1 / VOL. 2, NO. 6 ISSN 1430-4171
THE CHEMICAL EDUCATOR http://journals.springer-ny.com/chedr

S 1430-4171 (97) 06152-3

Generation and Observation of Cyclopentadienyl Anion: A Negatively Charged Aromatic Molecule

Instructions for Students

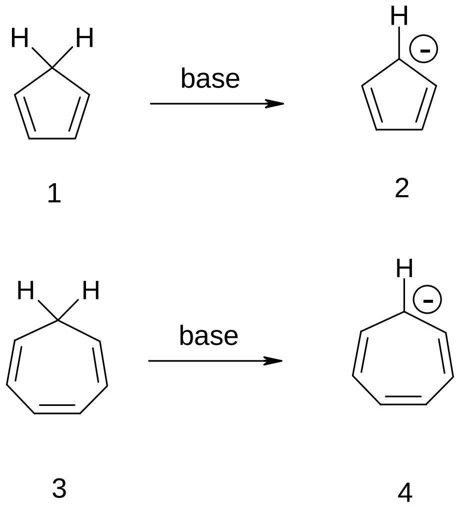
Gary W. Breton
Berry College, Mount Berry, GA 30149–5016; gbreton@berry.edu

Introduction

Aromaticity is a special property of cyclic molecules composed of a fully conjugated planar pi system containing a proper number of electrons within the pi circuit (which corresponds to those numbers satisfying the formula $4n+2$, where n is any integer [the Huckel rule]) [1, 2]. Compounds satisfying these prerequisites are observed to be especially stabilized relative to open–chain polyene reference compounds containing the same number of double bonds [1]. This general description of aromaticity encompasses not only neutral molecules (such as benzene, furan, pyrrole, etc.), but also those that are charged (anionic, cationic, multiply charged, or dipolar) [1–3]. Indeed, the strength of the theory of aromaticity is reflected in its ability to predict the unusual stability of such charged organic species. Aromaticity expresses itself in many forms, including (1) ease of generation of aromatic molecules from nonaromatic precursors, (2) generally low reactivity of aromatic systems, (3) tendency of aromatic molecules to undergo substitution reactions rather than addition, and (4) diamagnetic ring current effects in the ^1H NMR spectra [1].

In direct contrast to the aromatic stabilization of compounds with $4n+2$ pi electrons, it has been observed that cyclic compounds that contain a fully conjugated planar pi system composed of 4n electrons are *destabilized* relative to the corresponding open–chain polyene reference compound. Such molecules are said to be 'anti–aromatic' [1]. However, those compounds that are conformationally able to avoid planarity (e.g., cyclooctatetraene) evade the destabilization due to anti–aromaticity, and are simply referred to as 'non–aromatic' [1].

Consider the two cyclic polyene compounds cyclopenta–1,3–diene (**1**) and cyclohepta–1,3,5–triene (**3**). Diene **1** has a pK_a value of approximately 15 [4], while **3** has a pK_a



(1)

value of approximately 40 [5]. The large difference in pK_a values between the two indicates that anion **2** is more stable than anion **4**. Because of the relatively low pK_a of compound **1**, it is possible for us to generate anion **2** in a laboratory class, and obtain its ^1H NMR spectrum. We may then compare its spectrum to those of some representative aromatic, anti–aromatic and non–aromatic compounds and attempt to explain its unusual stability.

Experimental Procedure

Cautions. All manipulations should be performed in a manner so as to minimize physical contact with the chemicals involved, and in an adequate hood to ensure proper ventilation (especially during generation of the flammable H_2 gas). Sodium hydride is a flammable solid, and special precautions should be taken to prevent its contact with water. However, in our experience, we have encountered no difficulties weighing out and handling this compound in air when working in an expedient manner. Dimethyl sulfoxide should be handled carefully as it is readily absorbed through the skin.

*Formation of Anion **2***

Preheat a sand bath to 90 EC. Weigh into a clean dry NMR tube 10 mg (0.42 mmol) of NaH [6]. Add 0.5 mL of DMSO-d_6 via a Pasteur pipet and affix to the top of the NMR tube a drying tube which consists of a short piece of amber rubber tubing with a glass wool plug supporting a short column of Na_2SO_4. Place the apparatus into the preheated sandbath so that approximately one quarter of the solvent volume is submerged. Set the tube at an angle to allow for generation of a convenient convection current within the tube which will act to agitate the reaction mixture. The evolution of H_2 gas should be immediately observed upon mixture of the compounds. Once gas evolution has ceased (30–40 min), remove the apparatus from the bath and allow it to cool to room temperature. If time permits, obtain a ^1H NMR spectrum of the resulting clear, pale yellow solution. No signals other than those of residual monoprotio–dimethylsulfoxide (at * 2.50) should be present. To this solution CAREFULLY add 30 µL (0.43 mmol, d = 0.95 g/mL) of freshly 'cracked' cyclopentadiene (see below) via syringe. Shake the solution well for 5 min, and obtain a ^1H NMR spectrum. Finally, add to the NMR tube, via syringe, 32 µL (0.42 mmol) of CF_3CO_2H. Shake this solution, note any color change, and obtain the ^1H NMR spectrum of the resulting compound.

Cracking Cyclopentadiene

Cyclopentadiene is generated by heating the dimer of the compound ("dicyclopentadiene") which thermally reverts the dimer to the monomer. This process is called "cracking". To a 100–mL round-bottomed flask add 10 mL of dicyclopentadiene. Fit the flask with the necessary glassware for a fractional distillation (including a fractionating column), and heat the dimer to a vigorous boil. A distillate (**1**) will collect at a still head temperature of 40–45 EC which should be collected in an ice–cooled flask (to avoid thermal redimerization) to a volume of 3 mL. Keep this sample cold until ready for use.

Questions Concerning the Experiment

1. Draw all of the resonance forms contributing to the structure of aromatic anion **2**. Repeat the process for the cycloheptatrienyl anion **4**. Which has the greatest number of resonance forms?

*Generally, larger numbers of resonance forms indicate greater stability of the hybrid forms. However, the greater acidity of **1** relative to **3** indicates that anion **2** is considerably more stable than **4** despite this discrepancy in the number of resonance forms.*

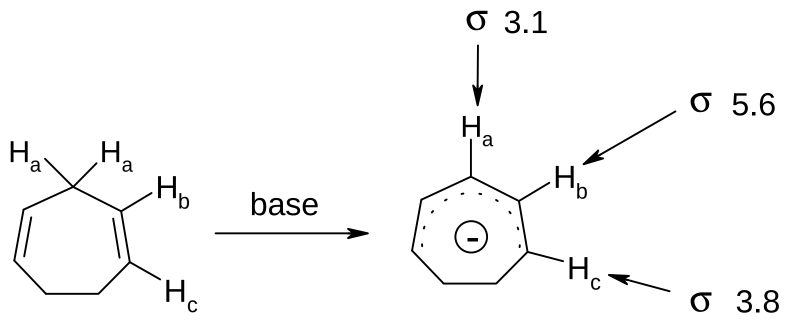
2. Use the prerequisites for aromaticity discussed in the Introduction to assess the potential for aromaticity of each of the two anions. Which of the two anions is aromatic? Which is more important, therefore, when assessing stability, aromaticity or number of resonance forms?

3. Anion **4** adopts a non-planar conformation. Why?

4. Look up, and report, the ^{1}H NMR spectrum of benzene. What characteristic do the NMR's of benzene and **2** share? Explain the significance of the lack of coupling of the protons on the rings.

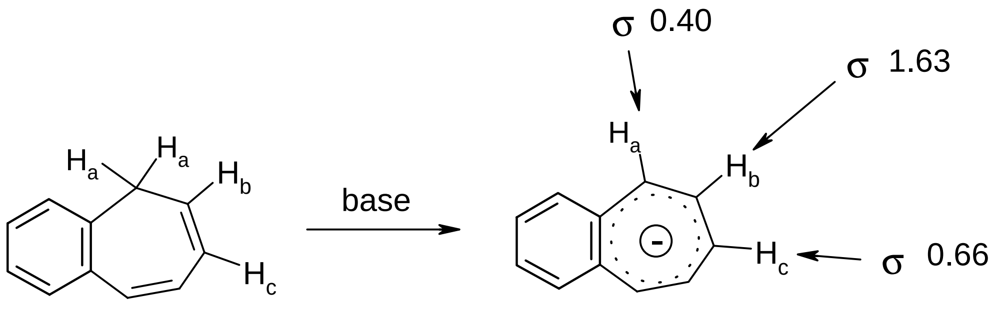
The chemical shifts of the ring protons for benzene and anion **2** *are quite different. With sufficient background information, and discussion, we may discern why this is so:*

5. Consider the NMR data reported below for the non-aromatic anion **5** [*7*]. Draw all contributing resonance forms for **5**. Which carbons bear the negative charge in the hybrid form. What effect does the negative charge have on the chemical shift of the attached protons relative to the protons on the uncharged carbons?



5

6. Consider the NMR data reported below for the anti–aromatic anion **6** [*8*]. Note that **6** is considered to be anti–aromatic because of the 8 electrons in its pi circuit and its essentially planar ring that is enforced by its fusion to the planar benzene ring. Draw all contributing resonance forms within



6

S 1430-4171 (97) 06152-3

the seven–membered ring of anion **6**. Which carbons bear the negative charge in the hybrid form? Note that all of the signals for the protons of anion **6** are significantly upfield of the proton signals of anion **5**. This shielding effect results from the paramagnetic ring current of the anti–aromatic ring. This is the opposite of the deshielding effect that the aromatic benzene ring has on its protons which shifts them downfield of the typical chemical shift for vinyl protons.

7. Using the information derived from questions 5 and 6 account for the chemical shift of the protons on anion **2** relative to those of benzene.

8. What product is formed from the reaction of CF_3CO_2H with anion **2**? Suggest a mechanism for the reaction. Assign the signals in the ^{1}H NMR to the protons on the product.

Acknowledgment

Acknowledgment is made to generous financial support provided by Berry College. Acknowledgment is also made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

References and Notes

1. (a) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry,* 3rd ed.; Harper and Row: New York, 1987; pp 35–51. (b) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part A*, 3rd ed.; Plenum Press: New York, 1993; pp 499–538.

2. Beyer, H.; Walter, W. *Organic Chemistry*, 22nd ed.; Albion Publishing Ltd.: Chichester, 1997; pp 655–659.

3. Reference 2, pp 647–648.

4. Streitweiser, A.; Langworthy, W. C.; Brauman, J. I. *J. Am. Chem. Soc.* **1963**, *85*, 1761–1763.
5. Taken as the average of values from reference 4 and Dauben, H. J.; Mahmoud, R. R. *J. Am. Chem. Soc.* **1963**, *85*, 3041–3042.

6. The sodium hydride, which was obtained as a 60% dispersion in mineral oil (Aldrich), should be rinsed several times with hexane prior to its use to remove the oil.

7. Bates, R. B.; Deines, W. H.; McCombs, D. A.; Potter, D. E. *J. Am. Chem. Soc.* **1969**, *91*, 4608.

8. Staley, S. W.; Orvedal, A. W. *J. Am. Chem. Soc.* **1973**, *95*, 3382–3384.