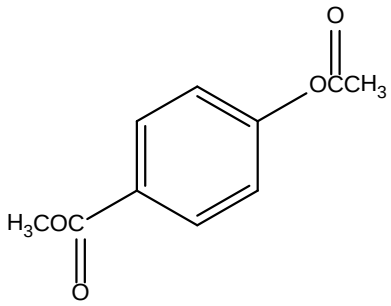
(iv) $CH(CH_3)_2/AlCl_3$

(8 marks/*markah*)

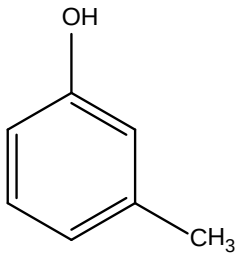
(b) Give the structure of the product(s) obtained from the reaction of each of the following compounds with $Br_2/FeBr_3$.

Berikan struktur hasil/hasil-hasil yang diperoleh dari tindak balas setiap sebatian berikut dengan $Br_2/FeBr_3$:

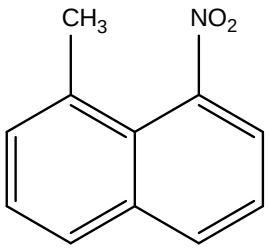
(i)



(ii)



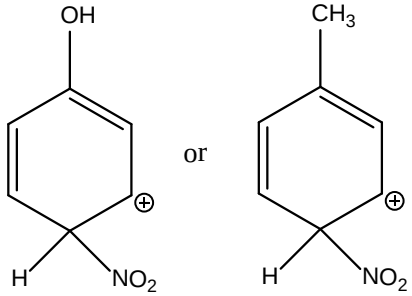
(iii)



(6 marks/*markah*)

(c) Which of the following carbocation intermediate is more stable? Explain your answer using resonance contributors.

Bahan perantaraan karbokation manakah antara berikut yang lebih stabil? Terangkan jawapan anda dengan menggunakan penyumbang resonans.

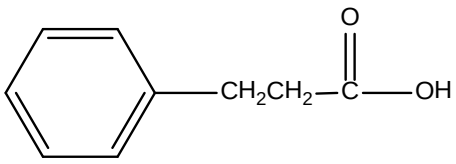


(6 marks/*markah*)

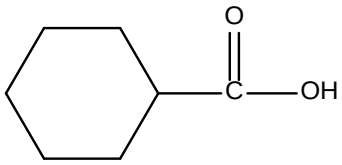
3. (a) Show how you would use the malonic ester synthesis to make the following compounds:

Tunjukkan bagaimana anda menggunakan sintesis ester malonik untuk menyediakan sebatian-sebatian berikut:

(i)



(ii)

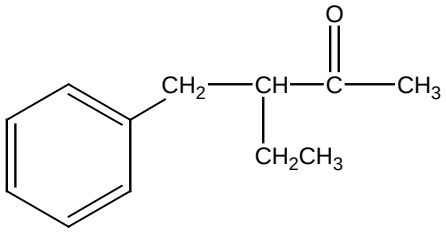


(10 marks/*markah*)

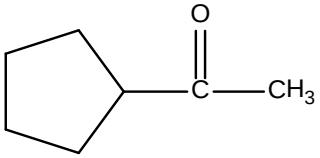
(b) Show how you would use the acetoacetic ester synthesis to make the following compounds.

Tunjukkan bagaimana anda menggunakan sintesis ester asetoasetik untuk menyediakan sebatian-sebatian berikut:

(i)



(ii)



(10 marks/*markah*)

4. (a) Sugar **X** is known to be a D-aldohexose. On oxidation with HNO_3, **X** gives an optically inactive aldaric acid. When **X** is degraded to an aldopentose, oxidation of the aldopentose gives an optically active aldaric acid. Determine the structure of **X** with adequate explanation.

*Gula **X** dikenali sebagai D-aldoheksosa. Pada pengoksidaan dengan HNO_3, **X** memberikan asid aldarik tidak beraktif optik. Apabila **X** terdegradasi ke aldopentosa, pengoksidaan aldopentosa memberikan asid aldarik beraktif optik. Tentukan struktur **X** dengan memberi penjelasan yang mencukupi.*

(10 marks/*markah*)

(b) Aldose **E** is optically active, but treatment with sodium borohydride converts it to an optically inactive alditol. Ruff degradation of **E** gives **F**, whose alditol is optically inactive. Ruff degradation of **F** gives optically active D-glyceraldehyde. Give the structures and names of **E** and **F** as well as their optically inactive alditols.

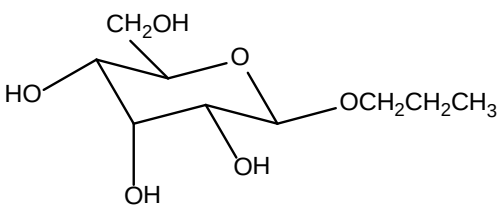
*Aldosa **E** adalah beraktif optik, tetapi pengolahan dengan natrium borohidrida menukarkannya kepada suatu alditolnya tidak beraktif optik. Degradasi Ruff terhadap **E** membentuk **F**, yang mana alditol adalah tidak beraktif optik. Degradasi Ruff terhadap **F** membentuk D-gliseraldehid yang beraktif optik. Berikan struktur dan nama **E** dan **F** serta alditol-alditolnya yang tidak beraktif optik.*

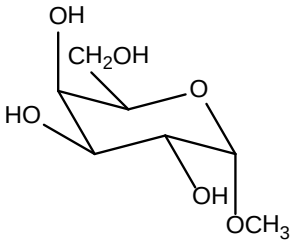
(10 marks/*markah*)

5. (a) Name the following compounds and indicate whether each is a reducing sugar or a non-reducing sugar.

Namakan sebatian-sebatian berikut dan nyatakan sama ada setiap daripadanya ialah gula penurun atau gula bukan penurun.

(i)



(ii) 

(6 marks/*markah*)

(b) Define each of the following terms and give an example.

(i) Erythro

(ii) Threo

Berikan definisi bagi setiap istilah-istilah berikut berserta satu contoh.

(i) Eritro

(ii) Threo

(4 marks/*markah*)

(c) The isoelectric point (pI) of histidine is pH 7.6. Draw the structures of the major forms of histidine at:

Takat isoelektrik (pI) untuk histidina ialah pH 7.6. Lukiskan struktur-struktur bentuk utama histidina pada:

(i) pH = 1

(ii) pH = 4

(iii) pH = 7.6

(iv) pH = 11

Explain briefly why the nitrogen in the histidine ring is a weaker base than the α-amino group.

Mengapakah nitrogen di gelang histidina adalah bes yang lebih lemah berbanding kumpulan α-amino? Jelaskan.

(10 marks/*markah*)

6. (a) Using solution-phase techniques, show how you would synthesise Ala-Val and then combine it with Ile-Leu-Phe to produce Ile-Leu-Phe-Ala-Val.

Dengan menggunakan teknik fasa-larutan, tunjukkan bagaimana anda mensintesis Ala-Val dan kemudian menggabungkannya dengan Ile-Leu-Phe untuk menghasilkan Ile-Leu-Phe-Ala-Val.

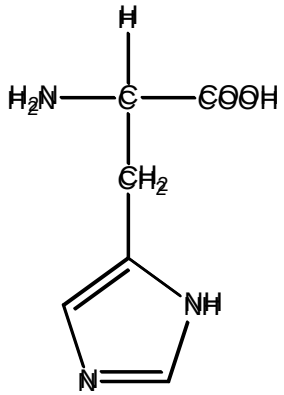
(15 marks/*markah*)

(b) Show how you would use the Strecker synthesis to produce aspartic acid.

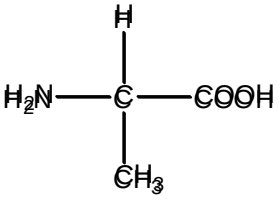
Tunjukkan bagaimana anda menggunakan sintesis Streckar untuk menghasilkan asid aspartik.

(5 marks/*markah*)

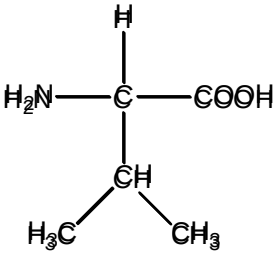
List of Amino Acids



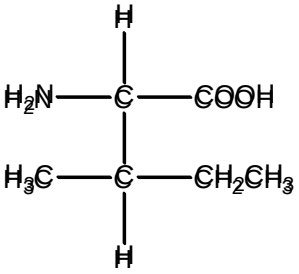
Histidine (His)



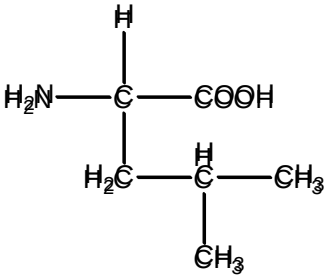
Alanine (Ala)



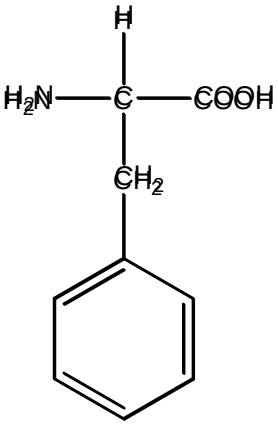
Valine (Val)



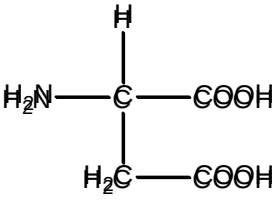
Isoleucine (Ile)



Leucine (Leu)

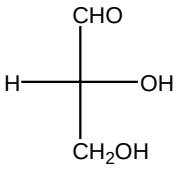


Phenylalanine (Phe)

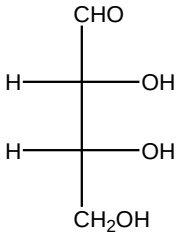


Aspartic Acid (Asp)

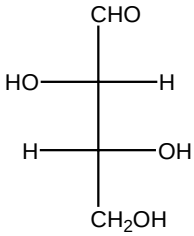
List of Sugars



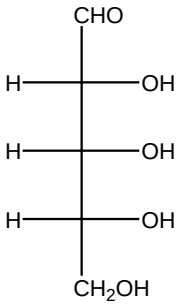
D-(+)-Glyceraldehyde



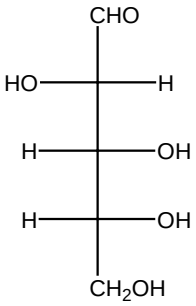
D-(-)-Erythrose



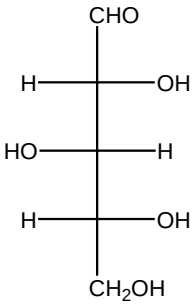
D-(-)-Threose



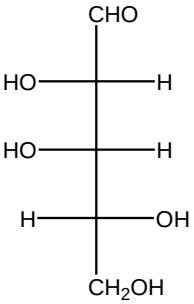
D-(-)-Ribose



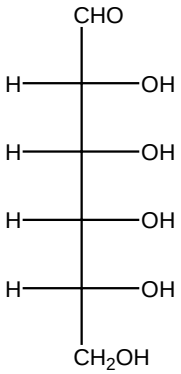
D-(-)-Arabinose



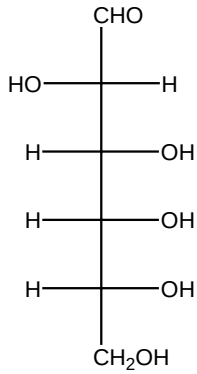
D-(+)-Xylose



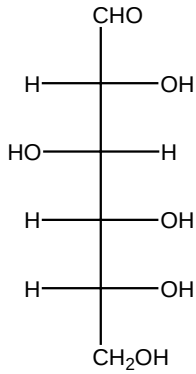
D-(-)-Lyxose



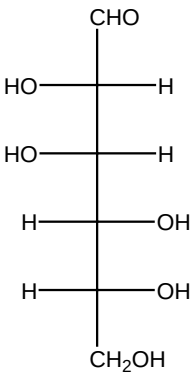
D-(+)-Allose



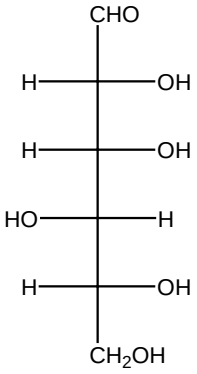
D-(+)-Altrose



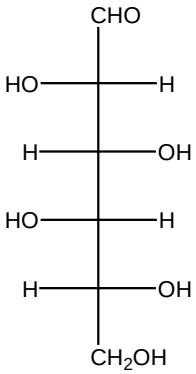
D-(+)-Glucose



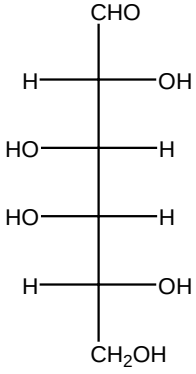
D-(+)-Mannose



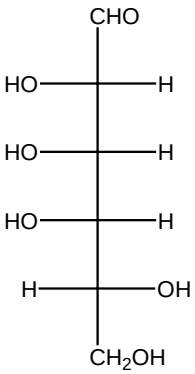
D-(-)-Gulose



D-(-)-Idose



D-(+)-Galactose



D-(+)-Talose

- oooOooo -