(a) (i) Compounds 2 and 3 are aromatic. Compound 1, pentalene, has 8 pi-electrons in a contiguous, cyclic set of p-orbitals perpendicular to the plane of the ring – it is therefore anti-aromatic according to the definition of Hückel (4n pi electrons, n = 2). It is highly unstable and dimerises at -100 °C. Compound 2, azulene, has 10 pi-electrons in a contiguous, cyclic set of p-orbitals perpendicular to the plane of the ring – it is therefore aromatic according to the definition of Hückel (4n+2 pi electrons, n = 2). It is a beautiful blue liquid with a significant dipole moment. Compound 3, phenanthrene, has 14 pi-electrons in a contiguous, cyclic set of p-orbitals perpendicular to the plane of the ring – it is therefore aromatic according to the definition of Hückel (4n+2 pi electrons, n = 3). It is a white crystalline solid.

Application of concepts from notes/lectures. We did not discuss these specific compounds in the course. Anticipated marking scheme: 1 mark for correct compounds, 1 mark for correct explanation based on Hückel’s rule.

(2 marks)

(ii) The pKa of propene (pKa ~44) is relatively low (compared to a saturated hydrocarbon such as propane, pKa ~50) due to allylic resonance of the resulting carbanion (conjugate base) upon deprotonation. The pka of cyclopropene might therefore have been expected to be similar. However, the cyclopropenyl anion is a 4 pi electron ring structure with a contiguous, cyclic set of p-orbitals perpendicular to the plane of the ring – it is therefore anti-aromatic according to the definition of Hückel (4n pi electrons, n = 2). Formation of this anion is therefore unfavourable and hence the unusually high pKa value of ~61.

The pKa of 1,4-pentadiene (pKa ~30) is relatively low (compared to a saturated hydrocarbon such as pentane, pKa ~50) due to double allylic resonance of the resulting carbanion (conjugate base) upon deprotonation. The pka of cyclopentadiene might therefore have been expected to be similar. However, the cyclopentadienyl anion is a 6 pi electron ring structure with a contiguous, cyclic set of p-orbitals perpendicular to the plane of the ring – it is therefore aromatic according to the definition of Hückel (4n+2 pi electrons, n = 1). Formation of this anion is therefore favourable and hence the unusually low pKa value of ~16.
Application of concepts from notes/lectures. We did not discuss these pKa’s in the course but I did present the difference in ease of deprotonation of cyclopropyl vs. cyclopropenyl phenyl ketones. Anticipated marking scheme: 1 mark for correct identification of cyclopropenyl anion conjugate base as anti-aromatic, 1 mark for identification of cyclopentadienyl anion conjugate base as aromatic (based on Hückel’s rule).

(2 marks)

(iii) The longest C-C bonds are found in cyclohexane (5) – standard C-C single bonds ~154 pm. The shortest is found in cyclooctatetraene (6) ~133 pm, which is typical of a standard C=C double bond. The C-C bonds in benzene (4) are all the same length and intermediate between typical single and double bond values, ~139 pm. This is because of pi-electron delocalisation due to the aromatic nature of benzene. Cyclooctatetraene (6) is non-aromatic; it would be anti-aromatic (8 pi-electrons, 4n where n = 2) if planar but it adopts a ‘tub’ shape to avoid this and thus has alternating bond lengths close to typical for single and double C-C bonds.

Application of concepts from notes/lectures. We did not explicitly discuss the bond lengths in cyclooctatetraene but did discuss that it was non-planar and did discuss the bond lengths in benzene. Anticipated marking scheme: 1 mark for correct answer, 1 mark for explanation of situation for cyclooctatetraene. Will accept the latter as having both the shortest and longest bonds if a reasonably logical argument is presented.

(2 marks)

(b) The expected major product of the reaction is:

Both Et and OMe substituents are o/p-directing, but the ether has the dominant/stronger directing influence because it results from conjugation of the oxygen lone pair as opposed to C-H/C-C bond sigma-conjugation. Mechanism of S₂Ar reaction also required – see below.
Problem Solving – this specific reaction was not discussed in lectures although electrophilic nitrination was. Anticipated marking scheme: 2 marks for correct product, 1 mark for $\text{NO}_2^+$ (nitronium ion) as electrophile; 3.5 marks for correct arrows for the reaction (standard $S_EAr$ mechanism) including Wheland intermediate resonance forms and associated explanation of regioselectivity.

(c) The expected major product of the reaction is:

The diazonium salt reacts as an electrophile at the terminal nitrogen of the diazonium function; the phenol reacts as a nucleophile through the para-position (predominantly, mainly for steric reasons) – a diazo dye is formed. The reaction is an $S_EAr$ reaction of the phenol.
Problem Solving – this specific reaction was not discussed in lectures although diazo dye formation was. Anticipated marking scheme: 3 marks for correct product (para-substituted phenol and (E) configured N=N bond), 3.5 marks for correct arrows for the reaction (standard S<sub>Ar</sub> mechanism) including Wheland intermediate resonance forms and associated explanation of regioselectivity and steric preference for (E) N=N bond.

(6.5 marks)