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Laboratories and Demonstrations

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

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The study of charged aromatic species greatly enhances discussions of the theory of aromaticity. The conveniently low acidity of cyclopentadiene (pK_a = 15) affords the opportunity to generate the aromatic cyclopentadienyl anion in an organic laboratory class. This experiment describes the preparation of a solution of deuterated dimethylsulfinyl anion in an NMR tube, followed by the addition of freshly prepared cyclopentadiene. The ^{1}H NMR spectrum of the resulting aromatic anion is compared with that of the isoelectronic (but uncharged) benzene, and contrasted with the spectra of several nonaromatic and antiaromatic compounds. Treatment of the anion with an equivalent of trifluoroacetic acid quantitatively affords cyclopentadiene.

Indeed, the strength of the theory of aromaticity is reflected in its ability to predict the unusual stability of such charged organic species.

Introduction

Aromaticity is a special property of cyclic molecules composed of a fully conjugated, planar π system containing a proper number of electrons within the π circuit (which

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corresponds to those numbers satisfying the formula $4n + 2$, where n is any integer [the Hückel rule]) [1, 2]. Compounds satisfying these prerequisites are observed to be especially stable 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: (a) ease of generation of aromatic molecules from nonaromatic precursors; (b) generally low reactivity of aromatic systems; (c) tendency of aromatic molecules to undergo substitution, rather than addition, reactions; and (d) diamagnetic ring current effects in the ^{1}H NMR spectra [1].

The contrast in the acidities of cyclopenta-1,3-diene (**1**) and cyclohepta-1,3,5-triene (**3**) is a remarkable illustration of aromaticity (Scheme 1).

Diene **1** has a pK_a of approximately 15 [4], while **3** has a pK_a of approximately 40 [5]. The difference between the two may be attributed to the formation of a stabilized aromatic anion (**2**) from **1**, and a nonaromatic anion (**4**) from **3**. Deprotonation of **1** gives a 6-electron aromatic π system akin to that of the quintessential aromatic compound, benzene. Deprotonation of **3**, however, affords an 8-electron π system. This number of electrons satisfies the Hückel formula $4n$, where n is any integer. In direct contrast to the stability of aromatic compounds with $(4n + 2)$ π electrons, it has been observed that cyclic compounds that contain a fully conjugated, planar π system composed of $4n$ electrons are *destabilized* relative to the corresponding open-chain polyene reference compounds. Such molecules are said to be antiaromatic [1]. However, those compounds that are conformationally able to avoid planarity (e.g., **4**, cyclooctatetraene) evade the destabilization due to antiaromaticity, and are simply referred to as nonaromatic [1].

The relatively low pK_a of **1** affords the opportunity to generate **2** in a laboratory class, to obtain its ^{1}H NMR spectrum, and to interpret the observed results in terms of a negatively charged aromatic system. We perform this experiment in our advanced organic chemistry course to coincide with a detailed study of aromaticity in lecture. While the generation of **2** is commonly performed in laboratory courses as part of the synthesis of ferrocene, it is typically done without observing it by NMR [6]. Our

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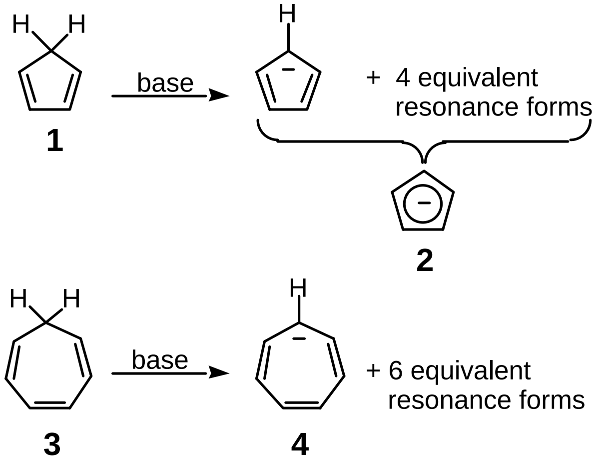

Scheme 1

SCHEME 1. AROMATICITY CONTRAST IN THE ACIDITIES OF CYCLOPENTA-1,3-DIENE (**1**) AND CYCLOHEPTA-1,3,5-TRIENE (**3**).

procedure affords a straightforward microscale approach to the generation of **2** in an apparatus (NMR tube) and medium (DMSO-d_6) directly amenable to its study by ^{1}H NMR spectroscopy. This experiment complements previously published experiments in which the aromatic tropylium cation is generated and investigated by ^{1}H NMR [7].

Experimental Procedure

Precautions

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 when generating 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 Cyclopentadienyl Anion

NaH (10 mg, 0.42 mmol) was weighed into a tared, oven-dried NMR tube, and 0.5 mL of DMSO-d_6 was added via a Pasteur pipet [8]. A drying tube, consisting of a short piece of amber rubber tubing with a glass-wool plug supporting a short column of

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Na_2SO_4, was fixed to the top of the tube, and the apparatus was placed in a preheated sand bath at 90 °C so that approximately one-quarter of the solvent volume was submerged. Setting the tube at a slight angle allowed for generation of a convenient convection current that adequately agitated the reaction mixture. The evolution of H_2 gas was observed immediately upon mixing the compounds. Once gas evolution had ceased (30–40 min), the apparatus was removed from the bath and allowed to cool to room temperature. A ^{1}H NMR spectrum of the resulting clear, pale-yellow solution may be obtained at this point (if time permits) to demonstrate the absence of any signals other than those of residual CD_3SOCHD_2 (Figure 1a). To this solution was **carefully** added 30 μL (d = 0.95 g/mL) of freshly cracked cyclopentadiene (see below) via syringe, and the contents were well shaken for 5 min. The color of the solution turned from yellow to dark green. A ^{1}H NMR spectrum (Figure 1b) of **2** was obtained (60 MHz): δ 5.35 (s).

After obtaining the spectrum (the solution typically turns brown by this time), 30 µL of CF_3CO_2H was added to the NMR tube via syringe. The solution immediately lightened in color. A ^{1}H NMR spectrum (Figure 1c and Figure 2) revealed the presence of cyclopentadiene (**1**) (60 MHz): δ 6.25 (m, vinyl protons, 4H), 2.86 (s, CH_2, 2H).

Cracking Cyclopentadiene

Dicyclopentadiene (10 mL) was added to a 100-mL round-bottom flask. The flask was fitted with glassware for a fractional distillation, and the dimer heated to a vigorous boil. Approximately 3 mL of **1** from the fraction that distilled from 40–45 °C was collected in an ice-cooled collection flask (to avoid thermal redimerization), and was used immediately.

Discussion

Sodium hydride reacts with DMSO at elevated temperatures to afford a solution of dimethylsulfinyl anion. Cyclopentadiene is quantitatively deprotonated under these conditions to afford anion **2,** which is readily observed in the ^{1}H NMR spectrum as a singlet. The spectrum is discussed with the class in terms of the chemical equivalence of the protons, and the observed chemical shift.

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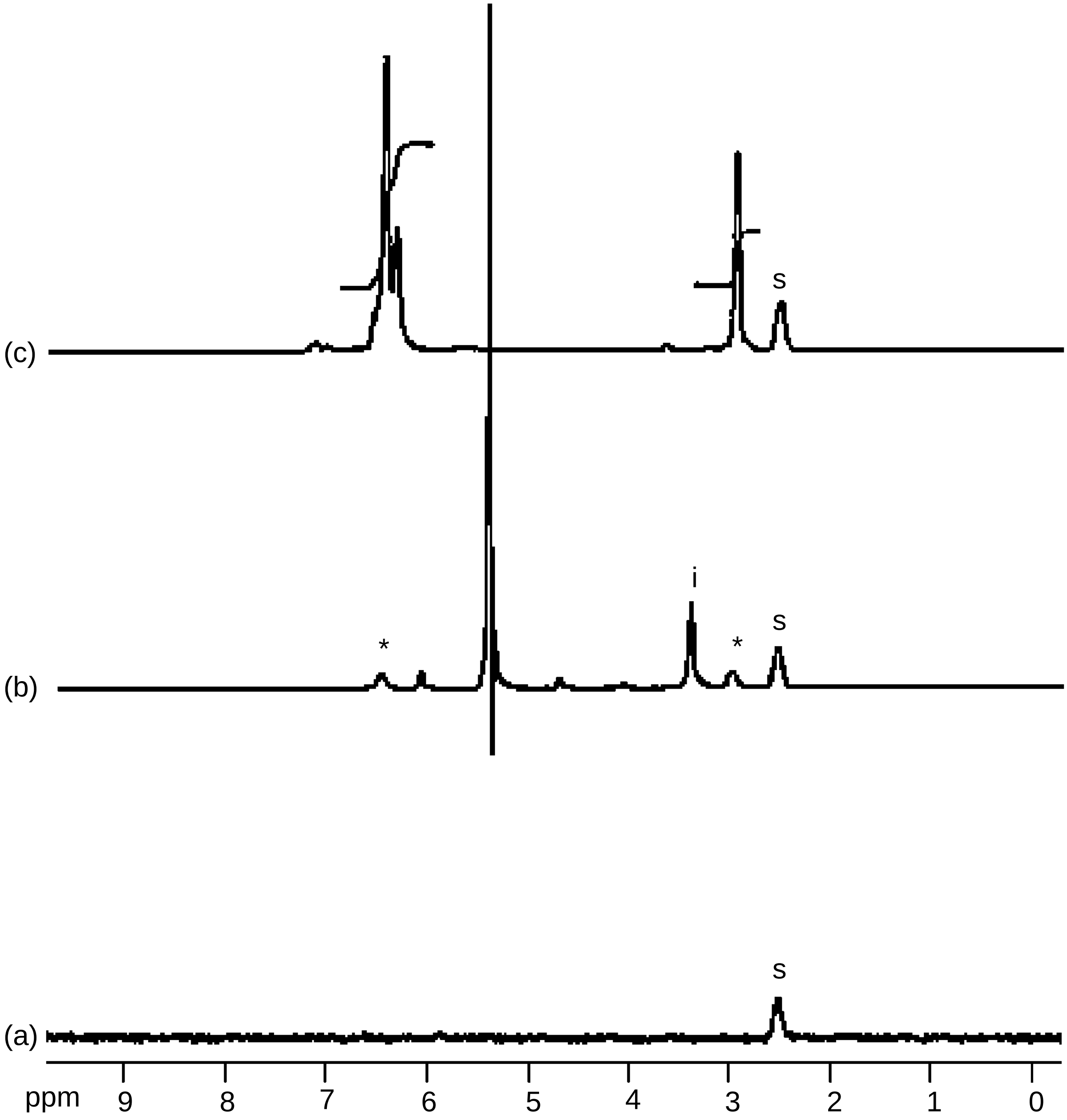

FIGURE 1. 60 MHz ^{1}H NMR SPECTRA IN DMSO–D_6. (A) SOLUTION OF DIMETHYLSUFINYL ANION BEFORE THE ADDITION OF CYCLOPENTADIENE. RESIDUAL CD_3SOCHD_2 IS DESIGNATED WITH AN “S”. (B) AFTER ADDITION OF CYCLOPENTADIENE TO THE ANION SOLUTION. THE SHARP SINGLET AT 5.35 PPM IS THAT OF AROMATIC ANION **2**. THE STARRED SIGNALS (*) BELONG TO RESIDUAL CYCLOPENTADIENE. THE SIGNAL MARKED WITH AN “I” IS AN UNKNOWN IMPURITY THAT WAS *UNIQUE TO THIS SAMPLE ONLY*. IT APPEARED NOT TO INTERFERE WITH THE SUBSEQUENT PROTONATION STEP. (C) RESULTING SOLUTION OF CYCLOPENTADIENE AFTER ADDITION OF AN EQUIMOLAR AMOUNT OF CF_3CO_2H TO THE NMR SAMPLE IN (B). NOTICE THAT NO **2** REMAINS IN THE SPECTRUM.

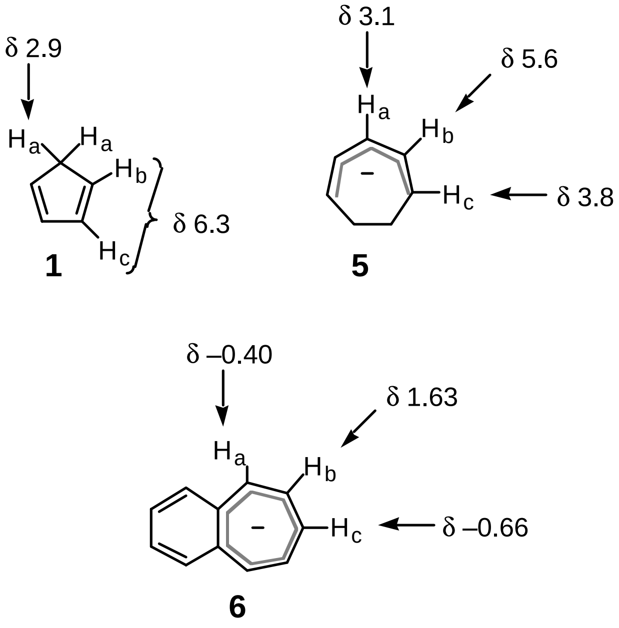

FIGURE 2. REFERENCE ^{1}H NMR SPECTRAL DATA FOR COMPOUNDS **1**, **5** [9], AND **6** [10].

Chemical Equivalence

Upon deprotonation of **1**, a single, symmetrical aromatic species (**2**) is formed that can be represented by five equally contributing resonance forms of equivalent energy (Scheme 1). The symmetry of **2** (D_{5h}) ensures that all of the protons are chemically equivalent. This may be contrasted with the chemical shifts of **1** (Figure 1c and Figure 2), which show two distinct broad multiplets at 6.3 ppm (protons H_b and H_c) and 2.9 ppm (H_a). The ^{1}H NMR spectrum of **1** may be conveniently obtained by addition of an equivalent of trifluoroacetic acid to a solution of anion **2** prepared as described above.

Chemical Shift

The first question from the bulk of the students upon obtaining the spectrum of **2** was: “Why isn't the singlet seen at 7 ppm (i.e., the chemical shift of benzene)?” Two effects are at work concurrently: the shielding effect of a negatively charged carbon on an attached proton, and the deshielding effect of the diamagnetic ring current of an aromatic ring. A negatively charged carbon typically shields an attached proton in the ^{1}H NMR spectrum (proton appears upfield). For example, the protons on the carbon

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atoms bearing the negative charge in the contributing resonance forms of the nonaromatic cycloheptadienyl anion, **5** (Figure 2, protons H_a and H_c), appear significantly upfield of the vinyl proton that does not bear the charge (H_b) [9]. However, since anion **2** is aromatic, the deshielding effect of the diamagnetic ring current shifts the proton signal downfield of the positions observed for **5**. The resulting shift is therefore upfield of uncharged benzene, but downfield of a nonaromatic anion. The spectrum may be further contrasted with the chemical shifts of benzocycloheptatrienyl anion, **6** (Figure 2), whose protons experience additional shielding effects relative to **5,** resulting from the paramagnetic ring current of its 8-electron antiaromatic π system [10]. Note that unlike the isoelectronic anion **4,** which is nonaromatic, **5** is antiaromatic because the ring's planarity is enforced by the fused benzene ring.

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

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