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Hyperaromatic Stabilization of Arenium Ions: A Remarkable *Cis* Stereoselectivity of Nucleophilic Trapping of β-Hydroxyarenium Ions by Water

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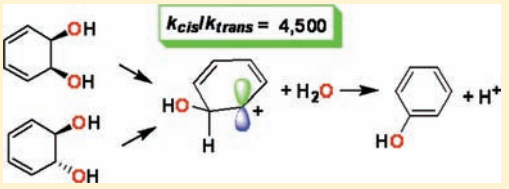
Supporting Information

ABSTRACT: *Cis*- and *trans*-1,2-dihydrodiol isomers of benzene undergo acid-catalyzed dehydration to form phenol. In principle the isomeric substrates react through a common β-hydroxybenzenium (cyclohexadienyl) carbocation. Notwithstanding, the isomers show a large difference in reactivity, k_{cis}/k_{trans} = 4500. This difference is reduced to k_{cis}/k_{trans} = 440 and 50 for the 1,2-dihydrodiols of naphthalene and 9,10-dihydrodiols of phenanthrene, respectively, and to 6.9 for the dihydrodiols of the nonaromatic 7,8-double bond of acenaphthylene. Because the difference in stabilities of *cis*- and *trans*-dihydrodiols should be no more than 2−3-fold, these results imply a high *cis* stereoselectivity for nucleophilic trapping of a β-hydroxyarenium cation by water in the reverse of the carbocation-forming reaction. This is confirmed by studies of the 10-hydroxy-9-phenanthrenium ion generated from aqueous solvolyses of the *trans*-9,10-bromohydrin derivative of phenanthrene and the monotrichloroacetate ester of the phenanthrene *cis*-9,10-dihydrodiol. The *cis* stereoselectivity of forward and reverse reactions is explained by the formation (in the "forward" reaction) of different conformations of carbocation from *cis*- and *trans*-dihydrodiol reactants with respectively β-C−H and β-C−OH bonds in pseudoaxial positions with respect to the charge center of the carbocation optimal for hyperconjugation. Formation of different conformations is constrained by departure of the (protonated) OH leaving group from a pseudoaxial position. The difference in stability of the carbocations is suggested to stem (a) from the greater hyperconjugative ability of a C−H than a C−OH bond and (b) from enhanced conjugation arising from the stabilizing influence of an aromatic ring in the no-bond resonance structures representing the hyperconjugation ($C_6H_6OH^+ \leftrightarrow C_6H_5OH\ H^+$). This is consistent with an earlier suggestion by Mulliken and a demonstration by Schleyer that the benzenium ion is subject to hyperconjugative aromatic stabilization. It is proposed that, in analogy with the terms homoconjugation and homoaromaticity, arenium ions should be considered as "hyperaromatic".

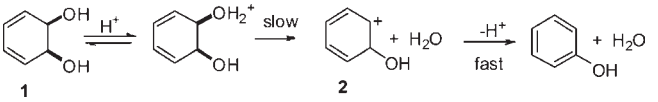


INTRODUCTION

Arene *cis*-dihydrodiols are products of oxidative biotransformations of aromatic molecules in bacterial cells.[12] They are prepared on a large scale[3] by employing bacterial cultures of genetically modified microorganisms, such as *Pseudomonas putida* UV4, where the enzyme responsible for further conversion to catechols during normal metabolism is blocked.[4] Their structure and chirality (e.g., of the dihydrodiols of monosubstituted benzenes) have made them valued as synthons in the preparation of a wide range of molecules including carbasugars, terpenes, inositols, and pyrethroids.[5]

A characteristic reaction illustrated for benzene *cis*-dihydrodiol **1** in Scheme 1 is dehydration in the presence of aqueous acid to yield phenol. Studies of this reaction,[6,7] and of the related dehydration of arene hydrates,[8,9] establish that it proceeds through formation of a carbocation intermediate (e.g., **2**) and that, in contrast to the analogous dehydration of alcohols yielding nonaromatic products, formation rather than reaction of the carbocation is rate-determining.[10] This is because loss of a proton from an arenium ion is accelerated by formation of a highly stabilized aromatic product or, in the case of β-hydroxyarenium ions such as **2**, by a hydride (NIH) shift leading to the keto tautomer of the phenolic product, which rapidly tautomerizes.[11]

Scheme 1



Arene *trans*-dihydrodiols are not accessible by bacterial fermentation but are accessible by chemical synthesis.[12−14] Benzene *trans*-1,2-dihydrodiol **3** for example may be prepared in four steps from 1,4-cyclohexadiene.[12] A remarkable finding is that although, like their *cis* isomers, they undergo acid-catalyzed dehydration to form phenols, they do so much more slowly. Thus, for the benzenedihydrodiols, k_{cis}/k_{trans} = 4500.

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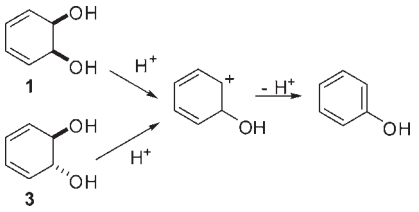
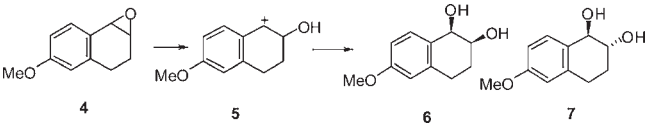
Scheme 2



Scheme 3



This large difference in reactivity is unexpected because apparently the two isomers react through a common carbocation intermediate **2** (Scheme 2). The difference in rates might therefore have been expected to reflect the difference in stabilites of *cis* and *trans* reactants which, based on MP2 calculations[15] and comparisons with indane and tetrahydronaphthalene dihydrodiols,[16] probably amounts to no more than a factor of 2- or 3-fold in reactivity. The much larger difference observed experimentally implies a substantial difference in energies of isomeric transition states.

A corollary of the high *cis*/*trans* reactivity ratio is that trapping of the β-hydroxybenzenium ion **2** with water as a nucleophile in the reverse of the carbocation-forming reaction should be subject to a comparable difference in selectivity, i.e., that a *cis*-dihydrodiol product **1** should be formed at least 1000 times more rapidly than its *trans* isomer **3**. This is a remarkable conclusion because β-hydroxycarbocations have been extensively studied as reactive intermediates, especially in connection with the mammalian metabolism of carcinogenic polycyclic aromatic hydrocarbons.[17] Typically they are formed from acid-catalyzed ring-opening of epoxides and react to form either predominantly *trans* or a mild excess of *cis* product.[18] Thus Whalen has shown that the epoxide of the 1,2-dihydro-7-methoxynaphthalene **4** reacts via benzylic cation **5** to yield 81% *cis*-diol and 19% *trans* product (Scheme 3).[19] Preference for the *cis*-diol **6** over the more stable *trans* isomer **7** was explained in terms of conformational factors or stabilization of the transition state for *cis* attack by hydrogen bonding between the attacking water nucleophile and β-hydroxy group.[16−20]

The ratio of *cis* to *trans* products in this example is small compared with the >1000-fold difference implied for trapping of the β-hydroxybenzenium ion **2**. It seems hardly possible that in aqueous solution such a large difference could be attributed to hydrogen bonding or simple conformational effects. In this paper we compare *cis*/*trans* reactivity ratios for acid-catalyzed dehydration of dihydrodiols of benzene, naphthalene, and phenanthrene and show that the magnitude of the *cis* stereoselectivity is correlated with the aromaticity of the double bond from which the dihydrodiol is derived.

It is not possible to confirm by direct experiment that nucleophilic trapping of a β-hydroxybenzenium ion yields the expected high ratio of *cis*/*trans* dihydrodiol products because the competing loss of a proton to form the aromatic phenolic product is much more favorable thermodynamically and kinetically. The same is true of β-hydroxynaphthalenium ions. However, in the case of the 10-hydroxy-9-phananthrenium ion, a little less than 10% of dihydrodiols is formed in competition with loss of a proton to yield the aromatic product.

Table 1. Rate Constants for Carbocation Formation from Benzene and Phenanthrene Dihydrodiols in Aqueous Solution at 25 °C

substrate	rate constant per OH group (M^{-1} s^{-1})
cis-benzene-1,2-dihydrodiol	0.055[a]
trans-benzene-1,2-dihydrodiol	1.21×10^{-5}
cis-phenanthrene-9,10-dihydrodiol	2.2×10^{-6}
trans-phenanthrene-9,10-dihydrodiol	4.4×10^{-8}

[a] From ref 6.

In this paper we show that the β-hydroxyphenanthrenium ion may be generated as a reactive intermediate from hydrolysis of the *trans*-9,10-bromohydrin of phenanthrene or the mono trichloracetate ester of the phenanthrene-*cis*-9,10-dihydrodiol. HPLC analyses of the products of the reactions of these substrates in water or aqueous acetonitrile confirm that the dihydrodiols formed are very predominantly of *cis* stereochemistry. The same is true of trapping with azide ions, which yields a *cis*-azido alcohol as product.[21]

These results point to an explanation for the difference in reactivity of *cis*- and *trans*-dihydrodiols in terms of hyperconjugative stabilization of an initially formed conformation of the carbocation which is more effective for a suitably oriented C−H than C−OH bond. The unusually large magnitude of the stabilization is suggested to come from the contribution of an aromatic component to the hyperconjugation, as previously proposed by Mulliken[22,23] and Schleyer.[24] As explained below, this reflects the stabilizing presence of an aromatic no-bond structure when the hyperconjugation is represented in terms of limiting resonance forms. In the following paper[25] further experimental evidence and computational studies supporting this interpretation are presented.

RESULTS

Dehydration of Arene Dihydrodiols. Acid-catalyzed dehydrations of *cis*- and *trans*-benzene and naphthalene-1,2-dihydrodiols and *cis*- and *trans*-phenanthrene-9,10-dihydrodiols were monitored spectrophotometrically. For the benzene and phenanthrenene dihydrodiols, the measured or extrapolated second-order rate constants are shown in Table 1. First-order rate constants are listed in Tables S1 and S2 (Supporting Informaion).

As shown in Scheme 4, for reactions of the naphthalene dihydrodiols **8** and their dimethyl ethers **9**, two products are possible corresponding to loss of the OH group at the 1- or 2-position to yield 2- and 1-naphthol or the corresponding ethers as products, respectively. Individual rate constants k_α and k_β were derived by combining the measured rate constants with measurements of product ratios for the two phenols or phenolic ethers by HPLC or GC. Measured product ratios and factored second-order rate constants for the dihydronaphthalene substrates are summarized in Table 2. First-order rate constants are in Tables S3 and S4.

It is noteworthy that the 2-position of the dihydronaphthalene reactants is consistently more reactive than the 1-position.

Scheme 4

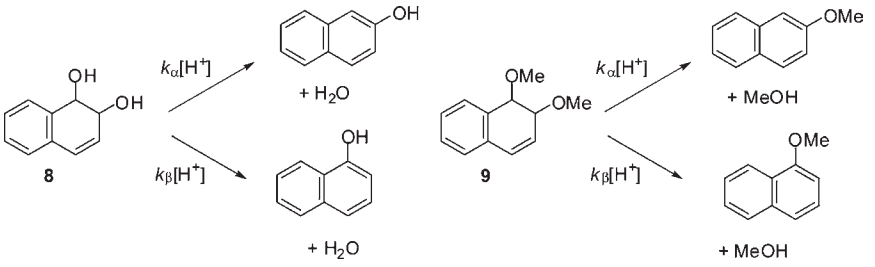
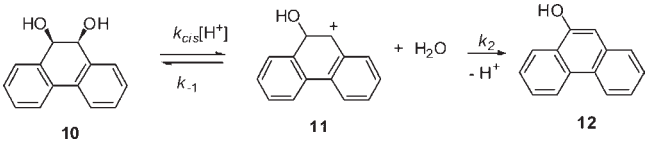


Table 2. Rate Constants and Product Fractions for Reactions of *cis*- and *trans*-2-Hydroxy-1,2-dihydro-1-naphthols 8 and Their Dimethyl Ethers 9 in Aqueous $HClO_4$ at 25 °C

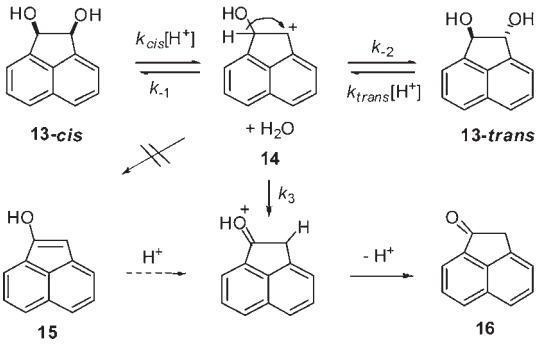
substituent	$[H^+]^a$ (M)	reaction^b time (h)	k_{obs} (M^{-1} s^{-1})	reaction at 1-position (%)	reaction at 2-position (%)	k_α (M^{-1} s^{-1})^c	k_β (M^{-1} s^{-1})^d
cis-1,2-OH, **8-*cis***	0.1	5	1.48×10^{-3}	4.7	95.3	7.0×10^{-5}	1.41×10^{-3}
trans-1,2-OH, **8-*trans***	2.0	15	4.00×10^{-6}	3.8	96.2	1.5×10^{-7}	3.85×10^{-6}
cis-1,2-OMe, **9-*cis***	2.0	3	1.70×10^{-4}	16.4	83.6	2.8×10^{-5}	1.42×10^{-4}
trans-1,2-OMe, **8-*trans***	2.0	12	9.4×10^{-7}	16.6	83.3	1.6×10^{-7}	7.83×10^{-7}

[a] Acid concentration for product analysis. [b] Reaction time for product analyses. [c] Rate constant for loss of OH or OMe from the 1-position. [d] Rate constant for loss of OH or OMe from the 2-position.

Scheme 5



Scheme 6



The difference is large enough that factored rate constants k_β for the 2-position are significantly more accurate. However, derived reactivity ratios for *cis* and *trans* reactants show rather small differences between the two positions: k_{cis}/k_{trans} = 357 (β) compared with 440 (α) for the diols **8** and k_{cis}/k_{trans} = 181 (β) compared with 175 (α) for the methyl ethers **9**. Thus, while a comparison with benzene and phenanthrene dihydrodiols seems most appropriate for reactions at the 1-position of the naphthalene dihydrodiols, it is unlikely that uncertainty in these measurements has a significant influence on the results.

In the case of the *cis*-phenanthrene-9,10-dihydrodiol **10**, the measured rate constant for formation of phenanthrol **12** requires a minor correction for the reversibility of formation of the 10-hydroxy-9-phenanthrenium ion intermediate **11** (Scheme 5) to yield the rate constant k_{cis} for formation of this ion. The value of k_{-1}/k_2 needed for the correction was determined from partitioning of the carbocation **11** generated by solvolysis of the phenanthrene-9,10-bromohydrin as described below. In principle, formation of the same ion from the *trans*-phenanthrene-9,10-dihydrodiol is also reversible. In practice, as also shown below, the "reverse" reaction yields very predominantly the *cis*-dihydrodiol, which reacts much more rapidly than the *trans*, so the measured rate constant needs no correction.

Isomerization of Acenaphthylene Dihydrodiols. Rate constants for acid-catalyzed carbocation formation from *cis*- and *trans*-7,8-dihydrodiols of acenaphthylene **13-*cis*** and **13-*trans*** were also measured. For these reactants the final product in concentrated solutions of aqueous perchloric acid is acenaphthenone **16**. The obvious pathway for formation of this product is acid-catalyzed dehydration of the dihydrodiols to form acenaphthenol **15**, followed by tautomerization to its keto tautomer. It might then have been expected that, in contrast to reaction of the arene dihydrodiols, and by analogy with dehydration of benzylic alcohols, carbocation formation and isomerization of *cis*- to *trans*-dihydrodiols would be substantially faster than formation of (acenaphthenol and) acenaphthenone. Consistent with this expectation, spectrophotometrically determined rate constants for dehydration of the *cis*- and *trans*-dihydrodiols have similar values in the acid concentration range 4−6 M $HClO_4$ (Table S5). However, HPLC analysis showed that, on the contrary, *cis*−*trans* isomerization was only a little faster than product formation. The most likely explanation for this behavior is that the acenaphthenone is formed directly from a carbocation intermediate by hydride rearrangement, as shown in Scheme 6.

Figure 1 shows the fractions of *cis*- and *trans*-dihydrodiols **13** and acenaphthenone **16** plotted as a function of time for reaction of the *cis* isomer in 6 M perchloric acid at 25 °C. It is clear that the

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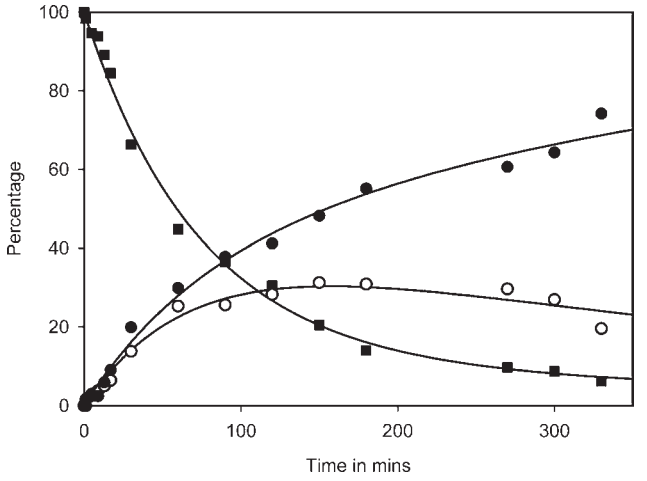
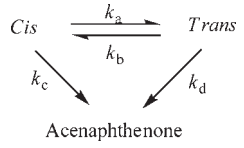


Figure 1. Plots against time of % *cis* (■) and *trans* (○) acenaphthylene-6,7-dihydrodiols (**13-*cis*** and **13-*trans***) and acenaphthenone (**16**, ●) for reaction of the *cis*-dihydrodiol isomer in 6 M aqueous $HClO_4$ at 25 °C. The full lines represent best fits of the points to a series first-order kinetic analysis based on Schemes 6 and 7.

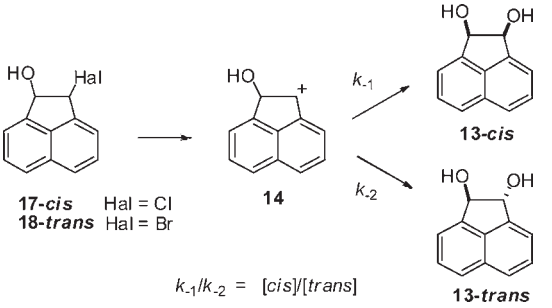
Scheme 7



isomers are equilibrated in competition with formation of acenaphthenone product, which in this case amounts to 70% of the reaction mixture at the longest reaction time. The reactions may be analyzed as series first-order processes involving two exponential terms based on the simplified reaction scheme shown in Scheme 7. Alternatively, the data may be treated by numerical integration. Details of the analysis are provided in the Experimental Section. The HPLC measurements are given in Tables S6−S9. Figure 1 shows a best fit of calculated to experimental data based on numerical integration.

The rate constants k_a, k_b, k_c, and k_d in Scheme 7 may be expressed in terms of the microscopic rate constants of Scheme 6, in which the *cis*−*trans* isomerization and formation of acenaphthenone are shown as occurring through a common 7-hydroxyacenaphthenium ion intermediate, **14**. In principle, this leads to determination of rate constants k_{cis} and k_{trans} and rate constant ratios k_{-1}/k_{-2} and k_{-1}/k_3. In practice, the ratio k_{-1}/k_{-2}, which corresponds in Scheme 6 to the ratio of rate constants for partitioning of the 7-hydroxyacenaphthenium ion **14** between formation of *cis*- and *trans*-dihydrodiol isomers **13-*cis*** and **13-*trans*** was measured independently. As shown in Scheme 8, the ion was generated by solvolysis of bromo- or chlorohydrins of acenaphthylene (**17-*cis*** or **18-*trans***) in water in the absence of acid. The ratio of *cis* to *trans* products formed, which corresponds to k_{-1}/k_{-2}, was measured by HPLC in acetate buffers and in the presence of unbuffered sodium azide (Tables S6 and S7). Both halohydrins furnished the same ratio, $k_{-1}/k_{-2} = 2.3$, and this was used in the kinetic analysis based on Schemes 6 or 7 to reduce the number of unknowns from four to three. Details of this analysis are given in the Experimental Section and Supporting

Scheme 8



Information. The measurements with sodium azide led to trapping of the ion **14** as *cis*- and *trans*-azido alcohols and will be described fully elsewhere.[21] There was no indication of formation of an epoxide (acenaphthylene-6,7-oxide) accompanying solvolysis of the acenaphthylene halohydrins, as was observed for solvolysis of the phenanthrene 9,10-bromohydrin described below.

Evaluation of the rate constants k_a and k_b in Scheme 7 from kinetic measurements at 5 and 6 M $HClO_4$ gave an average value of the constant for equilibration of the isomers, $K_{eq} = [trans]_{eq}/[cis]_{eq} = k_a/k_b = 2.7 \pm 0.2$. Combination of this value with k_{-1}/k_2 (Scheme 6) then gave as a ratio of rate constants for reaction of *cis* and *trans* dihydrodiols to form the common carbocation intermediate, $k_{cis}/k_{trans} = K_{eq}k_{-1}/k_{-2} = 6.9$. This is the most important result of the analysis in that it provides a comparison between values of k_{cis}/k_{trans} for dihydrodiols derived from aromatic and nonaromatic hydrocarbons.

It should be noted that partitioning of the β-hydroxyacenaphthenium cation **14** fomed from hydrolysis of the 7,8-halohydrins (**17-*cis*** or **18-*trans***) in the absence of acid did not lead to formation of acenaphthenone. As indicated below, measurements at 5 and 6 M $HClO_4$ gave some indication that the rate of formation of acenaphthenone increased relative to *cis*−*trans* equilibration of the dihydrodiol isomers (**13-*cis*** and **13-*trans***) as the acid concentration increased. Insofar as there seems little reason to expect the equilibrium ratio of *cis*- to *trans*-dihydrodiols to depend strongly on acid concentration, the above rate constant ratio (k_{cis}/k_{trans}) should be close to that in aqueous solution at 25 °C.

Partitioning of 10-Hydroxy-9-phenanthrenium Ions in Water. Solvolysis of the *trans*-9,10-bromohydrin of phenanthrene **19** gave as principal products 9-phenanthrol **12** and 9,10-phenanthraquinone **20**, together with 8% of predominantly *cis*-phenanthrene-9,10-dihydrodiols **10** (Scheme 9). The phenanthraquinone is an oxidation product of phenanthrol, and its proportion in HPLC samples increased with time. Under the reaction conditions, no phenanthraquinone is formed from the diol products. For the purpose of the analysis, therefore, it was assumed that the sum of concentrations of phenanthrol and phenanthraquinone represents the fraction of phenanthrol initially formed in the solvolyses.[26] Thus the ratio of concentrations of phenanthrol plus phenanthraquinone to *cis*-dihydrodiol was used to determine the ratio of forward to reverse rate constants, $k_2/k_{-1} = 14$, for reaction of the phenanthrenium ion intermediate **11** in the acid-catalyzed dehydration of the *cis*-dihydrodiol, as described above (Scheme 5).

The solvolyses were carried out in acetate buffers at pH 3.70, 4.55, and 5.10. Product analyses under these conditions are

Scheme 9

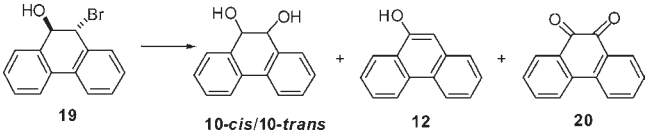


Table 3. Product Percentages from Reaction of *trans*-9-Bromo-10-hydroxy-9,10-dihydrophenanthrene (19) in Acetic Acid Buffers at 25 °C[a]

pH	% *cis*-dihydrodiol, **10-*cis***	% *trans*-dihydrodiol, **10-*trans***	$[c]/[t]^b$	% phenanthrol + quinone, **12** + **20**
5.10	6.65	1.25	5.3	92.1
4.55	6.73	0.80	9.0	92.5
3.70	6.70	0.60	11.2	92.7

[a] Measurements by HPLC at 270 nm with a substrate concentration of 1.0×10^{-3} M. [b] [**10-*cis***]/[**10-*trans***].

summarized in Table 3, and it can be seen that significantly more *cis*- than *trans*-dihydrodiol is formed, but that the proportion of *trans* product increases with pH. This behavior is consistent with formation of part of the *trans*-dihydrodiol from an epoxide intermediate[26] formed in a competing base-catalyzed reaction of the bromohydrin **19**, which should be favored with an increase in pH.

The intermediacy of an epoxide in the formation of the *trans*-dihydrodiol product **10-*trans*** was confirmed by measurements in azide buffers (to be reported in full elsewhere)[21] in which addition of 0.2 M sodium azide caused a decrease in the amount of *trans* dihydrodiol and an accompanying formation of the *trans* isomer of the azido alcohol 9-hydroxy-10-azido-9,10-dihydrophenanthrene. The amount of azido alcohol showed little increase as the concentration of sodium azide was increased from 0.2 to 0.8 M, consistent with its predominant formation from ring-opening of the epoxide and complete conversion of the epoxide to azido alcohol at >0.2 M concentration of sodium azide.

If this assessment is correct, the ratio of *cis*- to *trans*-dihydrodiols of 11.7 in Table 3 at the lowest pH represents a minimum value. This was confirmed by examination of phenanthrol and dihydrodiol products from the solvolysis of the monotrichloroacetate ester **21** of the *cis*-dihydrodiol of phenanthrene **10** (Scheme 10). These products are shown in Table 4 for solvolysis in water and acetonitrile−water mixtures. For this substrate there is no possibility of forming an epoxide. A complication is that there is an additional pathway to *cis*-dihydrodiol **10-*cis*** from hydrolysis of the trichloroacetate ester arising from attack of water at the carbonyl group. However, on the assumption that the ratio of diol to phenanthrol products formed from a phenanthrenium ion intermediate (**11**) is similar to that from the intermediate in the hydrolysis of the bromohydrin (**19**), the large fraction of phenanthrol in the products implies that a substantial proportion of the *cis*-dihydrodiol arises from attack of water on a phenanthrenium ion intermediate of the solvolysis reaction rather than the ester hydrolysis pathway. No *trans* isomer was observed, and from the minimum amount that could have been detected it was inferred that the ratio of *cis*/*trans* product from trapping the phenanthrenium ion must be ≥20.

Scheme 10

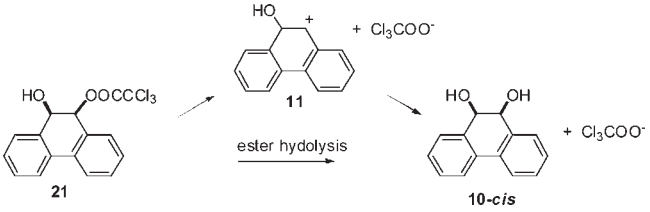


Table 4. Fractions of *cis*-Phenanthrene-9,10-dihydrodiol (10-*cis*) Formed from Solvolysis and Hydrolysis of *cis*-9-Trichloroacetoxy-10-hydroxy-9,10-dihydrophenanthrene (21) in Aqueous Acetonitrile at 25 °C[a]

% MeCN (v/v)	0	30	50	70	90
% *cis*-dihydrodiol[b]	21.2	15.6	9.72	6.04	3.09

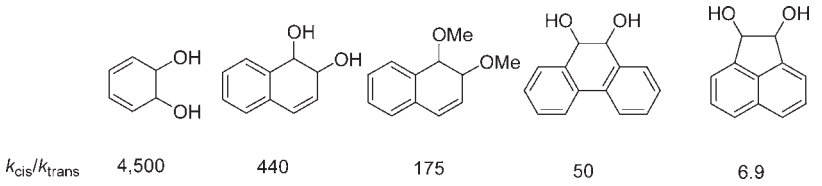
[a] Measurements by HPLC at 270 nm with a substrate concentration of 1.14×10^{-3} M. [b] The other products are phenanthrol **12** and phenanthraquinone **20**.

Solvolysis Rate Constants. Rate constant for solvolysis of the halohydrins of phenanthrene and acenaphthylene based on single measurements in aqueous solution were 5.8×10^{-3} s^{-1} for the *trans*-9,10-bromohydrin of phenanthrene **19**, $(9.6 \pm 1.0) \times 10^{-5}$ s^{-1} for the *cis*-7,8-chlorohydrin of acenaphthylene **17-*cis***, and $(1.48 \pm 0.15) \times 10^{-3}$ s^{-1} for the *trans*-bromohydrin **18-*trans*** of acenaphthylene. Solvolysis of the *cis*-trichloroacetate ester **21** in water occurred with a rate constant 1.9×10^{-3} s^{-1}. Rate constants for the phenanthrene derivatives were determined spectrophotometrically and for the acenaphthylene halohydrins from HPLC measurements given in Table S8. For the phenanthrene substrates, it is at first surprising that the phenanthrene *trans*-bromohydrin is only 3 times as reactive as the trichloroacetate ester, despite bromide being a much better leaving group than trichloroacetate ion. This probably reflects the different relative configurations of the two compounds and the greater reactivity of *cis* than *trans* stereochemistry for S_N1 reactions yielding an arenium ion, which is the principal topic of this paper.

DISCUSSION

Cis*/*Trans* Rate Ratios (k_{cis}/k_{trans}) for Arene Dihydrodiols.** Reactivity ratios for the acid-catalyzed dehydration of *cis*- and *trans*-dihydrodiols of benzene, naphthalene, and phenanthrene are shown in Chart 1, together with the corresponding ratio for the dihydrodiols of acenaphthylene. The rate constants refer to rate-determining carbon−oxygen bond-breaking of the *O*-protonated reactants to form carbocation intermediates. As explained in the Introduction, this is the rate-determining step of the directly measured dehydration reaction of the arene dihydrodiols. For the dihydrodiols of acenaphthylene, the ratio of rate constants was accessed indirectly from measurements of the ratio of *cis*- and *trans*-dihydrodiol products (**13-*cis and **13-*trans***) formed from reaction with water of the acenaphthylenium ion **14** generated from a bromo- or chlorohydrin precursor and the equilibrium constant between *cis* and *trans* isomers. The dihydrodiols of acenaphthylene were chosen for the comparison as being both representative of dihydrodiols of nonaromatic double

Chart 1. *Cis*/*Trans* Rate Ratios for Acid-Catalyzed Carbocation Formation from Arene Dihydrodiols



bonds and otherwise similar in structure to the "aromatic" dihydrodiols.

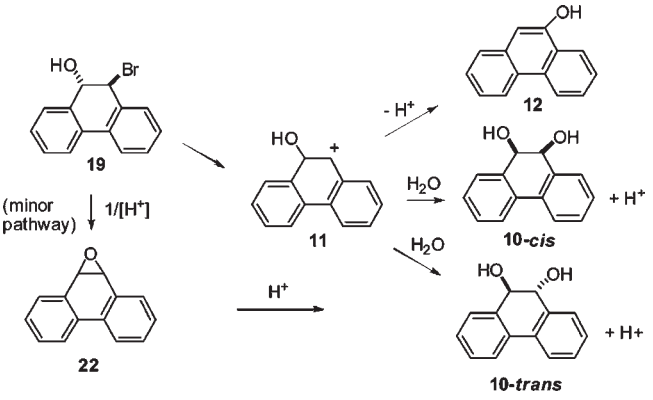
The comparison of values of k_{cis}/k_{trans} in Chart 1 illustrates their striking dependence on the aromatic character of the double bond from which the dihydrodiol is derived. Thus k_{cis}/k_{trans} decreases from 4500 for the dihydrodiols of benzene to 440 and 50 for those of naphthalene and phenanthrene and to 6.9 for those of acenaphthylene. The last comparison includes a factor of 3.0 arising from the difference in stabilities of the *cis* and *trans* dihydrodiol reactants, and this difference seems to be typical of such isomers,[16,27] for which measurements range from 4.3 for the 7,8-dihydrodiol of 4-methoxyacenaphthylene[27] to 1.5 for the 1,2-dihydrodiol of 6-methoxytetrahydronaphthalene.[16] A comparison of the naphthalene dihydrodiols with *cis*- and *trans*-1,2-dimethoxy-1,2-dihydronaphthalene, for which k_{cis}/k_{trans} = 175 (Table 2 and Scheme 4), suggests that the high *cis*/*trans* rate ratios are characteristic of β-oxygen substituents in general rather than specifically hydroxyl groups. The *cis*/*trans* rate ratios refer to the 1-position in the case of the dihydronaphthalenes, but similar ratios are observed for reactions at the 2-position (366 and 180 for 1,2-$(OH)_2$ and 1,2-$(OMe)_2$, respectively).

Before attempting to interpret the observed magnitudes and variation in k_{cis}/k_{trans}, we recall an implication of the small difference in stabilities of *cis*- and *trans*-dihydrodiol isomers noted in the Introduction, that the major part of the reactivity difference between the isomers should be expressed in the reverse reaction with water of a carbocation intermediate common to the reaction of *cis* and *trans* isomers for which the stereochemical difference of the reactants has been lost.

In principle, the carbocations may be generated from solvolysis reactions of diol derivatives with better leaving groups than OH at a sufficiently mild pH that the dehydration reaction does not occur. This is not practicable for the carbocation intermediates from the dehydration of benzene and naphthalene dihydrodiols because the carbocation loses a proton to form phenol or naphthol much more rapidly than it undergoes a nucleophilic reaction with water. However, in the case of phenanthrene 9,10-dihydrodiols, the carbocation leads not only to loss of a proton to form phenanthrol but also to competing nucleophilic attack to form *cis*- and *trans*-dihydrodiols.

Nucleophilic Trapping of the 10-Hydroxy-9-phenanthrenium Ion 11. The required carbocation may be generated solvolytically from reactions of the *trans*-9,10-bromohydrin of phenanthrene **19** or 9-monotrichloracetate of *cis*-9,10-dihydrodiol **21**. There is also extensive literature data on its formation from acid-catalyzed ring-opening of phenanthrene 9,10-oxide **22**[11,25,28] and its benzoannelated analogues,[11] to which we return below. In this work examination of the products of hydrolysis in aqueous solution of the bromohydrin **19** by HPLC showed, in addition to 9-phenanthrol **12**, 7% of *cis*-phenanthrenedihydrodiol **10-*cis***. The latter product we infer was derived from

Scheme 11



stereoselective nucleophilic attack of water on the 10-hydroxy-9-phenanthrenonium ion **11**, as shown in Scheme 11.

In practice, the 9-phenanthrol **12** in Scheme 11 is accompanied by its oxidation product 9,10-phenanthraquinone **20**, which was presumed to be formed from it.[26] More importantly, a small fraction of *trans*-dihydrodiol **10-*trans*** is also formed. However, the amount of *trans*-dihydrodiol depends on the pH, increasing at higher pH. From this dependence, and from the observation that the fraction of *trans*-dihdyrodiol is reduced by the addition of azide ion, it was inferred that this isomer was formed partly via conversion of the bromohydrin to phenanthrene-9,10-oxide **22**, followed by opening of the epoxide ring as shown in the lower pathway of Scheme 11. Studies of the pH dependence of products from the ring-opening of phanthrene oxide in aqueous solution by Bruice[28] and Whalen[26] have shown that, at the relevant pH, about 15% of *trans*-dihydrodiol is formed, in addition to phenanthrol as the predominant product and a small amount of *cis*-dihydrodiol.

From measurements at low enough pH to prevent formation of an epoxide, or in the presence of 0.2 M or greater concentration of sodium azide which traps the epoxide as an azido alcohol,[21] the ratio of *cis*/*trans*-dihydrodiols [**10-*cis***]/[**10-*trans***] arising from solvolysis of the *trans*-bromohydrin is 14.4 ± 1.9. The predominant formation of *cis*-dihydrodiol is confirmed by HPLC analysis of the products of solvolysis of the 9-trichloroacetate ester of phenanthrene-9,10-dihydrodiol (**21**), a reaction which cannot lead to formation of an epoxide. While part of the *cis*-dihydrodiol formed must arise from direct hydrolysis of the trichloroacetate ester through water attack at the carbonyl group (Scheme 10), provided that the ratio of diol/phenanthrol formed from a carbocation intermediate (**11**) is similar to that from the intermediate in the hydrolysis of the bromohydrin **19**, the large fraction (79%) of phenanthrol in the products confirms that the major part of the reaction proceeds via the carbocation. Failure to detect the formation of any *trans*-dihydrodiol in this case implies that the ratio of *cis*/*trans* products is ≥20. This indeed is greater

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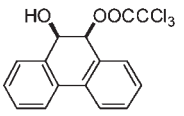
than the ratio of dihydrodiols formed from the *trans*-bromohydrin, for which the *trans* isomer was clearly detectable. It is noteworthy too that trapping with azide ion led to the formation of no *trans*-azido alcohol from trichloroacetate ester.[21]



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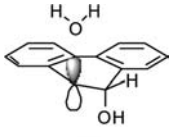
23

For comparison, an independent study of solvolysis of the methylated bromohydrin *trans*-9-methoxy-10-bromo-9,10-dihydrophenanthrene **23**, for which there is also no possibility of forming an epoxide, gave a ratio of *cis*- to *trans*-9-methoxy-10-hydroxy-9,10-dihydrophenanthrene products of 14 ± 2.[21] The measured reactivity ratio for dehydration of these solvolysis products was k_{cis}/k_{trans} = 50 ± 20. The large uncertainty in this ratio derives in part from the need to separate the dehydration reaction from the competing acid-catalyzed loss of methanol.[21]

It is clear that these results are consistent with the high *cis*/*trans* reactivity ratio for acid-catalyzed dehydration of the 9,10-dihydrodiols of phenanthrene **10** if allowance is made for a reasonable difference in stability of the isomeric reactants. A trapping ratio of 14 between nucleophilic attack of water on the 9-hydroxy-10-phenanthrenonium ion **11** to yield *cis*- and *trans*-dihydrodiols implies a rather high ratio of 55/14 = 3.9 for the equilibrium between these diols. However, as we have seen, the ratio is measurably less if based on trapping of the carbocation generated from solvolysis of the *cis*-trichloroacetate ester of phenanthrene-9,10-dihydrodiol **21** rather than 9,10-*trans*-bromohydrin **19**.

Indeed a much larger discrepancy is apparent if we compare the carbocation generated from these substrates with that from acid-catalyzed ring-opening of phenanthrene-9,10-oxide **22**.[11,26] This reaction too has been presumed to occur with the intermediacy of the 9-hydroxy-10-phenanthrenonium ion **11**. However, in contrast to the solvolytic reactions, the predominant dihydrodiol is not the *cis* isomer but the *trans*. In the pH range of our own studies (3.5−5.5), the products comprise 15% *trans*-dihydrodiol, ∼5% *cis*-dihydrodiol, and 80% phenanthrol.[26] This is markedly different from the product distribution from the bromohydrin **19** (7% *cis*- and <0.5% *trans*-dihydrodiol) despite the fact that formally the same carbocation intermediate is formed. In methanolic solution the fraction of *trans*-9-methoxy-10-hydroxy product from acid-catalyzed ring-opening of phenanthrene oxide increases to 54% (and *cis* to 9%).[11]

Differences in product distribution from carbocations generated from epoxide and halohydrin precursors have been well documented by Whalen.[26,29−31] Sayer has suggested that acid-catalyzed ring-opening of the epoxide yields intitially a carbocation in an unstable conformation (**24**) which is trapped by water to form a *trans*-dihydrodiol in competition with conversion to a more stable conformer which gives mainly the *cis* isomer.[11] This is consistent with an interpretation offered for the predominant formation of *trans*-diols from hydrolysis of benzylic epoxides which ring-open to form relatively unstable carbocations.[19]



24

An alternative possibility is that the *trans* product arises from nucleophilic attack on the protonated epoxide, leading to a concerted mechanism for ring-opening. This would be consistent with the probable instability of the 9-hydroxy-10-phenanthrenium ion intermediate **11**.[7,21] However, it is not easily reconciled with the absence of a significant S_N2 pathway for hydrolysis of the 9,10-bromohydrin **19** implied by a lack of kinetic dependence on the strongly nucleophilic azide ion.[21] Such a combination of poorer leaving group and stronger nucleophile should allow detection of a bimolecular reaction.

Also consistent with the relative instability of the 9-hydroxy-10-phenanthrenium ion, particularly for a conformation in which the OH group occupies a pseudoaxial position (see below), is the probability that nucleophilic trapping of the ion occurs at or close to the limit of solvent relaxation.[7,21] Whalen has suggested that in these circumstances the reaction may reflect the structure of the solvation shell of the reactant or the presence of a "preassociated" solvent molecule in the solvation shell of the carbocation.[20] Indeed the discrepancy in behavior is consistent with the established principle that a leaving group may provide some protection from "frontside" attack for a short-lived carbocation. As illustrated in structure **24**, in the case of the epoxide this naturally leads to formation of *trans* product from the initial conformation of the carbocation.

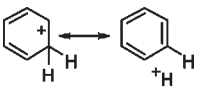
While we do not illustrate the corresponding conformations of carbocation (ion pairs) from reaction of the bromohydrin and trichloroacetate ester, it is evident that shielding from the departing bromide ion in the former case would lead to *cis* product. We will see below that the trichloroacetate ester is expected to yield directly a stable conformation for the carbocation, in which a hyperconjugating hydrogen in a β-axial position renders it uniquely prone to nucleophilic trapping leading to *cis* product. In terms of Sayer's account of ring-opening of phenanthrene oxide, this would also correspond to the more stable structure into which the initially formed conformation from the epoxide (**24**) was converted in competition with trapping as *trans*-dihydrodiol **10-*trans*** and 9-phenanthrol **12**.[11]

Hyperconjugation of Arenium Ions. The above results confirm that there is a complementary relationship between *cis*/*trans* reactivity ratios for acid-catalyzed conversion of arene dihydrodiols to β-hydroxycarbocations and the *cis*/*trans* selectivity of nucleophilic attack by water (and azide ion[21]) on the ions themselves. Similar product ratios of *cis*/*trans* dihydrodiols and azido alcohols from the trapping reactions implies that the *cis*/*trans* selectivity depends primarily on the influence of the β-hydroxyl group of the carbocation rather than on the nature of the nucleophile or leaving group.

Although the complementary relationship between reactivity and product partitioning is established only for the 10-hydroxy-9-phenanthrenium ion **11**, it is a reasonable inference that it applies also to β-hydroxybenzenium and -naphthalenium ions, even though nucleophilic trapping of these cations cannot be observed directly because of competing loss of a proton to form the aromatic molecule. This brings us back to the question, why are these rate ratios correlated with the stability of the aromatic molecule from which the dihydrodiols derive?

The small difference in stabilities of the *cis*- and *trans*-arene dihydrodiols themselves implies that differences in reactivity are expressed in the transition states for formation (or in the reverse direction nucleophilic trapping) of a β-hydroxycarbocation intermediate. The dilemma for attempts to interpret the differences is how it can be linked to aromaticity for transition states of reactions in which neither the dihydrodiol reactant nor carbocation intermediate appears to be aromatic.

As briefly indicated in the Introduction, the dilemma may be resolved by recognizing that the carbocation intermediates themselves are "aromatic". This is most simply expressed by writing valence bond resonance structures for hyperconjugation of the CH_2 group of the benzenium ion (**25a** ↔ **25b**). The effectiveness of this resonance can then be supposed to be a consequence of the stabilizing influence of an aromatic ring for the no-bond resonance structure **25b**. As already indicated, the importance of this was recognized by Mulliken at an early stage in his consideration of hyperconjugation.[22] However, it was not possible to assess reliably the magnitude of this stabilization until a much later date. As indicated in the following paper[25] and demonstrated earlier by Schleyer and co-workers,[24] a calculated structure shows the two methylene hydrogens of the benzenium ion to be equivalent, with both implicated in the hyperconjugation, and a stabilization energy about half that of benzene.



25a **25b**

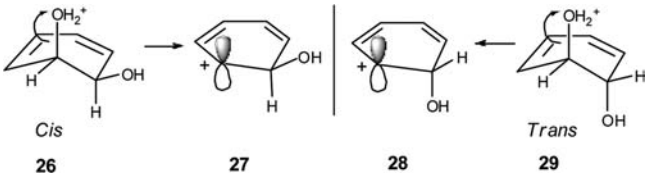
The main purpose of this and the following paper[25] is to present experimental evidence of the aromaticity of arenium ions. An attempt at overall assessment of the work and, to a lesser extent, computational results (including estimates of magnetic ring currents) will also be presented in the following paper. In the present paper we aim to show that the stereochemical results can indeed be interpreted by supposing that the arenium ion intermediates are strongly stabilized by hyperconjugation

Origin of the Dependence of the Reactivity of Arene-1,2-dihydrodiols on Stereochemistry. The very high *cis*/*trans* rate ratios for reaction of vicinal arene dihydrodiols may be understood if reactions of *cis* and *trans* isomers lead initially to different conformations of a β-hydroxy carbocation intermediate. The argument that they do so depends on an S_N1 displacement of the protonated hydroxyl leaving group of the dihydrodiol reactant occurring from a pseudoaxial orientation in the transition state. This was proposed by Goering for carbocation-forming reactions of cyclohexenol derivatives because it maximizes overlap between the incipient orbital of the carbocation and the adjacent π-bond.[32]

As shown in Scheme 12 for reaction of the of the *cis* isomer of the dihydrodiol reactant **26**, departure of the leaving group in an axial trajectory leads directly to a conformation of the carbocation **27** in which the C−H bond of the β-CHOH group is in a pseudoaxial position, favorably oriented for hyperconjugation with the adjacent positive charges. In this conformation the C−OH occupies a pseudoequatorial location. The conformation is consistent with MP2 calculations for the gas phase, which show the tetrahedral carbon to be out of the plane of the cyclopentadienyl cation fragment of the ring by 10.5°.

For reaction of the *trans* isomer **28**, the positions of C−H and C−OH bonds are reversed. Now it is the C_2−OH bond which is in a pseudoaxial position while the C_2−H is pseudoequatorial (**29**). We infer that the difference in reactivity arises as a consequence of the much less favorable hyperconjugating capacity of a C−OH than C−H bond and the fact that the aromatic character of the hyperconjugation makes the energies of the two conformations particularly sensitive to this change. In principle, the experimental results do not distinguish "less favorable hyperconjugating capacity" for C−OH from positive destabilization by this group. However, we defer discussion of this point to the following paper.[25]

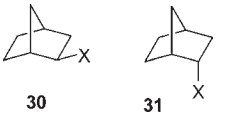
Scheme 12



26 **27** **28** **29**

It seems likely that the unstable conformation of the carbocation initially formed from *trans*-arene dihydrodiols relaxes rapidly to the more stable conformation. Nevertheless the influence of the higher energy of this conformation is expressed in the transition states of reactions leading directly to it. In the reverse reaction of the carbocation with a nucleophile, we infer that this will normally occur by attack of the nucleophile on the more stable conformation and will yield a product in which the bonding of the nucleophile and β-OH is *cis*. However, a fraction of reaction can be expected to occur through the small concentration of the energetically less favorable conformation to yield *trans* product.

An example of analogous behavior well known in carbocation chemistry is provided by the difference in reactivity of norbornyl reactants possessing *exo* or *endo* leaving groups. Although the formation of structurally differentiated carbocation intermediates from *endo* and *exo* reactants **30** and **31** was envisaged by Winstein and Trifan,[33] it seems possible in this case that there is no energy minimum for a less stable (unbridged) conformation of the norbornyl cation and that the difference in reactivity arises from an inability to express fully the stabilization arising from σ-bond delocalization in the *endo* transition state.[34] Nevertheless, the analogy between C−C bond participation in formation of the norbornyl cation from *exo* reactant and C−H participation for formation of a β-hydroxycarbocation from a *cis*-dihydrodiol remains close. Indeed it should be noted that the discrete existence of the conformation **28** is by no means definitely established. Thus attempts to calculate MP2 energies for this conformation without geometric constraint, at least in the gas phase, indicate the absence of a local minimum and give the more stable conformation instead.[25] In this case too, therefore, there may exist only one stable conformation for the carbocation in solution, but nevertheless a marked difference in energy of isomeric transition states.

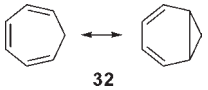


30 **31**

Hyperaromaticity. The term "hyperaromaticity" has been used in the titles of this and the following paper for two reasons. First, it emphasizes the importance of a concept which hitherto has received only limited attention. Second, it captures its key features by implying an analogy between the relationship of hyperaromaticity to hyperconjugation and of homoaromaticity to homoconjugation.

The term "homoaromaticity" was introduced by Winstein[35] as an extension of homoconjugation to apply to structures which,

from their stability and number of electrons involved in homocyclic delocalization, could be inferred to be aromatic. Thus the relationship between homo (homologous) conjugation and aromaticity parallels that between ordinary (π) conjugation and aromaticity. It should be noted that while both homoaromaticity and hyperaromaticity are conveniently described in terms of no-bond resonance structures, as illustrated above for the benzenium ion **26** and below for cycloheptatriene **32** (both of which are six-electron pseudoaromatics), the analogy does not imply a closer relationship than between homo- and hyperconjugation. In general the latter two concepts have been treated as distinct. However, we can recognize that in terms of energetic or magnetic effects, as well as breadth of implications for organic chemistry, a case can be made that hyperaromaticity is of significance comparable to if not greater than that of homoaromaticity.[25]



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SUMMARY

The greater reactivity of *cis*- than *trans*-arene dihydrodiols toward acid-catalyzed formation of β-hydroxy carbocation intermediates, and the marked dependence of this reactivity difference upon the aromatic stability of the arene (benzene 4500 > naphthalene 440 > phenanthrene 50), offers evidence of aromaticity of the carbocations themselves. The difference in reactivity is suggested to stem from (a) the initial formation of intermediates (or at least transition states) in which C−H and C−OH bonds respectively are located in axial positions with respect to the carbocation center optimal for hyperconjugation and (b) the greater hyperconjugating ability of the C−H than C−OH bond.

EXPERIMENTAL SECTION

Materials. The *cis*-1,2-dihydrodiols of benzene and naphthalene were prepared by biotransformations of the parent aromatic molecules using whole cell oxidation by a mutant strain (UV4) of the bacterium *Pseudomonas putida*.[2] They were purchased from the School of Chemistry, Queen's University of Belfast, as solutions in ethyl acetate. The *cis*-dihydrodiols of phenanthrene (9,10)[36] (**10-*cis***) and acenaphthylene (6,7)[37] (**13-*cis***) and the *trans*-dihydrodiols of benzene,[13] naphthalene (1,2),[12] phenanthrene (9,10)[14] (**10-*trans***), and acenaphthylene (6,7)[38] (**13-*trans***) were synthesized using literature methods, as were *cis*-1-chloro-2-hydroxyacenaphthene[39] (**17-*cis***), *trans*-1-bromo-2-hydroxyacenaphthene[40] (**18-*trans***), and the monotrichloroacetate ester of *cis*-9,10-dihydroxy-9,10-dihydrophenanthrene[41] (**21**). The preparation of the *trans*-9,10-bromohydrin of phenanthrene was described in an earlier paper.[1]

Cis- and *trans*-1,2-dimethoxy-1,2-dihydronaphthalenes were prepared as follows.

trans-1,2-Dimethoxy-1,2-dihydronaphthalene. Sodium hydride (40 mg, 1.4 mmol) was added to a solution of *trans*-1,2-dihydroxy-1,2-dihydronaphthalene (0.1 g, 0.61 mmol in DMF, 5 mL). Dimethyl sulfate (0.18 g, 1.5 mmol) was added slowly over 10 min, and the mixture was stirred for 20 h at room temperature. The reaction was quenched with acetic acid (0.1 mL) and diluted with water (20 mL) followed by extraction with diethyl ether (2 × 15 mL). After washing with water and drying (Na_2SO_4), the ether was removed under reduced pressure to yield the crude product, which was purified by column chromatography to give a pale yellow liquid (80 mg, 73%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.38 (s, 3H), 3.48 (s, 3H), 4.2 (m, 1H), 4.28 (d, J = 4.36 Hz, 1H), 6.07 (dd, J = 9.8, 2.95 Hz, 1H), 6.54 (dd, J = 9.7, 1.75 Hz, 1H), 7.12−7.38 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 56.7, 56.8, 76.3, 77.9, 126.9, 127.1, 127.7, 128.1, 128.2, 132.9, 133.0.

cis-1,2-Dimethoxy-1,2-dihydronaphthalene. The preparation was as described for the *trans* isomer above. The product was obtained as a mixure of the two monomethylated products, which were separated by column chromatography (diethyl ether−hexane mixture) to yield the desired product (0.25 g, 43% from 0.5 g of dihydrodiol, R_f = 0.71, 20% ethyl acetate in pentane): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.38 (s, 3H), 3.48 (s, 3H), 4.21 (m, 1H), 4.28 (d, J = 3.9 Hz, 1H), 6.07 (dd, J = 9.9, 2.0 Hz, 1H), 6.53 (d, J = 9.6 Hz, 1H), 7.12−7.38 (m, 4H); m/z (EI) 191.2 (M^+).

Kinetics and Product Analyses. First-order rate constants k_{obs}, for reaction of benzene, naphthalene, and phenanthrene dihydrodiols measured in aqueous solutions of perchloric or hydrochloric acids, are recorded as a function of acid concentration in Tables S1−S3. For benzene and naphthalene *cis*-dihydrodiols, the measurements were in dilute solutions of acid, and second-order rate constants were obtained from the slopes of plots of k_{obs} against acid concentration or the intercepts of plots of $k_{obs}/[H^+]$ against acid concentration. For the corresponding *trans*-dihydrodiols and for the *cis*- and *trans*-9,10-dihydrodiols of phenanthrene, the first-order rate rate constants were measured in concentrated solutions of perchloric acid, and second-order rate constants were extrapolated to dilute solution as (antilogs of) intercepts of plots of $\log(k_{obs}/[H^+])$ against the acidity parameter X_o.[42,43]

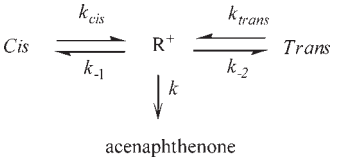
As shown in Scheme 5, for the *cis*-dihydrodiol of phenanthrene $k_{obs} = k_{cis}[H^+]/(1 + k_{-1}/k_2)$, where k_1 is the rate constant for formation of the carbocation **11** and k_2 and k_{-1} correspond to rate constants for reaction of the carbocation to form phenanthrol **12** and re-form reactant, respectively. The ratio k_{-1}/k_2 was determined as described below by generating the 9-hydroxyphenanthrenium ion **11** from solvolysis of the *trans*-9,10-bromohydrin of phenanthrene or the monotrichloroacetate ester of the *cis*-phenanthrene-9,10-dihydrodiol **10** and measuring the product ratio of phenanthrol **12** to dihydrodiol **13** at sufficiently mild pH that the dihydrodiol was not converted to the phenol. Based on formation of 7% *cis*-phenanthrene dihydrodiol and 92% phenanthrol, k_{-1}/k_2 = 1.08.

Because of extrapolation from concentrated acid solutions as plots of $\log(k_{obs}/[H^+])$ against X_o, individual rate constants for phenanthrene dihydrodiols were subject to appreciable uncertainty, $(4.1 \pm 1.1) \times 10^{-6}$ M^{-1} s^{-1} for the *cis*-dihydrodiol and $(8.2 \pm 2.6) \times 10^{-8}$ M^{-1} s^{-1} for the *trans*, thus the implied uncertainty in the *cis*/*trans* ratio is large. However, extrapolation of measured *cis*/*trans* rate constant ratios of 101, 95, and 85 at 6.0, 5.0, and 4.0 M $HClO_4$ leads to a ratio of 47 ± 1.0, which after correction for reversibity of dehydration of the *cis* isomer becomes 50 ± 1.0.

Acenaphthylene Dihydrodiols. A more complex case is presented by the equilibration of *cis*- and *trans*-acenaphthylene dihydrodiols, especially because, as shown in Scheme 6, isomerization is accompanied by irreversible conversion of both isomers to acenaphthenone. However, the reactions are conveniently monitored by HPLC (Tables S9−S12), and a kinetic analysis may be based on Scheme 6 (shown in abbreviated form as Scheme 13), in which k denotes the rate constant for (the presumed) reaction of the 2-hydroxyacenaphthenium ion (R^+) to form acenaphthenone.

As shown in Figure 1, reaction of the *cis*-dihydrodiol as reactant leads to an intital increase in concentration of the *trans* isomer and then a decrease as this is converted to acenaphthenone. Relative concentrations of dihydrodiols and acenaphthenone as a function of time at 5 and 6 M $HClO_4$ for both *cis*- and *trans*-dihydrodiols as reactants are listed in Tables S7 and S8. The acenaphthenone concentration is corrected for a 3:1 greater extinction coefficient than the dihydrodiols at the wavelength of analysis.

Scheme 13



The kinetic behavior can be described in terms of a double exponential dependence of concentration on time for both the *cis*- and *trans*-diols, as shown in eqs 1 and 2. As usual, the coefficients of the exponentials are complicated but can nevertheless be expressed in terms of the four rate constants k_a, k_b, k_c, and k_d in Scheme 7 or the microscopic rate constants shown in Schemes 6 and 13, namely k_{cis} and k_{trans} and rate constant ratios k_{-1}/k_{-2} and k_{-1}/k_3. The relationships between the two sets of rate constants are $k_a = k_{cis}/x$, $k_b = k_{trans}(k_{-1}/k_{-2})/x$, $k_c = k_{cis}(k_3/k_{-2})/x$, and $k_d = k_{trans}(k_3/k_{-2})/x$, where $x = 1 + (k_{-1}/k_{-2}) + (k_3/k_{-2})$. As explained above, the four unknowns are reduced to three by direct determination of $k_{-1}/k_{-2} = 2.3$ from partitioning of the 7-hydroxyacenaphthenium ion (R^+), generated from aqueous solvolysis of acenaphthylene halohydrins, between *cis*- and *trans*-dihydrodiol products.

The kinetic dependence of the concentration of the *cis* isomer may be described by a best fit of eq 1,

$$[cis] = Q\, e^{-\lambda_1 t} + (A - Q)\, e^{-\lambda_2 t} \quad (1)$$

where $Q = (a_1 - (p - q)/2)A/q$, A is the initial concentration of the *cis* isomer as reactant taken as 100 (%), $p = a_1 + b_2$, $q = (p^2 - 4\sqrt{(a_1 b_2 - b_1 a_2)})$, $a_1 = k_{cis}(1 - z)$, $a_2 = wzk_{cis}$, $b_1 = zk_{trans}$, $b_2 = (1 - wz)k_{trans}$, $z = 1/(1 + w + v)$, $w = k_{-2}/k_{-1}$, and $v = k_3/k_{-1}$.

Similarly the kinetic dependence of the *trans* isomer formed from reaction of the *cis* and reacting on to acenaphthenone can be fitted by eq 2,

$$[trans] = P_1\, e^{-\lambda_1 t} + P_2\, e^{-\lambda_2 t} \quad (2)$$

where $P_1 = \{a_1 - (p + q)/2\}Q/b_1$ and $P_2 = \{a_1 - (p - q)/2\}(A - Q)/b_1$. The fraction (%) of acenaphthenone is given by $100 - [cis] - [trans]$. In practice, the numerical integration program 'Berkeley Madonna' used for Scheme 7 proved effective in providing a best fit to concentrations of the *cis*- and *trans*-dihydrodiols and acenaphthenone siumtaneously. Plots of percent reactant, intermediate, and product against time for the *cis*-dihydrodiol reacting in 6 M $HClO_4$ are shown in Figure 1 and illustrate the quality of fit of calculated to experimental data. Values of k_a, k_b, k_c, and k_d based on Scheme 7 are listed in Table S13.

The derived microscopic rate constants at 6 and 5 M $HClO_4$ for *cis*- and *trans*-dihydrodiol reactants are shown in Table 6. The agreement between sets of measurements with *cis*- and *trans*-dihydrodiol isomers respectively as reactants is satisfactory at 6 M $HClO_4$ but not at 5 M. In practice, the slower-reacting *trans* isomer was monitored to only 50% reaction in the 5 M acid. The rate constants based on this measurement are deemed less reliable than for the *cis* reactant and are shown in parentheses. However, both measurements are consistent with the expectation, based on failure to detect acenaphthenone from partitioning of the acenaphthenium ion in water in the absence of acid, that k_3/k_{-1} should decrease with decreasing acid concentration.

Product Analyses. Product analyses for reaction of *cis*- and *trans*-naphthalene-1,2-dihydrodiols (**9**) and their dimethyl ethers were carried out by GC or HPLC to determine the fraction of isomeric phenols and methyl ethers formed from loss of OH or OMe at the 1- and 2-positions of the reactant (Scheme 4). Typically 7−10 mg of substrate in 1 mL of acetonitrile was added to 10 mL of aqueous $HClO_4$. After an appropriate reaction time (usually 10 half-lives) the acid was neutralized with aqueous sodium carbonate and extracted with ethyl acetate followed by concentration of the solution under reduced pressure. Analyses were carried out on a reverse-phase C18 HPLC column with aqueous acetonitrile (1:1 v/v) as mobile phase and a flow rate of 0.25−1 mL/min or, in the case of the *cis*-1,2-dihydrodiol, by GC. Retention times and response factors of products were checked from known samples. Acid-catalyzed dehydration (or loss of MeOH) occurred more readily at the 2-position than the 1-position. The ratio of rate constants for reaction at the 1- and 2- positions, k_α/k_β, is given by the ratio of concentrations of the 2- and 1-substituted phenolic or methyl ether products. These product fractions are recorded in Table S3.

Table 6. Rate Constants ($M^{-1}\,s^{-1}$) from Isomerization of *Cis* and *Trans* Isomers of Acenaphthylene 6,7-Dihydrodiol and Conversion to Acenaphthenone at 5 and 6 M $HClO_4$ at 25 °C (with $k_{-1}/k_2 = 2.3$)

$[HClO_4]$	reactant	K_{eq}	k_{cis}/k_{trans}	k_{cis} (s^{-1})	k_{-1}/k_3
6 M	*cis*	2.3	5.3	4.3×10^{-4}	2.2
6 M	*trans*	2.2	5.0	3.8×10^{-4}	2.5
5 M	*cis*	3.4	7.7	5.0×10^{-5}	3.8
5 M	*trans*	2.6	6.0	(9.8×10^{-5})	(7.3)

Ratios of *cis*- to *trans*-dihydrodiol products formed from solvolyses of halohydrins of phenanthrene and acenaphthylene and from solvolysis of the monotrichloroacetate of phenanthrene 9,10-*cis*-dihydrodiol were also determined by HPLC. In each case the measurements were combined with studies of trapping of the presumed β-hydroxy carbocation intermediates in the solvolysis reactions by azide ions. As already indicated, the azide trapping will be described in a separate paper.[25] However, the ratios of *cis*- to *trans*-dihydrodiols obtained at different concentrations of azide ions for the chloro- and bromo-6,7-halohydrins of acenaphthylene are summarized in Tables S6 and S7.

■ ASSOCIATED CONTENT

Supporting Information. First-order rate constants for acid-catalyzed dehydration of dihydrodiols (Tables S1−S5); product ratios of *cis*- to *trans*-dihydrodiols from solvolysis of acenaphthylene halohydrins (Tables S6, S7); HPLC monitoring of the solvolysis reactions (Table S8); HPLC data (Tables S9−S12) and rate constants (Table S13) for equilibration and reaction of *cis*- and *trans*-acenaphthylene-6,7-dihydrodiols in 5 and 6 M $HClO_4$; and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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