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Generation, Characterization, and Diazo-Coupling Reaction of Cycloheptatrienols[1]

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Three isomeric cycloheptatrienols, cyclohepta-1,3,5-trien-1-ol (**1**), cyclohepta-1,3,5-trien-2-ol (**2**), and cyclohepta-1,3,5-trien-3-ol (**3**), were generated by controlled acid-catalyzed hydrolysis or methanolysis of their corresponding trimethylsilyl enol ethers in DMSO. ^{1}H NMR spectroscopic studies indicate that ketonization of **1**−**3** all took place by α-protonation to give cyclohepta-3,5-dien-1-one (**4**), cyclohepta-2,4-dien-1-one (**5**), and cyclohepta-2,5-dien-1-one (**9**), respectively. **9** is not stable at room temperature and isomerized to **4** via enol **1** as an intermediate. The diazo-coupling reaction of these enols with *p*-substituted-benzenediazonium ions **10** was also studied, and three different behaviors were observed. **1** reacted at the α-position(s) with 1 and 2 equiv of **10** to give intramolecularly H-bonded 2-(*p*-substituted-phenylhydrazono)cyclohepta-3,5-dien-1-ones **15** and 2,7-bis(*p*-substituted-phenylhydrazono)cyclohepta-3,5-dien-1-ones **16**, respectively. Coupling of **2** with *p*-chlorobenzenediazonium ion (**10d**) proceeded through its valence tautomer bicyclo[4.1.0]hepta-2,4-dien-2-ol (**20**), to give 4-(*p*-chlorophenylhydrazono)bicyclo[4.1.0]hept-3-en-2-one (**24d**). Diazo-coupling of enol **3** with **10a,b** yielded both **15a,b** and **16a,b**, the same products as the coupling reaction of **1**. Our results suggest that the most probable reaction pathway of **3** is instead of undergoing direct coupling, it is isomerized first to enol **1** which then reacted. Kinetics for the three coupling reactions were also studied by conventional and stopped-flow UV/vis spectroscopy. The reaction constant ($\rho = 1.15$) for the diazo-coupling reaction of **1e**, the enolate anion of **1**, is much smaller than that for the same reaction of phenolate anion ($\rho = 4.2$), suggesting that the formation of the transition state in the reaction of **1e** has a greater activation energy than that for the aromatic phenolate anion. This observation and the dramatic difference in reactivity toward electrophilic additions are considered as evidence for *the lack of significant homoaromatic stabilization in the cycloheptatriene derivatives.*

Introduction

Although phenol, a cyclic trienol, derived from the aromatic hydrocarbon benzene is well known, the cyclic trienols derived from the potential homoaromatic hydrocarbon cycloheptatriene have been unknown until quite recently. We have previously reported that cyclohepta-1,3,5-trien-1-ol (**1**) and cyclohepta-1,3,5-trien-3-ol (**3**) could be generated in aqueous DMSO solutions.[2] Enol **1** also exists in a *ca.* 35% equilibrium with its keto isomer cyclohepta-3,5-dien-1-one (**4**) in pure DMSO.[2] The equilibrium constant K_E for enolization (**4** $\rightleftharpoons$ **1**) has been determined to be 1.2×10^{-3} in aqueous solution,[2] which is between that of phenol (1×10^{11})[3] and vinyl alcohol (2×10^{-7}),[4] indicating that although **1** is much less stable than the former, it is more stable than the latter. It is not clear whether such stabilization originates solely from π-conjugation of the triene system or if there is also an additional contribution from homoaromaticity resulting from cyclic 6π-conjugation across the methylene bridge.[5] Homoaromaticity has been sometimes claimed[6] and sometimes rejected[7] to be present in cycloheptatriene. Recent *ab initio* calculations carried out by Cremer and his co-workers[8,9] indicated that the equilibrium geometry of cycloheptatriene does not adopt a pure boat conformation but a perturbed one comprising of 77% boat and 23% chair form. As a result, the triene part of the seven-membered ring is flattened, and hence π-delocalization is improved and cycloheptatriene is stabilized. However, these authors cautiously pointed out that it is not

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(1) A preliminary communication on this work has appeared; see: Lew, C. S. Q.; Tang, T.-H.; Capon, B.; Csizmadia, I. G. *J. Chem. Soc., Chem. Commun.* **1995**, 175.

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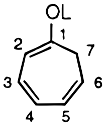
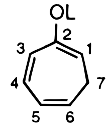
necessary to invoke homoaromaticity to explain the stability of cycloheptatriene.[9]



1



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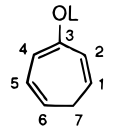
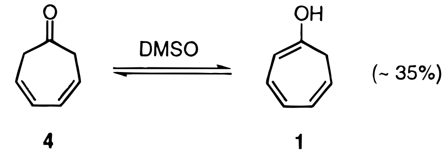


3

L = H or D



4 **1**

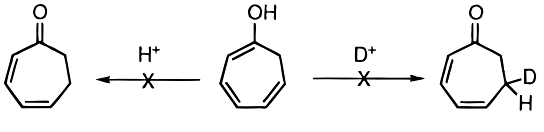
In order to shed more light on the role of homoaromaticity in the stabilization of cycloheptatriene derivatives, we have carried out a systematic study on the electrophilic addition reactions of all three isomers of cycloheptatrienol (**1**−**3**).[1] This paper presents in detail the generation and characterization of these enols in solutions. In addition, results of kinetic and mechanistic investigations of their diazo-coupling reactions are reported and compared with that of phenol. Our results indicate that *there is no significant homoaromatic stabilization in these cycloheptatrienols.*

The development of many convenient methods for the generation of simple enols[10] in greater than equilibrium amounts in solutions has led to a resurgence of interests in these chemically and biologically important reactive intermediates in recent years.[11,12] However, apart from ketonization,[13] few of their reactions have been studied directly.[14] To the best of our knowledge, this work represents the first *direct* investigation of the diazo-coupling reaction of simple enols in solutions.

Results and Discussion

(A) Generation and Characterization of Cycloheptatrienols in Solution. Under carefully controlled conditions, many simple enols can be generated thermally in solution by hydrolysis of certain precursors which react to give enols faster than these enols ketonize.[11] Currently, there are two types of precursors which have been widely used for such a purpose.[11] The first type derives from orthoesters or ketene acetals and is generally used for the generation of reactive enols such as vinyl alcohol.[4,15] For less reactive enols, trimethylsilyl enol ethers, the second type of precursors, have been proven to be more useful.[16] There are several advantages in using the latter. For example, the synthesis is simple and straightforward.[17] Moreover, the hydrolysis products derived from the leaving group are either trimethylsilanol or hexamethyldisiloxane[16,18] which have ^{1}H and ^{13}C NMR signals near zero ppm, and therefore, complications in the NMR spectra are minimized. This allows one to follow the subsequent reactions of the enols easily. In the present study, all the cycloheptatrienols **1**−**3** were generated from their corresponding trimethylsilyl enol ethers.

[*O*-D]Cyclohepta-1,3,5-trien-1-ol (1, L = D). Trienol **1** (L = H) has been considered in the past and rejected as an intermediate in the isomerization of cyclohepta-3,5-dien-1-one (**4**) to cyclohepta-2,4-dien-1-one (**5**).[19] The *O*-D form (**1**, L = D) was generated from its trimethylsilyl enol ether **6** in DMSO-d_6:CD$_3$OD (95:5, v/v) at 25 °C. Under these conditions **1** was formed efficiently after the addition of CF$_3$CO$_2$D (final concentration 1.5×10^{-4} M). Thus, the signal of the trimethylsilyl group at δ 0.18 was replaced by that of the trimethylsilanol at δ 0.07 and hexamethyldisiloxane at δ 0.06,[18] the signals of the ring protons of the starting substrate **6** by a new set of signals at similar chemical shifts (Scheme 1).[20] **1** ketonized to [2-D]cyclohepta-3,5-dien-1-one (**4a**) slowly before the conversion of **6** to **1** was complete. By the end of the methanolysis which took about 10 min, the reaction mixture contained about 85% **1** and 15% **4a**. Ketonization continued, and the mixture arrived at a final equilibrium containing about 27% **4a** at 1.5 h. There appeared to be no formation of [6-D]cyclohepta-2,4-dien-1-one (**5a**).



5 **1** **5a**

Experiments had also been carried out to generate **1** through hydrolysis of **6** in DMSO-d_6 using DCl/D$_2$O as catalyst; however, the results were less satisfactory. The problem appears to be related to the faster rates of hydrolysis of **6** and ketonization of **1** under these conditions. The best result was obtained in a DMSO-d_6:D$_2$O (98:2, v/v) mixture containing 5×10^{-6} M DCl; the hydrolysis took approximately 7 min, at the end of which there was about 70% **1** and 30% **4a**. Note that the maximum amount of enol **1** obtained at the end of the hydrolysis of **6** in these experiments (DMSO-d_6:D$_2$O/DCl) is less than that in the DMSO-d_6:CD$_3$OD/CF$_3$CO$_2$D experiment described above.

[*O*-D]Cyclohepta-1,3,5-trien-2-ol (2, L = D). Trienol **2** (L = D) was generated from its trimethylsilyl derivative **7** in DMSO-d_6:D$_2$O (95:5, v/v) which contained DCl (5.66×10^{-4} M) at 25 °C. The trienol was formed quantitatively after 10 min, almost free of its keto from [7-D]-cyclohepta-2,4-dien-1-one (**5b**). Ketonization of **2** to **5b** took a period of 2 h (Scheme 2).[20]

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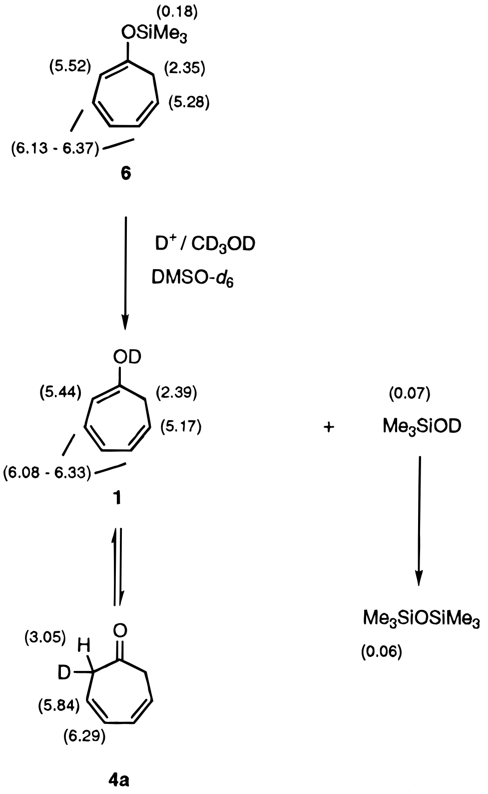
(20) NMR spectra are included as Supporting Information.

Scheme 1. Generation of [*O*-D]Cyclohepta-1,3,5-trien-1-ol (1) in a DMSO-d_6:CD_3OD (95:5, v/v) Mixture Containing 1.5 × 10^{-4} M CF_3CO_2D at 25 °C[a]

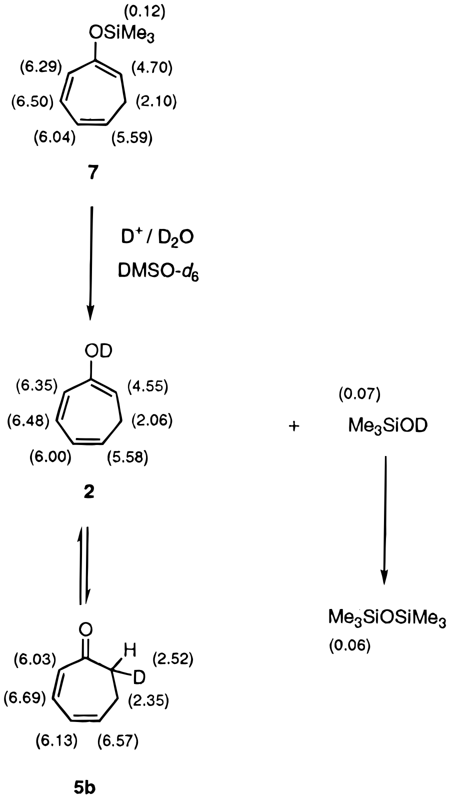


[a] Data in parentheses represent 270 MHz ^{1}H NMR chemical shifts.

[*O*-D]Cyclohepta-1,3,5-trien-3-ol (3, L = D). Trienol **3** (L = D) was generated from its trimethylsilyl derivative **8** in DMSO-d_6:D_2O (97.5:2.5, v/v) which contained DCl (5 × 10^{-3} M) at 25 °C. It took 5 min under these conditions for the trimethylsilyl enol ether to be converted into the trienol (L = D) which then tautomerized to [7-D]-cyclohepta-2,5-dien-1-one (**9a**) (Scheme 3).[20] The ketonization of **3** to **9a** was sufficiently slow that at the end of the hydrolysis, the reaction mixture contained almost quantitatively **3**. However, the ^{1}H NMR spectrum obtained after the reaction mixture was allowed to stand overnight at room temperature was very similar to that of the equilibrated mixture resulting from the ketonization of [*O*-D]cyclohepta-1,3,5-trien-1-ol (**1**, L = D) in DMSO-d_6:CD_3OD (95:5, v/v) (*vide supra*). In an independent experiment in which the trimethylsilyl derivative **8** was hydrolyzed under the same conditions except that HCl/H_2O was used as the acid catalyst, cyclohepta-3,5-dien-1-one (**4**) was the only isolated product. It appeared that cyclohepta-2,5-dien-1-one (**9**) was not stable and isomerized to **4**, probably via **1** as an intermediate under these conditions. Support of this hypothesis was obtained by monitoring the changes by ^{1}H NMR spectroscopy in CD_3CN:H_2O (97:3, v/v) which contained 6 × 10^{-5} M HCl: a distinct and stepwise conversion from the trienol **3** (L = H) to ketone **9**, then to trienol **1** (L = H), and finally to ketone **4** was observed (Scheme 3).[20]

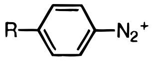
As discussed in the previous section, no evidence for the presence of **9** was found in the ketonization of **1**. Therefore, the rate of ketonization of **1** to **9** is much slower than that of **1** to **4**. It is concluded that the activation energy for the former process must be much higher than that of the latter (Figure 1).

Scheme 2. Generation of [*O*-D]Cyclohepta-1,3,5-trien-2-ol (2) in a DMSO-d_6:D_2O (95:5, v/v) Mixture Containing 6 × 10^{-4} M DCl at 25 °C[a]



[a] Data in parentheses represent 270 MHz ^{1}H NMR chemical shifts.

(B) Diazo-Coupling Reactions of the Cycloheptatrienols. Three different types of behaviors were encountered in the diazo-coupling reactions of cycloheptatrienols **1**−**3** with *p*-substituted-benzenediazonium ions **10**. In this section they are discussed separately.



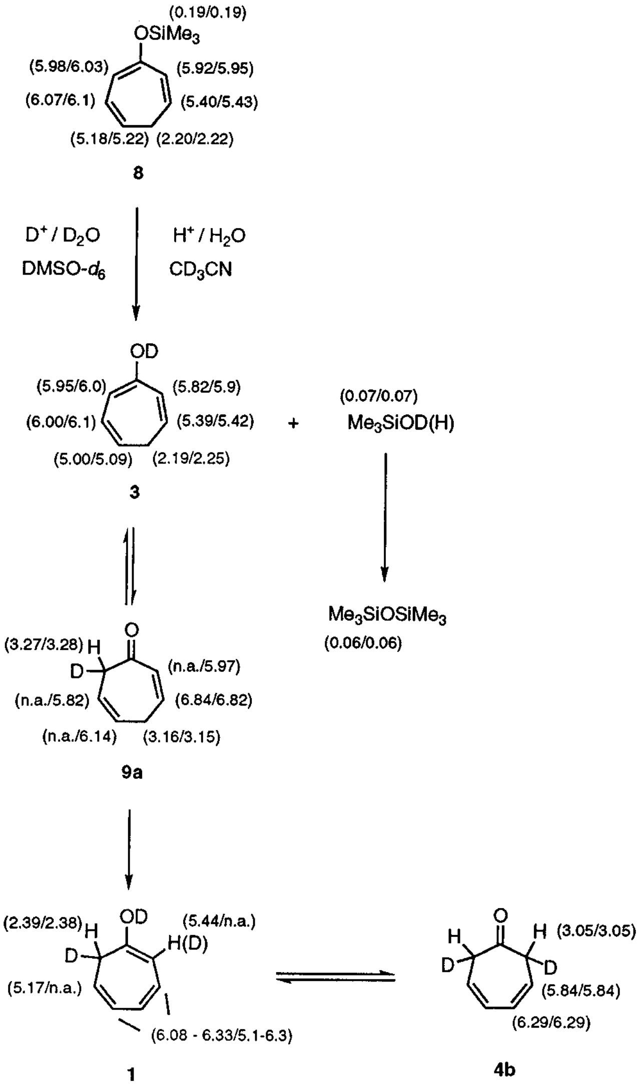
10

	R
a	H
b	CH_3
c	OCH_3
d	Cl

(a) Cyclohepta-1,3,5-trien-1-ol (1). Isolation of Products. The diazo-coupling reaction was carried out by mixing a DMSO solution of cyclohepta-1,3,5-trien-1-ol (**1**), generated as described in the previous section, with an aqueous solution of the benzenediazonium ions **10a**−**d** at 5 °C. Products were isolated by extracting the reaction mixtures with chloroform and purified by flash column chromatography. There are two major products which were formed by reacting with 1 and 2 equiv of **10**, respectively. The monocoupling products are the intramolecularly H-bonded forms of 2-(*p*-substituted-phenylhydrazono)cyclohepta-3,5-dien-1-ones **15**, and the biscoupling products are 2,7-bis(*p*-substituted-phenylhydrazono)cyclohepta-3,5-dien-1-ones **16**.

When **1** was allowed to react with 1 equiv of **10a**−**d** for 5−15 min, **15a**−**d** were isolated as the major products

Scheme 3. Generation of [*O*-D]Cyclohepta-1,3,5-trien-3-ol (3) at 25 °C in a DMSO-d_6:D_2O (97.5:2.5, v/v) Mixture Containing 5 × 10^{-3} M DCl and in a CD_3CN:H_2O (97:3, v/v) Mixture Containing 6 × 10^{-5} M HCl[a]



[a] The first data in parentheses represent the 270 MHz ^1H NMR chemical shifts in the DMSO-d_6:D_2O/DCl experiment. The second data in parentheses represent the 270 MHz ^1H NMR chemical shifts in the CD_3CN:H_2O/HCl experiment.

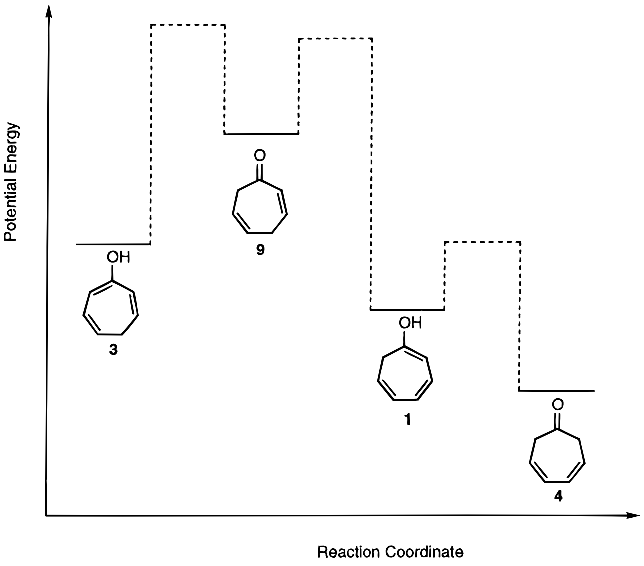
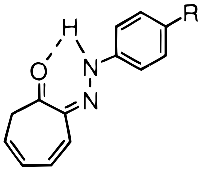


Figure 1. Schematic representation of the energy profile of the acid-catalyzed ketonization of cyclohepta-1,3,5-trien-3-ol (**3**).

(*ca.* 60%). Trace amounts of **16a**–**d** were isolated as dark red solids or detected on the silica gel column by their characteristic purple colors. Longer reaction time (*ca.* 30–60 min) only improved the yields of both **15a**–**d** and **16a,b** moderately to *ca.* 65% and 5%, respectively. When 2 equiv of benzenediazonium ions **10a,b** were allowed to react with **1** for 45–60 min, the biscoupling products **16a,b** were isolated as the major products (*ca.* 45%) along with small amounts of the monocoupling products **15a,b** (*ca.* 15%). Full spectroscopic data of **15a**–**d** and **16a,b** are given in the Experimental Section. The presence of significant amounts of possible enol–azo tautomeric structures (**17a**–**d**) was excluded based on the facts that the signals at δ 189.58–189.79 and 140.01–142.35 in the ^{13}C NMR spectra showed the presence of carbonyl and hydrazono groups and that additional ^1H NMR signals which can be ascribed to the methylene protons of **17a**–**d** (*i.e.*, doublets at δ ~2) were not detected. The ^{15}N NMR spectrum of the unsubstituted compound prepared from ^{15}N-enriched aniline had a signal at δ −213.6 (CH_3NO_2 as an external standard) which is also consistent with structure **15a** and excludes azo structure **17a** for which δ (^{15}N) would be expected to be in the range 0–100.[21] The presence of strong intramolecular H-bonds was indicated by a signal at δ *ca.* 14 in the ^1H NMR spectrum.[22]



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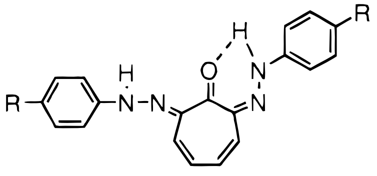
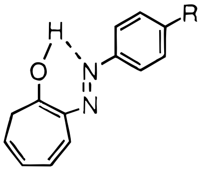


16



17

	R
a	H
b	CH_3
c	OCH_3
d	Cl

For the biscoupling products **16a,b**, the presence of a carbonyl group was indicated by a signal at δ *ca.* 186 in the ^{13}C NMR spectra. The ^1H NMR spectrum showed the presence of one intramolecularly H-bonded NH group (δ *ca.* 15) and one intermolecularly H-bonded NH group (with solvent, δ *ca.* 10).[22] The presence of two different hydrazono groups in **16a** (R = H) was also indicated by the ^{15}N NMR spectrum of the compound obtained from ^{15}N-enriched aniline which showed signals for the nitrogens attached to the phenyl rings at δ −209.8 and −224.6. Weaker signals at δ −20.5 and −42.8 were

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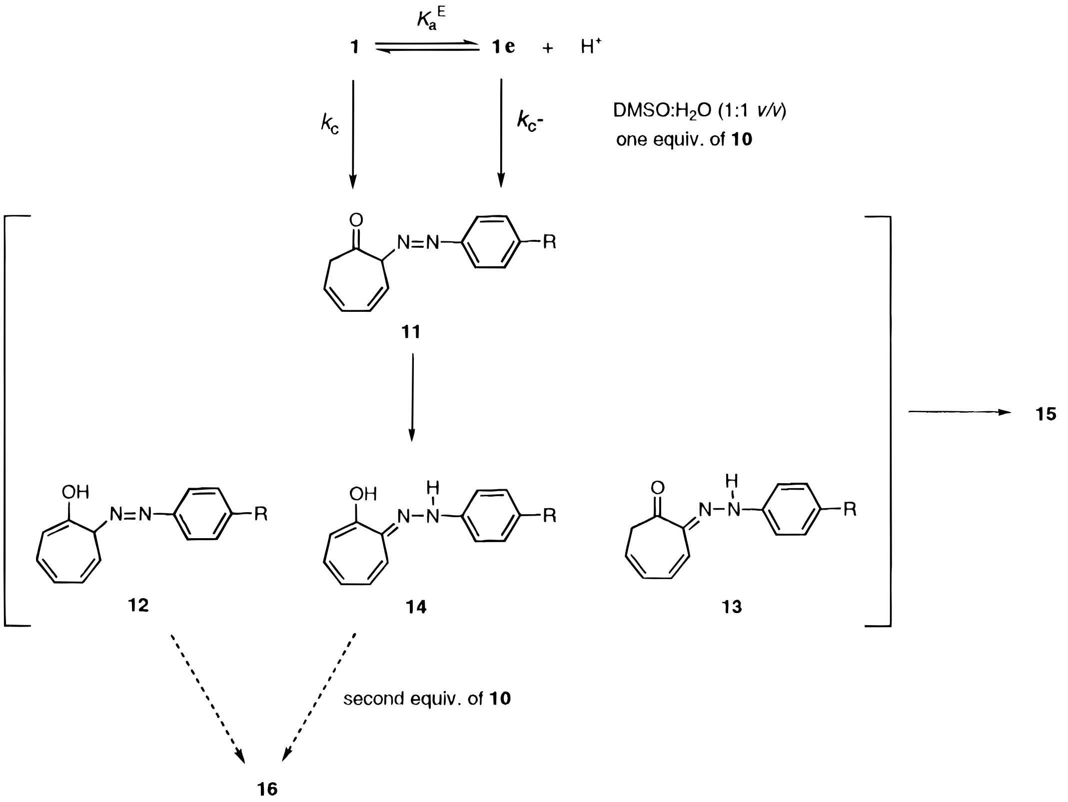
Scheme 4. Proposed Scheme for Diazo-Coupling Reaction of Cyclohepta-1,3,5-trien-1-ol (1) in DMSO:H$_2$O (1:1, v/v)



also observed and attributed to the double-bonded nitrogens of hydrazono groups.[21] These presumably arose from scrambling of the nitrogen atoms in the diazonium ions.[23]

Kinetics of the Diazo-Coupling Reaction. Kinetics of diazo-coupling reactions of cyclohepta-1,3,5-trien-1-ol (**1**) with benzenediazonium ions **10a–d** were studied in DMSO:H$_2$O (1:1, v/v) mixtures at 20 °C. When the reaction of **1** (5×10^{-3} M) with **10a** (5×10^{-4} M) was followed by UV spectroscopy, an absorption band with $\lambda_{max} = 400$ nm was detected in the first scan (<2 min). This signal was assigned to a monocoupling product based on a time-dependent product analysis. However, it is clear that this was not the isolated product 2-(phenylhydrazono)cyclohepta-3,5-dienone (**15a**) which has λ_{max} at 412 nm. Control experiments indicate that the detected product ($\lambda_{max} = 400$ nm) underwent further reaction with **10a** at a rate significantly faster than the isolated product ($\lambda_{max} = 412$ nm) under the same conditions.[24] Therefore, it is concluded that the detected product must either be an enol or a ketone which enolizes faster than the isolated product. Possible structures are **11a**, **12a**, **13a**, or **14a** (see Scheme 4).

The kinetics of the initial coupling were measured by following the formation of the product(s) at 400 nm using stopped-flow UV spectroscopy. The observed pseudo-first-order rate constants were more than 100 times greater than the first-order rate constants for ketonization under similar conditions (*i.e.*, at the same [H$^+$] and in the same solvent system) and were inversely proportional to the concentration of hydronium ions. Plots of k_{obs} versus 1/[H$^+$] yielded straight lines with finite values of slopes and intercepts, indicating that both the un-ionized (**1**) and ionized (**1e**) forms undergo reaction. Presumably, the diazo-coupling reactions of **1** and **1e** both took place at the α-position to give the monocoupling products **11**, **12**, **13**, or **14**, which either were isolated as the intramolecularly H-bonded compounds **15** or underwent further reactions with another equivalent of benzenediazonium ions **10** to give the biscoupling products **16** (Scheme 4).

According to Scheme 4, the observed rate constant for the formation of the coupling product measured at 400 nm is given by the following equation:

$$k_{obs} = \left(\frac{k_{c^-} K_a{}^E}{[H^+]} + k_c\right)[E] \qquad (1)$$

by taking the ionization of enol **1** into account. In this equation, k_c and k_{c^-} represent the rate constants for coupling of **1** and its enolate ion **1e**, respectively. [E] stands for the concentration of enol **1**, and $K_a{}^E$ is the dissociation constant of **1**. [E] and $K_a{}^E$ are related to [E$^-$], the concentration of **1e** by eq 2:

$$E_a{}^E = \frac{[E^-][H^+]}{[E]} \qquad (2)$$

Equation 1 indicates that the slope of the plots of k_{obs} versus 1/[H$^+$] is equal to $k_{c^-}K_a{}^E$[E] and the intercept is equal to k_c[E]. A summary of the $k_{c^-}K_a{}^E$ and k_c values is given in Table 1. It is obvious that determination of k_{c^-} requires the $E_a{}^E$ value of **1** which, unfortunately, is not available in the literature and is difficult to measure directly due to the instability of **1** in either water or

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[23] Hegarty, A. F. In *The Chemistry of Diazonium and Diazo Groups*; Patai, S., Ed.; John Wiley & Sons: Chichester, 1978; Part 2, Chapter 12, p 526.

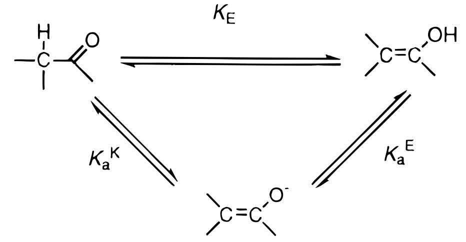
[24] Capon, B.; Lew, C. S. Q. Unpublished results.

Table 1. Rate Constants for the Diazo-Coupling Reaction of Cyclohepta-1,3,5-trien-1-ol (1) and Its Enolate Anion 1e[a]

benzene-diazonium ion	*p*-substituent R	**1e** $(k_{c^-}K_a^E)$ (M s^{-1})	**1e** k_{c^-} (10^9 M^{-1} s^{-1})[b]	**1** k_c (10^2 M^{-1} s^{-1})
10a	H	3.91	1.56	4.88
10b	CH_3	1.48	1.07	2.66
10c	OCH_3	0.98	0.71	1.97
10d	Cl	2.15	2.83	10.61
			$\rho_{enolate} = 1.15$	$\rho_{enol} = 1.46$

[a] 20 °C, DMSO:H_2O (1:1, v/v), [**1**] = 2×10^{-3} M, [**10**] = 2.5×10^{-4} M. Pseudo-first-order kinetics were observed. Errors are ± 5%. [b] Estimated values. See text for discussion.

DMSO:H_2O mixtures. The K_a^E constant, however, is related to other equilibrium constants K_a^K and K_E in the following thermodynamic cycle by eq 3:



$$K_a^E = \frac{K_a^K}{K_E} \tag{3}$$

For simple enols, these two constants (K_a^K and K_E, in wholly aqueous solution) are related to each other by a linear equation reported by Kresge and Keeffe:[13]

$$pK_a^K = 1.39 \times pK_E + 8.06 \tag{4}$$

By using eqs 3 and 4 and a K_E (**4** ⇌ **1**) value of 8.9×10^{-3} determined in DMSO:H_2O (1:1, v/v) at 20 °C,[24] the K_a^E value of **1** was estimated to be about 1.38×10^{-3} M in the same solvent system. This estimation is based on an assumption that the equilibrating and ionizing behaviors of enol **1** and its keto from **4** in DMSO:H_2O (1:1, v/v) are approximately the same as in a wholly aqueous solution. Indeed, the K_E constant in water (1.2×10^{-3})[2] is of the same order of magnitude as that in the DMSO:H_2O (1:1, v/v) (8.9×10^{-3}).[24] The k_{c^-} values obtained based on the thus estimated K_a^E value (1.38×10^{-3} M) are also listed in Table 1. However, it must be pointed out that they might only represent the lower limits of the k_{c^-} values since DMSO acts as a base in water and hence facilitates the ionization.

The reaction constants ρ_{enol} and $\rho_{enolate}$ were determined from Hammett plots to be 1.46 and 1.15, respectively. This implies that the transition state of the reaction of the more reactive enolate ion **1e** with the diazonium ions **10** lies earlier on the reaction coordinate than that of the reaction of the less reactive enol. This conclusion is similar to that made for the *C*-protonation of the ionized and un-ionized forms of vinyl alcohol based on the Bronsted coefficient[4c] and is the result to be expected on the basis of the Hammond postulate.[25]

(b) Cyclohepta-1,3,5-trien-2-ol (2). Isolation and Identification of the Product of the Reaction with *p*-Chlorobenzenediazonium ion. When cyclohepta-1,3,5-trien-2-ol (**2**) was allowed to react with 1 equiv or an excess amount of *p*-chlorobenzenediazonium ion (**10d**)[26] in DMSO:H_2O (1:1, v/v) at −5 to 0 °C for 1 h, a yellow-orange solid was the only isolated product after extracting the reaction mixture with chloroform followed by evaporating the solvent and running a flash column chromatography (85% yield). The ^1H NMR spectrum showed the presence of two olefinic protons at δ 5.84 (dd, $J = 10.17, 1.71$ Hz) and 6.95 (dd, $J = 10.17, 1.95$ Hz), four protons bound to saturated carbon (δ 1.01, 1.72, 2.23, 2.74 (m)), and four aromatic protons (δ 7.23). This clearly could not be a derivative of a cycloheptadiene (or of a cycloheptatriene). Elemental analysis and the mass spectrum showed that only 1 equiv of the diazonium ion had coupled. In view of the known tendency of cycloheptatriene derivatives to undergo valence tautomerism into bicyclo[3.2.0]heptadiene[27] and bicyclo[4.1.0]-heptadiene[28] derivatives, the possibility of reaction through structures **18**−**20** was considered to yield **21d**, **22d**, **23d**, and **24d**.

Of these only **24d** is consistent with the spectroscopic data. The ^1H NMR spectrum shows that the protons attached to the saturated carbons are not adjacent to the olefinic protons as only long-range couplings are present. A computer simulation (NMRCALC)[29] using the coupling constants in the Experimental Section shows good agreement with the experimental spectrum (Figure 2).

It is interesting that the presumed intermediate bicyclo[4.1.0]hepta-2,4-dien-2-ol (**20**) undergoes exclusive coupling at the γ-position. Protonation of dienols normally only occurs exclusively at the γ-position when the dienol system is planar,[30] which suggests that the dienol system of **20** is probably planar.

Kinetics of the Reaction with *p*-Chlorobenzenediazonium Ion. When the formation of the product was followed at $\lambda = 400$ nm with the concentration of enol ($5-10 \times 10^{-3}$ M) maintained at least 10 times greater than that of **10d** (5×10^{-4} M), pseudo-zeroth-order kinetics were observed. Moreover, the pseudo-zeroth-order kinetics are independent of the concentration of **10d** in a separate experiment in which the concentration of enol **2** was fixed (but maintained at least 10 times higher than the concentration of **10d**). These observations indicate that the rate-determining step is the valence tautomerism of **2** to bicyclo[4.1.0]hepta-2,4-dien-2-ol (**20**) and that the diazo-coupling of **20** (or its anion) is rapid under these conditions. The first-order rate constant for the valence tautomerism (at 20 °C) was

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(25) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334. For a discussion, see: Farcasiu, D. *J. Chem. Educ.* **1975**, *52*, 76.

(26) Diazo-coupling of enol **2** with other *p*-substituted benzenediazonium ions **10a**−**c** gives similar results.[24]

(27) (a) Chapman, O. L.; Borden, G. W. *Proc. Phys. Chem.* **1963**, 221. (b) Borden, G. W.; Chapman, O. L.; Swindell, R.; Tezuka, T. *J. Am. Chem. Soc.* **1967**, *89*, 2979. (c) Tezuka, T.; Kikuchi, O.; Houk, K. N.; Paddon-Row, M. N.; Santiago, C. M.; Rondan, N. G.; Williams, J. C., Jr.; Gandour, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 1367.

(28) (a) Vogel, E. *Pure Appl. Chem.* **1969**, *20*, 237. (b) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 402.

(29) Simulation was performed by using the PC version of NMR-CALC program (M. D. Johnston, Jr,. Dept. of Chem., Univ. of Florida, 1984).

(30) (a) Rogers, N. A. J.; Sattar, A. *Tetrahedron Lett.* **1965**, 1471; **1964**, 1311. (b) Malhotra, S.; Ringold, H. J. *J. Am. Chem. Soc.* **1965**, *87*, 3228. (c) Heap, N.; Whitham, G. A. *J. Chem. Soc. B* **1966**, 164. (d) Morrison, H.; Kurowsky, S. R. *Chem. Commun.* **1967**, 1098. (e) Whalen, D. L.; Weimaster, J. F.; Ross, A. M.; Radhe, R. *J. Am. Chem. Soc.* **1976**, *98*, 7319. (f) Pollack, R. M.; Mack, J. P. G.; Blotny, G. *J. Am. Chem. Soc.* **1987**, *109*, 3138. (g) Capon, B.; Guo, B. Z. *J. Am. Chem. Soc.* **1988**, *110*, 5144.

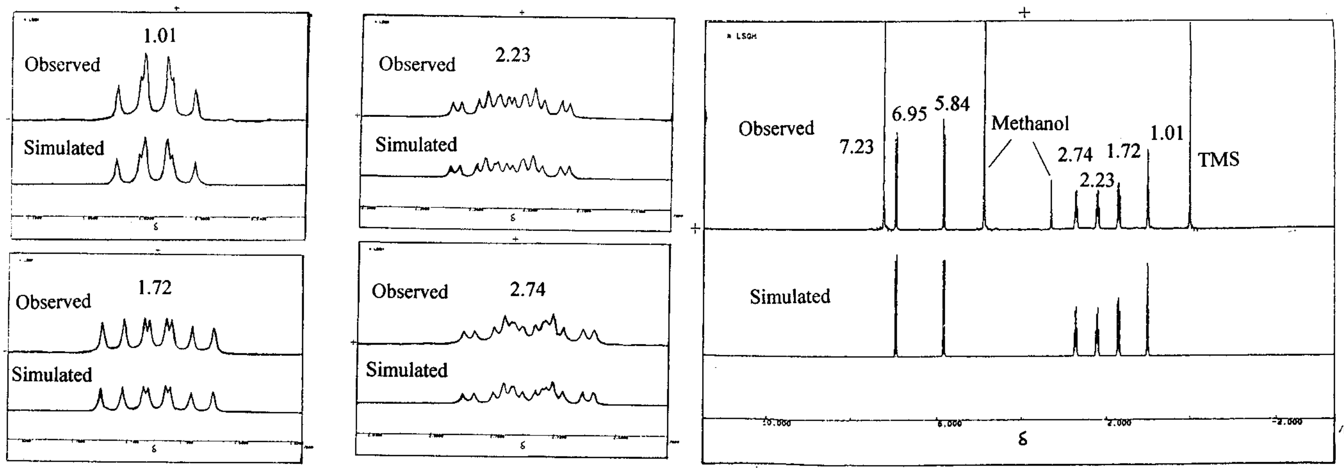
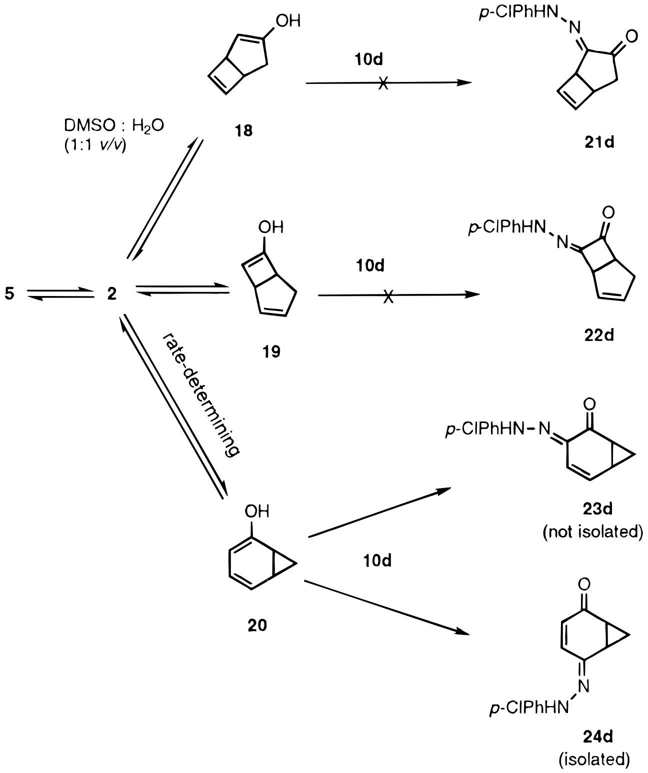


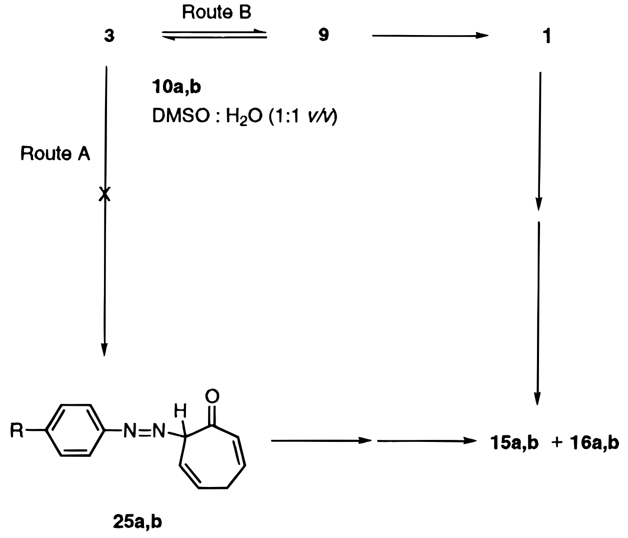
Figure 2. Observed (270 MHz, in CD_3OD) and simulated ^1H NMR spectra of **24d**.

calculated from the zeroth-order rate constant, 1.6×10^{-2} M s^{-1}, to be 3.2 s^{-1}.



(c) **Cyclohepta-1,3,5-trien-3-ol (3).** Coupling of cyclohepta-1,3,5-trien-3-ol (**3**) with 1 equiv of benzenediazonium ions **10a,b** for 2 h yields the same isolated products **15a,b** (20%, 22%) and **16a,b** (45%, 46%) as that of the cyclohepta-1,3,5-trien-1-ol (**1**) under similar conditions. There are two possible pathways for the formation of the products: direct coupling at the α-position to give **25a,b** followed by double-bond migration (route A, Scheme 5) or tautomerizing to enol **1** which then undergoes diazo-coupling in the same way discussed previously (route B, Scheme 5). When the reaction of 2.5×10^{-4} M **10a** with 5×10^{-3} M **1** was followed by UV spectroscopy, the observed pseudo-first-order rate constant for the formation of coupling product as observed at 400 nm (2.5×10^{-4} s^{-1}) is about 10 times less than that of the ketonization of **3** (2.3×10^{-3} s^{-1}) under the same conditions.[24] Based on an assumption that the direct coupling product **25a** absorbs at 400 nm,[31] it is reasonable to suggest that route B is the actual reaction pathway. In other words, the reaction most probably took place by rate-determining tautomerism of enol **3** to enol **1**, via cyclohepta-2,5-dien-1-one (**9**) as an intermediate (route B). Such a tautomerism was directly observed by ^1H NMR spectroscopy and is discussed in the previous section of this paper.

Scheme 5. Proposed Scheme for Diazo-Coupling Reaction of Cyclohepta-1,3,5-trien-3-ol (3) in DMSO:H$_2$O (1:1, v/v)



Concluding Remarks

26, **20**, and **27** are the respective norcaradiene valence tautomers of the three cycloheptatrienols **1**−**3**. The equilibrium between cycloheptatrienes and norcaradienes normally highly favors the monocyclic cycloheptatriene form, except under a few occasions such as when the 7-position is substituted with electron-withdrawing group(s).[28,32] The fact that only **20** was trapped by the diazonium ions can be attributed to its greater stability or/and its higher activity toward the electrophilic diazonium ion. Our preliminary *ab initio* calculations suggest

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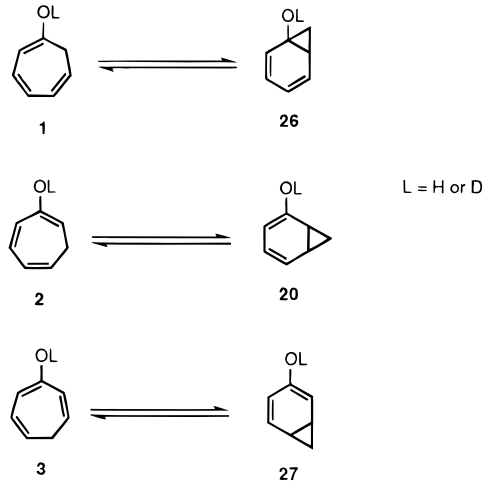
[31] Azo compounds with the structure Ph−N=N−CR_3 are known to have absorption λ_{max} at ~400 nm; see: Porter, N. A.; Marnett, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 4361.

[32] Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1989**, *89*, 1225.



that hydroxy group (or hydroxide group formed upon deprotonation), when substituting at the 2-position, has a small stabilization effect on norcaradiene.[1] A similar effect has been reported for trimethylsiloxy groups substituted at the 2- and 5-positions.[33] Indeed, the formation of **20** would be expected to be more favorable than that of **27** because the lone pair on the oxygen of the hydroxy/hydroxide group in **20** is continuously conjugated with the planar cyclohexa-1,3-diene moiety, whereas that of the hydroxy/hydroxide group in **27** is in a cross-conjugation situation. Similarly, the formation of **26** would be expected to be least favorable due to loss of continuous conjugation of the lone pair on the oxygen of the hydroxy/hydroxide group with the triene moiety. In terms of reactivity, it would be difficult to predict and compare the reactivity of **26** which is a homoenol[34] with that of **20** and **27** which are both dienols. Of the two dienols, the α-position of the enolic double bond in **27** is sandwiched between the hydroxy group and the cyclopropyl moiety whereas both the α- and γ-positions in **20**, where the electrophilic attack of diazonium ion is expected,[35] are in a more open situation. In other words, there would be greater steric hindrance to the approaching diazonium ion in the reaction of **27**, and therefore, it should be less reactive than **20**

The exclusive trapping of **20** found in this study is interesting in view of the formation, *in effectively a single step*, of a [4.1.0] bicyclic compound incorporated with an enone functionality. This finding might have potential applications in organic synthesis, particularly of natural products containing a cyclopropyl group.[36]

The present study establishes that ketonization of the three isomeric cycloheptatrienols **1**−**3** all took place by α-protonation to give cycloheptadienones **4**, **5**, and **9**, respectively. However, **9** is not stable at room temperature and isomerized to **4** via enol **1** as an intermediate. In addition, **1**−**3** reacted with benzenediazonium ions in three different manners. This dramatic difference in reactivities toward electrophilic addition can be considered as evidence for *the lack of significant homoaromatic stabilization in cycloheptatrienes* and is consistent with the results of recent theoretical calculations.[8,9,37] Additional evidence comes from kinetic studies of enol **1**. The reaction constant (ρ value) for the coupling of the enolate ion **1e** determined in this study ($\rho = 1.15$) is obviously much less than that for the coupling of phenolate ion[38] ($\rho = 4.2$) and is close to that for the coupling of the enolate ion derived from acetone[39] ($\rho = 1.89$), suggesting that it requires a much greater energy of activation for the formation of the transition state from the aromatic phenolate ion than **1e**.

Experimental Section

General. Deionized water was distilled and degassed. Aniline were purified by recrystallization from ethanol. Freshly double distilled (over CaH_2) spectroscopic grade DMSO (Aldrich) was used in all kinetic studies. Other commercial chemicals were used as received. δ values for ^{15}N NMR were measured against external CH_3NO_2. Accurate masses were determined on a VG 7070F MICRO-MASS spectrometer. Elemental analyses were performed at the Butterworth Laboratories Ltd., U.K. Melting and boiling points were not corrected.

Preparation of Trimethylsilyl Enol Ethers. The trimethylsilyl enol ethers **6**−**8** were prepared from the corresponding homocyclic ketones cyclohepta-3,5-dien-1-one (**4**),[40] cyclohepta-2,4-dien-1-one (**5**),[19b,41] and cyclohepta-2,6-dien-1-one[40a] by the following procedure:

Trimethylsilyl trifluoromethanesulfonate (1.22 g, 5.5 mmol) was added, with caution by using a syringe, to a stirring solution of the homocyclic ketone (5 mmol) and triethylamine (0.61 g, 6 mmol) in dry *n*-hexane (15 mL) under dry nitrogen atmosphere. Stirring was continued until two immiscible layers were formed. The lower layer was usually darkish brown in color. The upper clear layer was separated with a syringe, and the solvent was removed under reduced pressure. The products were purified by vacuum distillation using a microdistillation setup equipped with a 5 cm Vigreux column (for **6** and **7**) or a silica gel column chromatograph using dichloromethane as an eluent (for **8**).

1-[(Trimethylsilyl)oxy]cyclohepta-1,3,5-triene (6): bp 54−56 °C, 4 mmHg; ^1H NMR (CCl_4, 90 MHz) δ 0.20 (s, 9 H, $OSiMe_3$), 2.40 (d, 2 H, CH_2), 5.33 (m, 1 H), 5.56 (t, 1 H), 6.05 (m, 1 H), 6.22 (m, 2 H); ^1H NMR (DMSO-d_6, 270 MHz) δ 0.18 (s, 9 H, $OSiMe_3$), 2.35 (d, 2 H, CH_2), 5.28 (dt, 1 H, H-6, $J_{5,6} = 9.03$ Hz, $J_{6,7} = 7.08$ Hz), 5.52 (d, 1 H, H-2, $J_{2,3} = 4.88$ Hz), 6.37−6.13 (m, 3 H, H-3,4,5). Anal. Calcd. for $C_{10}H_{16}OSi$: C, 66.61; H, 8.95. Found: C, 66.42; H, 9.50.

2-[(Trimethylsilyl)oxy]cyclohepta-1,3,5-triene (7): bp 61−63 °C, 5 mmHg; ^1H NMR (DMSO-d_6, 270 MHz) δ 0.12 (s, 9 H, $OSiMe_3$), 2.10 (dd, 2 H, CH_2, $J_{7,1} = 7.08$ Hz, $J_{7,6} = 6.83$ Hz), 4.70 (dt, 1 H, H-1, $J_{1,3} = 1.95$ Hz), 5.59 (dt, 1 H, H-6, $J_{6,5} = 9.53$ Hz), 6.04 (dd, 1 H, H-5, $J_{5,4} = 5.37$ Hz), 6.29 (dd, 1 H, H-3, $J_{3,4} = 11.72$ Hz), 6.50 (dd, 1H, H-4); HRMS for $C_{10}H_{16}OSi$ calcd 180.0970, found 180.0943.

3-[(Trimethylsilyl)oxy]cyclohepta-1,3,5-triene (8): ^1H NMR (CCl_4, 90 MHz) δ 0.20 (s, 9 H, $OSiMe_3$), 2.22 (t, 2 H, CH_2, $J = 6$ Hz), 5.53−5.03 (m, 2 H, H-3,5), 6.2−5.73 (m, 3 H, H-1,2,4); ^1H NMR (DMSO-d_6, 270 MHz) δ 0.19 (s, 9 H, $OSiMe_3$), 2.20 (dd, 2 H, CH_2, $J_{7,1} = 6.84$ Hz, $J_{7,6} = 6.60$

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[33] Klarner, F.-G.; Schmidt, E. K. G.; Rahman, M. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 138.

[34] Nickon, A.; Lambert, J. L. *J. Am. Chem. Soc.* **1966**, *88*, 1905 and references cited therein.

[35] The fact that only the γ-coupling product **24d** was isolated suggests that the reaction at the α-position of **21** is much slower. Similar phenomena have been observed in the diazo-coupling reactions of phenols; see ref 22, p 546.

[36] Yamazaki, S.; Tanaka, M.; Yamahuchi, A.; Yamabe, S. *J. Am. Chem. Soc.* **1994**, *116*, 2356 and references cited therein.

[37] (a) Schulmann, J. M.; Disch, R. L.; Sabio, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 7696. (b) Williams, R. V.; Kurtz, H. A.; Farley, B. *Tetrahedron* **1988**, *44*, 7455.

[38] Sterba, V.; Valter, K. *Collect. Czech. Chem. Commun.* **1972**, *37*, 1327.

[39] Machacek, V.; Machackova, O.; Sterba, V. *Collect. Czech. Chem. Commun.* **1970**, *35*, 2954.

[40] (a) Garbisch, E. W., Jr. *J. Org. Chem.* **1965**, *30*, 2109. (b) Schuster, D. I.; Plamer, J. M.; Dickerman, S. C. *J. Org. Chem.* **1966**, *31*, 4281. (c) Schuster, D. I.; Sckolnick, B. R.; Lee, F.-T. H. *J. Am. Chem. Soc.* **1968**, *90*, 1300.

[41] Hine, K. E.; Childs, R. F. *J. Chem. Soc., Chem. Commun.* **1972**, 144.

Hz), 5.18 (dt, 1 H, H-6, $J_{6,5} = 9.53$ Hz), 5.40 (dt, 1 H, H-1, $J_{1,2} = 9.76$ Hz), 5.92 (dd, 1 H, H-2, $J_{2,4} = 1.95$ Hz), 5.98 (dd, 1 H, H-4, $J_{4,5} = 6.59$ Hz), 6.07 (dd, 1 H, H-5). Anal. Calcd. for $C_{10}H_{16}OSi$: C, 66.61; H, 8.95. Found: C, 66.39; H, 8.87.

Generation of Enols. Typically, to *ca*. 5 mg of the trimethylsilyl enol ether in a NMR tube was added *ca*. 0.5 mL of dry (freshly opened ampule) DMSO-d_6. A ^{1}H NMR spectrum was recorded first as a reference for the later hydrolysis experiments. An appropriate amount of acid was then added using a syringe, and the progress of the hydrolysis was monitored by ^{1}H NMR spectroscopy. When the hydrolysis was complete, the solution was either used immediately or stored in liquid nitrogen to avoid further ketonization.

Isolation of Diazo-Coupling Product 2-(Phenylhydrazono)cyclohepta-3,5-dien-1-one (15a). Aniline (1.4 g, 1.5 mmol) was diazotized with concd HCl (0.5 mL) and $NaNO_2$ (0.11 g, 1.6 mM) in water (20 mL) at −5 to 0 °C. A solution of cyclohepta-1,3,5-triene (**1**) (1.4 mmol) in DMSO (20 mL) generated as described above was added, and the resultant mixture was stirred for 3−5 min. Water (50 mL) was added, and the product was extracted with diethyl ether (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated, and the residue was purified by flash chromatography (silica gel, light petroleum) (40−60 °C):diethyl ether = 3:1, v/v; $R_f = 0.75$) to yield a bright yellow-green oil as a major product (yield 65%): ^{1}H NMR ($CDCl_3$, 270 Hz) δ 3.19 (d, 2 H, $J = 6.59$ Hz, CH_2), 5.74 (m, 1 H, H-6), 6.19−6.25 (m, 2 H, H-4,5), 6.53 (d, 1 H, $J = 11.72$ Hz, H-3), 7.07−7.37 (m, 5 H, aromatic Hs), 14.09 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 43.73 (C-7), 115.35, 129.41, 120.50, 124.12, 124.82, 128.83, 129.39, 129.41, 135.23, 142.35 (C-2), 189.35 (C=O); ^{15}N NMR ($CDCl_3$) δ −213.6; MS *m/e* 212 (M^+), 120 ($M^+ - C_6H_5NH$), 106 ($M^+ - C_6H_5NHN$), 91 ($C_6H_5N^+$), 77 ($C_6H_5^+$); UV (DMSO) $\lambda_{max} = 415$ nm; exact mass calcd for $C_{13}H_{12}N_2O$ (M^+) 212.0945, found 212.0988. Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.55; H, 5.70. Found: C, 73.14; H, 5.89.

In this experiment, **16a** was also isolated as a minor product (5%, $R_f = 0.1$) using the same eluent system.

2-(*p*-Methylphenylhydrazono)cyclohepta-3,5-dien-1-one (15b): prepared as above, bright yellow oil (yield 60%); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 2.32 (s, 3 H, Me), 3.17 (d, 2 H, $J = 6.71$ Hz, CH_2), 5.73 (m, 1 H, H-6), 6.17−6.25 (m, 2 H, H-4,5), 6.53 (d, 1 H, $J = 11.60$ Hz, H-3), 7.13 (d, 2 H, $J = 8.02$ Hz, aromatic Hs), 7.24 (d, 2 H, $J = 8.02$ Hz, aromatic Hs), 14.14 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 20.90 (Me), 43.67 (C-7), 115.35, 120.41, 124.44, 128.78, 129.36, 129.96, 133.94, 134.81, 140.01 (C-2), 188.97 (C=O); MS *m/e* 226 (M^+), 120 ($M^+ - CH_3C_6H_4NH$), 106 ($M^+ - CH_3C_6H_4NHN$), 105 ($CH_3C_6H_4N^+$), 91 ($CH_3C_6H_4^+$); UV (DMSO) $\lambda_{max} = 422$ nm; exact mass calcd for $C_{14}H_{14}N_2O$ (M^+) 226.1106, found 226.1074.

2-(*p*-Methoxyphenylhydrazono)cyclohepta-3,5-dien-1-one (15c): prepared as above, bright yellow-orange oil (yield 65%); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 3.16 (d, 2 H, $J = 6.71$ Hz, CH_2), 3.79 (s, 3 H, OMe), 5.76 (m, 1 H, H-6), 6.16−6.24 (m, 2 H, H-4,5), 6.52 (d, 1 H, $J = 11.72$ Hz, H-3), 6.88 (d, 2 H, $J = 9.03$ Hz, aromatic Hs), 7.13 (d, 2 H, $J = 9.03$ Hz, aromatic Hs), 14.05 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 43.55 (C-7), 55.54 (OMe), 114.75, 120.31, 124.18, 128.76, 129.38, 129.59, 135.54, 135.99, 140.53 (C-2), 188.58 (C=O); MS *m/e* 242 (M^+), 121 ($M^+ - CH_3OC_6H_4NH$), 120 ($M^+ - CH_3OC_6H_4NHN$ or $CH_3OC_6H_4N^+$), 107 ($CH_3OC_6H_4^+$); exact mass calcd for $C_{14}H_{14}N_2O_2$ (M^+) 242.1055, found 242.1049.

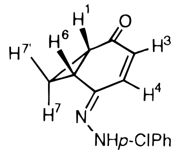
2-(*p*-Chlorophenylhydrazono)cyclohepta-3,5-dien-1-one (15d): prepared as above, green-orange oil (yield 60%); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 3.20 (d, 2 H, $J = 6.71$ Hz, CH_2), 5.76 (m, 1 H, H-6), 6.20−6.28 (m, 2 H, H-4,5), 6.50 (d, 1 H, $J = 11.90$ Hz, H-3), 7.24−7.31 (m, 4 H, aromatic Hs), 14.01 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 43.75 (C-7), 116.39, 120.60, 125.34, 128.85, 128.96, 135.56, 138.81, 139.91, 140.05 (C-2), 189.79 (C=O); MS *m/e* 248 (M^+ for ^{37}Cl), 246 (M^+ for ^{35}Cl), 127 ($M^+ - ClC_6H_4NH$), 125 ($M^+ - ClC_6H_4NHN$ or $ClC_6H_4N^+$), 120 ($ClC_6H_4^+$); exact mass calcd for $C_{13}H_{11}ClN_2O$ (M^+) 246.0560, found 246.0531.

2,7-Bis(phenylhydrazono)cyclohepta-3,5-dien-1-one (16a). Cyclohepta-1,3,5-trien-1-ol (**1**) was allowed to react with 2 equiv of benzenediazonium ion **10a** as described above for the reaction with 1 equiv but with a longer reaction time (50 min). The product **16a** shows a purple color on the silica gel column and was isolated as a dark red solid in the same way as described above (yield 35%): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.10 (d, 1 H, $J = 12.91$ Hz, H-3 or H-4), 6.58 (d, 1 H, $J = 12.91$ Hz, H-3 or H-4), 6.77−6.99 (m, 2 H, H-4,5), 7.06−7.46 (m, 10 H, aromatic Hs), 10.77 (br s, 1 H, nonchelated NH), 14.49 (br s, 1 H, chelated NH); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 112.87, 113.96, 115.16, 121.43, 123.80, 126.70, 129.05, 129.38, 131.90, 135.32, 139.23, 142.00, 143.62, 143.75, 186.34 (C=O); ^{15}N NMR (DMSO-d_6, 270 MHz) δ −20.5, −42.8, −209.8, −224.6; MS *m/e* 316 (M^+), 224 ($M^+ - C_6H_5NH$), 211 ($M^+ - C_6H_5NHN$), 91 ($C_6H_5N^+$), 77 ($C_6H_5^+$); exact mass calcd for $C_{19}H_{16}N_4O$ (M^+) 316.1317, found 316.1287. Anal. Calcd for $C_{19}H_{16}N_4O$: C, 72.14; H, 5.10. Found: C, 72.14; H, 5.22.

2,7-Bis(*p*-methylphenylhydrazono)cyclohepta-3,5-dien-1-one (16b): prepared in the same way as above, dark red solid (yield 40%); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 2.25 and 2.28 (*p*-Me), 6.07 (d, 1 H, $J = 13.12$ Hz, H-3 or H-4), 6.54 (d, 1 H, $J = 13.12$ Hz, H-3 or H-4), 6.71−6.95 (m, 2 H, H-4,5), 7.10 and 7.23 (d, 2 H, $J = 8.54$ Hz, aromatic Hs), 7.18 and 7.33 (d, 2 H, $J = 7.33$ Hz, aromatic Hs), 10.68 (br s, 1 H, nonchelated NH), 14.53 (br s, 1 H, chelated NH); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 20.37 and 20.26 (*p*-Me), 112.57, 113.93, 115.10, 126.35, 129.50, 129.85, 130.28, 131.77, 133.06, 134.98, 138.86, 139.70, 141.52, 143.75, 186.31 (C=O); MS *m/e* 344 (M^+), 238 ($M^+ - CH_3C_6H_4NH$), 224 ($M^+ - CH_3C_6H_4NHN$), 105 ($CH_3C_6H_4N^+$), 91 ($CH_3C_6H_4^+$); exact mass calcd for $C_{21}H_{20}N_4O$ (M^+) 344.1629, found 344.1609.

15a,b and **16a,b** were also isolated from the diazo-coupling reactions of cyclohepta-1,3,5-trien-3-ol (**3**) under similar conditions. ^{15}N-Enriched samples of **15a** and **16a** were prepared from ^{15}N-enriched aniline which was in turn prepared by nitration of benzene with nitric acid (40% ^{15}N) followed by reduction with a mixture of tin and concentrated hydrochloric acid.

5-(*p*-Chlorophenylhydrazone)bicyclo[4.1.0]hept-3-en-2-one (24d): yellow-orange solid; mp 135−37 °C; ^{1}H NMR (methanol-d_4, 270 MHz) δ 1.01 (m, 1 H, $J_{7,7'} = 4.31$ Hz, $J_{7,6} = 5.27$ Hz, $J_{7,1} = 5.48$ Hz, H-7), 1.72 (m, 1 H, $J_{7',6} = 9.49$ Hz, $J_{7',1} = 8.50$ Hz, H-7′), 2.23 (m, 1 H, $J_{6,1} = 7.16$ Hz, $J_{6,3} = 1.71$ Hz, H-6), 2.74 (m, 1 H, $J_{1,4} = 1.95$ Hz, H-1), 5.84 (d, 1 H, $J_{4,3} = 101.7$ Hz, H-4), 6.95 (d, 1 H, H-3), 7.23 (s, 4 H, aromatic); ^{13}C NMR (67.8 MHz, methanol-d_4) δ (assignment based on ^{1}H−^{13}C COSY spectrum) 14.72 (C-7), 15.51 (C-6), 25.96 (C-1), 116.02 (aromatic), 124.09 (C-3), 126.81 (aromatic), 130.06 (aromatic), 141.20 (aromatic), 144.18 (C-4), 144.75 (C-5), 199.23 (C-2); HRMS for $C_{13}H_{11}ClN_2O$ calcd 246.0560, found 246.0533. Anal. Calcd for $C_{13}H_{11}ClN_2O$: C, 63.55; H, 4.10; Cl, 14.43; N, 11.40. Found: C, 63.47; H, 4.61; Cl, 14.41; N, 11.69.



24d

Kinetic Studies. Enol solutions were freshly prepared as described in the previous section. The relative amount of enol and ketone was estimated from the ^{1}H NMR spectroscopic data. Once the conversion of the trimethylsilyl ether to the enol form was complete, the NMR solution was immediately diluted to the required concentration with vigorously dried DMSO (freshly doubly distilled over CaH_2) and was used immediately for kinetic studies. For diazo-coupling reaction of enol **1**, the 37% equilibrium mixture of **1** with its keto form cyclohepta-3,5-dien-1-one (**4**) in pure DMSO was also used as a more convenient stock solution of **1**.

The coupling kinetics were studied either on a stopped-flow (HI-TECH SFA-11) accessory linked to a single-beam UV spectrometer (LKB 2238 Uvicord SII) or on a Shimadzu UV-250 spectrometer, monitoring at a fixed wavelength (400 nm). Eighty absorbance data were recorded at selected time intervals and transmitted to an APPLE IIe microcomputer via an IEEE interface for data analysis.

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Supporting Information Available: ^{1}H NMR spectra for the generation of **1**–**3** and ^{1}H–^{13}C HETCO and ^{1}H–^{1}H COSY NMR spectra of **24d** (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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