CHEM40006: Reactivity at Carbon Centres - Aromatic Chemistry

TUTORIAL PROBLEMS

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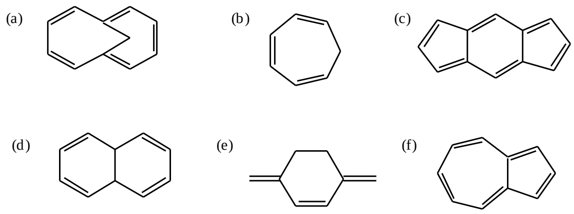
1. Which of the following neutral hydrocarbons display aromatic character?

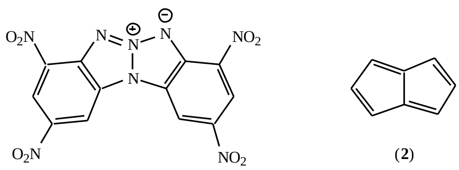
   For those which do, state the number of π-electrons participating in the aromaticity and sketch a predicted 1H NMR spectrum.



2. Professor G. Olah (chemistry Nobel prize winner 1995) and his collaborators exposed benzene to the 'super-acid' system HF-SbF_5 in the non-nucleophilic solvent SO_2ClF-SO_2F_2 in an NMR tube and observed a new ^{1}H NMR spectrum: δ 5.69 (2H), 8.22 (2H), 9.42 (1H) and 9.58 (2H) ppm. Propose a structure for this species.

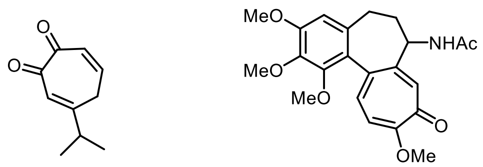
3. Thermal stability is a highly desireable property for explosive materials as it helps to safeguard weapons from accidental fire or sabotage. It is especially important for the warheads of guided missiles which become very hot due to air-resistance at high velocity. 2,4,8,10-Tetranitrobenzotriazolo[1,2-a]benzotriazol-6-ium inner salt (**1**) commonly known as y-tacot, was developed in the 1960's as a high melting point (mp 400°C) 'aromatic' explosive. Draw an orbital representation of the core azapentalene unit of y-tacot showing the orbitals involved in the aromaic system and the number of participating p-electrons from each ring atom.

   Is the 'parent' pentalene system (**2**) aromatic?



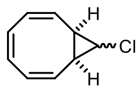
(1)

4. The molecule on the left is a natural product of the Taiwanese cedar called hinokitiol; it enolises readily to give a much more thermodynamically stable tautomer. Draw this tautomer and explain why it is particularly stable. The molecule on the right is the natural product colchicine, used to treat gout. Suggest why its ketone group undergoes particularly facile protonation.

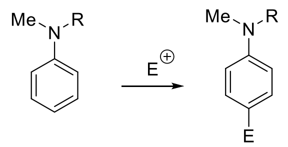


hinokitiol colchicine

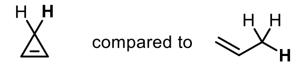
5. Suggest why the halogen-metal exchange reaction of the below cyclopropylchloride might be particularly favourable?



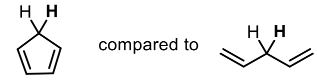
6. Explain why the following reaction goes rapidly when R = Me but very slowly when R = *t*-Bu.



7. The pKa values of the indicated protons in two pairs of molecules are shown below. Rationalise the differences observed.

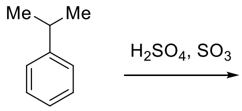


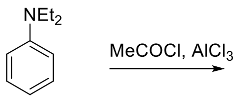
pKa ~61 pKa ~44

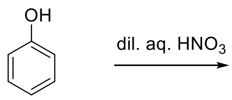


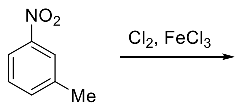
pKa ~16 pKa ~30

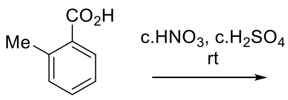
8. Draw the expected major products of the following reactions:

(a)


(b)


(c)


(d)


(e)


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