species which reacts with Rh(I). The preceeding mechanistic discussion clearly eliminates this possibility. Furthermore Tobey and West[16] have shown that alcoholysis of C_3Cl_4 does not lead to dichlorocyclopropenone but rather to a mixture of acrylic acid esters via ring opening of an unstable cyclopropane intermediate which could not lead to a product of the type isolated.

On the basis of this proposed mechanism, synthetic studies are currently in progress to prepare metallocyclobutenes similar to intermediate V and to demonstrate the subsequent insertion step. It is interesting to note that, since IV can add to the Rh(I) complex in two ways to produce V as well as its geometric isomer, one may a priori expect a mixture of two products resulting from CO cis migration[3a] into two different Rh—C bonds. In our studies no evidence for the isomeric 2,3-dione has been found, although platinum complexes of this type have been prepared by a different route.[17]

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(6) $Rh(H_2O)Cl(PMe_2Ph)_2(C_4O_2Cl_2)$: monoclinic; $P2_1/c$; unit cell parameters are a = 8.924 (8) Å, b = 18.965 (10) Å, c = 14.775 (12) Å, β = 102.90 (8)°, V = 2445.2 Å^3. The structure was solved by the heavy-atom method and refined by iterative Fourier and least-squares analyses to a final residual of $R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.046$ for the 2878 independent reflections with $I > 2\sigma(I)$.
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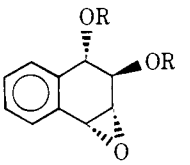
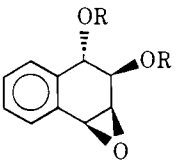
The Importance of Intramolecular Hydrogen Bonding on the Reactivity of Tetrahydro Diol Epoxides

Sir:

The chemistry of the tetrahydro diol epoxides (TDE) of polycyclic aromatic hydrocarbons is presently of much concern. This is due to the fact that these compounds have been proposed to be the ultimate carcinogenic and mutagenic derivatives of the ubiquitous benzo[*a*]pyrene[1] as well as benz[*a*]-anthracene.[2] Both syn- and anti-TDE isomers are produced in the metabolism of benzo[*a*]pyrene through the combined action of cytochrome P-450 and epoxide hydrase.[3] Many workers[4] have suggested that intramolecular hydrogen bonding between epoxide oxygen and hydroxyl group in the syn isomers provides assistance to ring opening. The anti isomer, in its most stable conformation, possesses no such structural feature. The



R = –H (DE-1)
R = –CH_3 (DME-1)



R = –H (DE-2)
R = –CH_3 (DME-2)

relevant syn and anti structures for the compounds of this study are abbreviated as DE-1 and DE-2, respectively. Herein the chemistry[5] of DE-1 and DE-2 is compared with that of their dimethyl ethers (i.e., DEM-1 and DEM-2) to delineate the relative importance of conformation as opposed to internal hydrogen bonding in determining the rates for epoxide ring opening. The NMR coupling constant of H_1 and H_2 of both DE-1 and DME-1 is at ~3 Hz, in accord with their diequatorial conformation, so that the *trans*-hydroxyl and *trans*-methoxyl groups must be diaxial. The J value for both DE-2 and DME-2 is ~9, implying a conformation in which the *trans*-hydroxyl and *trans*-methoxyl groups are diequatorial. These results dictate that the conformation of DE-1 is that of DME-1 and that of DE-2 is the same as DME-2 under the solvent conditions used in these NMR studies.[5]

In the present study we have determined the acid (k_H) and spontaneous or water-catalyzed (k_0) rate constants for solvolysis of DE-1, DE-2, DME-1, and DME-2 and the second-order rate constants for nucleophilic attack of β-mercaptoethanol anion (k_s) upon the various substrates as a function of the composition of dioxane–water mixed solvent. We would expect the effect of any intramolecular hydrogen bonding to be accelerated upon decrease in the protic nature of the solvent. Values of k_H and k_0 (Table I) were obtained from plots of the logarithm of the first-order rate constants (k_{obsd}) of solvolysis vs. the pH values at which the k_{obsd} values were determined. Examination of Table I reveals that in water the k_H values for both DE-1 and DME-1 are less than those for both DE-2 and DME-2, while exactly the reverse is true for the k_0 constants. Conformation, therefore, rather than internal hydrogen bonding, appears to be the feature of importance in determining both the spontaneous and acid-catalyzed solvolysis rate constants in water. (The observation that k_0 for DE-1 is twice that for DME-1 might be interpreted as a small contribution of 0.4 kcal M^{-1} to $\Delta G^{\ddagger}$ due to hydrogen bonding.) Transfer from water to 75% dioxane–water (v/v) has little effect on the ratio of k_H values for *syn*- and *anti*-hydroxyl compounds, while the value of k_H for the *syn*-methoxyl compound is actually enhanced over that for its anti isomer (Tables I and II).[6,7] Again, however, there is no apparent influence of the *syn*-hydroxyl group of DE-1 upon rate. Jerina and co-workers,[8] working with the bay region syn and anti diol epoxides of benzo[*a*]pyrene (BP-1 and BP-2, respectively), have suggested

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Table I. Rate Constants for H_3O^+ Catalyzed (k_H, $M^{-1}\,s^{-1}$) and Spontaneous (k_0, s^{-1}) Solvolysis (30 °C, μ = 1.0 with KCl) and Attack of β-Mercaptoethanol Anion (k_s, $M^{-1}\,s^{-1}$) in 0% (μ = 1.0) and 75% (μ = 0.1) Water–Dioxane (v/v), 30 °C

substrate	k_H[a] 0%	k_H[a] 75%	$k_0 \times 10^5$,[a] 0%	k_s, 0%[a]	k_s, 75%[b]
DE-1	6	0.22	8.5	0.64	3.33
DME-1	5	0.052	4.0	0.13	0.08
DE-2	40	1.90	1.1	0.51	0.18
DME-2	25	0.049	1.1	0.62	0.28

[a] 0% and 75% dioxane–water (v/v). All rate constants were obtained spectrophotometrically (Cary 15, 3-cm path length) at the λ_{max} of the substrates: DE-2, 269 nm; DE-1, 272 nm; DME-2, 271.5 nm; DME-1, 272.5 nm. [b] Reactions were followed by 250 nm.

Table II. Ratios of k_s and k_H Constants as a Function of the Protic Nature of the Solvent

	vol. % dioxane 0	25	50	75
		k_s Ratios		
DE-1/DE-2	1.2	3.2	7.9	18.5
DME-1/DME-2	0.20			0.28
		k_H Ratios		
DE-1/DE-2	0.15			0.12
DME-1/DME-2	0.2			1.0

internal hydrogen bonding to account for the 30-fold greater value of k_0 for BP-1 relative to BP-2. A similar explanation has been offered by Keller et al.[9] to account for the differences in k_H values of BP-1 and BP-2 in 50% (v/v) dioxane–water. We too have suggested internal hydrogen bonding to account for our previous results[4c] with DE-1 and DE-2. In view of our present findings, the influence of internal hydrogen bonding in determining k_H (in either water or water–dioxane) and k_0 (in water) must be *seriously questioned*.

The reaction of β-mercaptoethanol anion with the various substrates was studied under argon in degassed dioxane–water mixtures and the kinetic results of these determinations are presented in Tables I and II. At 0 to 50% dioxane the k_s values were determined from reactions pseudo first order in thiol employing thiol dilutions at several pH values:

$$k_{obsd} = k_H a_H + k_0 + k_s[S_T][K_a/(K_a + a_H)] \quad (1)$$

The slope obtained from plots of k_{obsd} vs. total thiol concentration (i.e., $[S_T]$) were each divided by the fraction of thiol anion to provide k_s. For the k_s values determined in 75% dioxane–water, the reactions were performed under the conditions of pseudo first order in epoxide:

$$k_{obsd} = k_s[\text{epoxide}][K_a/(K_a + a_H)] \quad (2)$$

The values of K_a were determined at each dioxane concentration by spectrophotometric titration and the fitting of plots of thiol anion absorbance vs. pH to theoretical titration curves (pK_a values obtained follow: 0% dioxane, pK_a = 9.23; 25% dioxane, pK_a = 10.10; 50% dioxane, pK_a = 10.60; 75% dioxane, pK_a = 11.68 (pH meter reading)[6]).

Examination of Table I reveals that in pure water the values of k_s for DE-1, DE-2, and DME-2 are essentially identical. There appears to be no assistance to nucleophilic epoxide ring opening by intramolecular hydrogen bonding. The smaller value of k_s for DME-1 may be due to steric hindrance to ring opening by a methoxyl group. In 75% dioxane the value of k_s for DE-1 clearly exceeds the k_s values for the other substrates and again a small steric hindrance is seen in DME-1. It may also be seen from Table I that the value of k_s for DE-1 actually increases on decrease of the protic nature of the solvent. Since water is an excellent hydrogen-bonding solvent, one might have anticipated that, at best, any intramolecular hydrogen bonding between the epoxide oxygen and the hydroxyl group would serve only to buffer the decrease in k_s on decrease in the water content of the solvent. The increase in k_s may reflect a lessened solvation of both epoxy oxygen and hydroxyl groups. This would then allow expression of the entropic advantage of an internal hydrogen bond. The increasing advantage of the *syn*-hydroxyl group participation with decrease in the protic nature of the solvent is best appreciated by comparison of the ratios of k_s for DE-1/DE-2 vs. DME-1/DME-2 (Table II). Inspection of Table II reveals that the ratio of the values of k_s for the methyl derivatives remains invariant with solvent composition. In contrast the value of k_s for the *syn*-hydroxyl isomer increases over that for the *anti*-hydroxyl isomer, in a progressive manner, on decrease in the protic nature of the solvent.

Hydrogen bond assisted nucleophilic attack in mixed organic–aqueous solvents has been proposed to account for the enhanced rate of oxirane ring opening for the antileukemic drug tripdiolide,[10] the analeptic drug picrotoxinin,[11] and epoxy steroids.[12] Jerina and co-workers[4b] have suggested anchimeric assistance in BP-1 and DE-1 (as opposed to BP-2 and DE-2) in nucleophilic addition of *p*-nitrothiol phenolate when employing dry *tert*-butyl alcohol with ~5% Me_2SO. Their preliminary work in water–ethanol had actually shown DE-2 to have a slightly greater reactivity toward nucleophilic attack than DE-1. From our present results we find that, although kinetically absent in the solvolysis reactions, the *syn*-hydroxyl of DE-1 can provide an accelerating effect toward nucleophilic attack but then only in mixed organic–aqueous solvents.

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(6) The glass electrode was calibrated for the 25 and 50% dioxane–water concentrations (pH meter reading minus 0.08 for both concentrations). However, at 75% dioxane a calibration correction was not obtainable and therefore determined pH's are actually pH meter readings. As a result, the same acidic 75% dioxane–water solution (pH 1.74) for determination of k_H and the same bicarbonate–carbonate buffer solution (pH 11.00) for determining the k_s constants were employed for all four substrates. For this reason rate constants in 75% dioxane should be regarded only as relative numbers useful for comparison, not as absolute constants.
(7) Unfortunately, owing to the very small absorbance changes, values of k_0 were not obtainable in 75% dioxane.

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Carbon Acidity. 59. First and Second Ion-Pair Acidity Constants for 9,10-Dihydroanthracene with Cesium Cyclohexylamide[1]

Sir:

Although dimetalated and even more highly metalated hydrocarbons are not uncommon,[2] no equilibrium constants for such higher metalations have previously been measured. We report here both the first and second acidity constants for 9,10-dihydroanthracene (DHA) expressed as pK_{CsCHA} values in the cesium cyclohexylamide (CsCHA)-cyclohexylamine (CHA) system.[3]

The procedure for measuring the spectra of the cesium salts was essentially that used previously,[4] and the relevant data are summarized in Table I. Commercially obtained DHA was purified by recrystallization from ethanol followed by vacuum sublimation. UV analysis showed the presence of <0.01% anthracene. The absorptions of 9,10-dihydroanthracyl 9 anion[5] (DHA^-) and 9,10-dihydroanthracene 9,10 dianion[6] (anthracene dianion, A^{-2}) lie well separated in the visible region with extinction coefficients of comparable magnitude and permit the determination of the pK leading to the dianion. Formation of the dianion with CsCHA is rapid and quantitative; successive additions of base yielded a constant final absorption value with an isosbestic point between the monoanion and dianion peaks. No absorptions due to anthracene radical anion were observed.[7] The λ_{max} values of the tight ion-paired and solvent-separated lithium salts of DHA^- occur at 400 nm and 450 nm, respectively;[8] we find that the cesium salt absorbs at 444 nm. Extrapolating from the ion-pair studies of Hogen-Esch and Smid,[9] this value is about what one would expect for a contact ion pair with a cation of large radius.

The pK measurement technique is based on competitive equilibria with cesium cyclohexylamide (CsCHA) in cyclohexylamine (CHA):[4,10]

$$AH_2 + I_1{}^-Cs^+ \rightleftharpoons AH^-Cs^+ + I_1H \quad (1)$$

$$K_1 = [I_1H][AH^-Cs^+]/[AH_2][I_1{}^-Cs^+] \quad (2)$$

$$\log K_1 = pK_{CsCHA}(I_1H) - pK_{CsCHA}(AH_2) \quad (3)$$

$$Cs^+AH^- + I_2{}^-Cs^+ \rightleftharpoons A^{-2}Cs_2{}^+ + I_2H \quad (4)$$

$$K_2 = [I_2H][A^{-2}Cs_2{}^+]/[AH^-Cs^+][I_2{}^-Cs^+] \quad (5)$$

$$\log K_2 = pK_{CsCHA}(I_2H) - pK_{CsCHA}(AH^-Cs^+) \quad (6)$$

Determination of the second pK_{CsCHA} value involved a more indirect technique than usual because the indicators used and DHA^- absorb at the same wavelength. Therefore, the 444-nm peak had to be factored into the two components by calculating the concentration of A^{-2} from the 633-nm peak and deriving the DHA^- concentration from mass balance with the initial quantity of anthracene (eq 7-9) where ϵ_1, ϵ_2, and ϵ_3 refer to the independently determined extinction coefficients of 9,10-dihydroanthracylcesium (AH^-Cs^+), indicator (I^-Cs^+), and 9,10-dihydroanthracene dicesium ($A^{-2}Cs_2{}^+$) in that order. Several runs were made with each of three indicators, DpTM, DXM, and DmTM, and consistent results were obtained.

Table I. Absorbance and pK_{CsCHA} Values of Indicators and DHA

hydrocarbon,[a] RH	λ_{max} (R^-Cs^+), nm	$10^{-3}\epsilon$	pK_{CsCHA} (per H)[b]
BDPM	573	44.3	30.2
DXM	448	37.7[c]	36.3
DpTM	446	44.0	35.1
DmTM	447	47.9	34.8
DHA	444	24.2	30.3
DHA^-Cs^+	633	18.3	34.1

[a] Abbreviations follow: BDPM, *p*-biphenylyldiphenylmethane; DXM, bis(2,4-dimethylphenyl)methane (or dixylylmethane); DpTM, di-*p*-tolylmethane; DmTM, di-*m*-tolylmethane; DHA, 9,10-dihydroanthracene; DHA^-, 9,10-dihydroanthracyl anion. [b] Error limits are within ±0.2. [c] This value was redetermined and is a correction to the previously published number.[10]

$$[AH^-Cs^+] = [AH_2]_0 - [A^{-2}Cs_2{}^+] \quad (7)$$

$$[I_2{}^-Cs^+] = (Abs_{444} - \epsilon_1[AH^-])/\epsilon_2 \quad (8)$$

$$[A^{-2}Cs_2{}^+] = Abs_{633}/\epsilon_3 \quad (9)$$

The first pK_{CsCHA} of DHA, 30.3, is not significantly different from that previously measured for 9,9-dimethyl-9,10-dihydroanthracene (30.25).[10] This result provides a check on the present experimental technique and shows that the effects of a dimethylmethylene bridge are similar to a simple methylene bridge in this system, but the truly novel result of the present work is the discovery of such a small difference of only 4 pK units between the first and second dissociations; with a pK_{CsCHA} of 34.1, DHA^-Cs^+ is almost as acidic as diphenylmethane itself (pK_{CsCHA} = 33.4).[10]

One factor contributing to this relatively high acidity is the high delocalization of the dianion. Anthracene dianion is a 16-electron system with a considerable paratropic ring current;[11] however, this anti-aromatic character clearly does not seriously offset the net stabilization provided by the delocalized π system and illustrates the point made by Haddon, Kaplan, and Marshall[12] that classification of aromatic character by any one criterion does not necessarily reflect on the other properties. Ring current effects in particular are so sensitive to small perturbations that they have little correlation with thermodynamics.[13]

The other important factor in this system is that the dianion is undoubtedly a contact ion triplet in which the cesium cations are located on opposite sides of the anthracene dianion.[14] The electrostatic stabilization in such a system is clearly of dominating importance. The quantitative resultant of these effects as given in the present experiments also helps to rationalize the polymetalation observed in many organolithium compounds.[2]

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