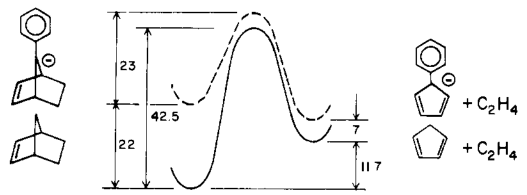

Figure 2. Free energy diagram for norbornene (ref 3a) and approximate free energy diagram for the 7-phenylnorbornenyl anion. Energies are shown in kilocalories per mole.

yield of norbornadiene was obtained.[12] Related Grignard and alkyl lithium reagents have proved to be elusive for synthetic purposes.[13] Base catalyzed exchange studies of norbornenyl systems[14] indicate that the 7-norbornenyl anion is an intermediate with finite lifetime. However, the claim[15] that the 7-norbornenyl anion was generated by oxidative nitrogen loss must be treated with caution, because of the implicit requirement that anion inversion be faster than carbanion quench by solvent water.

A crude analysis of reaction energetics is instructive. Walsh and Wells[3] have established that ethylene loss from norbornene requires 42.5 kcal/mol activation energy (extrapolated to 25 °C). A lower limit of 38 kcal/mol may be inferred for acetylene loss from 7-phenylnorbornadiene.[3d] In striking contrast, the ethylene loss from 7-phenylnorbornenide ion has an activation energy ≤ 23 kcal/mol. A comparison of energetics is shown in Figure 2. The relative energies of the carbanions were estimated from pK_a data and are accurate to ± 3 kcal/mol at best.[16] The significant conclusion to be drawn is that *anions are efficient bond-breaking species* provided the thermodynamics are favorable. Reference 17 lists several recent examples of this principle. A wide variety of classical anionic condensation reactions (e.g., Robinson annulation) are based on this principle as they rely on facile reversibility for their success.[18]

The importance of the counterion in controlling anion reactions has been noted repeatedly.[17b,d,e,i] The preparation and subsequent reaction of 7-norbornenyl Grignard reagents[13] is indicative that counterion control is also significant in the present case. Finally it is interesting to compare the carbanion with its heterocyclic analogues. Diels-Alder reactions are rare in pyrrole chemistry, not because addition is difficult, but because the reverse reaction occurs readily.[19] By contrast furan and especially isobenzofuran are efficient dienes in the Diels-Alder reaction.[20] The combination of lower aromatic stabilization in the diene and the high degree of lone pair localization on oxygen in the adduct are presumably responsible.[21]

We are currently investigating the synthetic and mechanistic potential of the cleavage. Incorporation of an appropriate norbornadiene as a dienophile in a Diels-Alder reaction followed by anion generation and the retroreaction should provide a convenient acetylene equivalent for Diels-Alder processes.

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Elizabeth S. Bowman, Graham B. Hughes,[22] John B. Grutzner*
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received June 11, 1976

Molecular Beam Chemistry: Reactions of Cs^+ with Chlorobenzene and the Electronic State of the Phenyl Cation

Sir:

Crossed molecular beam scattering experiments with Cs^+ on α-, *o*-, *m*- and *p*-chlorotoluene have recently been reported.[1,2] The results suggest that the product $C_7H_7^+$ is benzyl in the first case and tropylium for the others.[3] Moreover, the stripping process responsible for the forward scattering of the $C_7H_7^+$ leaves these ions with little internal excitation, while the repulsive or knock-out process responsible for the backward scattering produces excited benzyl ion in the α case and excited tropylium in the meta and para cases. The data suggest, in fact, that these ions are in their first excited singlet states. Further evidence for the strong electronic correlation in these systems is that over the range of collision energies from 0 to 15 eV, the only products that are observed ($C_7H_7^+$, $C_5H_5^+$, and $C_4H_3^+$) are those which have singlet (ground) states. We report here results of similar experiments with chlorobenzene,

$$Cs^+ + C_6H_5Cl \rightarrow CsCl + C_6H_5^+ \qquad (1)$$

$$\rightarrow CsCl + C_2H_2 + C_4H_3^+ \qquad (2)$$

These reactions, like the chlorotoluene reactions, are endoergic (by 4.4 eV for (1) and 7.7 eV for (2)[4]). The phenyl ion should resemble the tolyl ion, except that rearrangement to a "stable" singlet structure like tropylium is not possible.[5]

The experimental procedure is described in detail elsewhere.[1,6] Briefly, the Cs^+ ion beam and the thermal (300 K) C_6H_5Cl beam sources are mounted from a rotatable platform

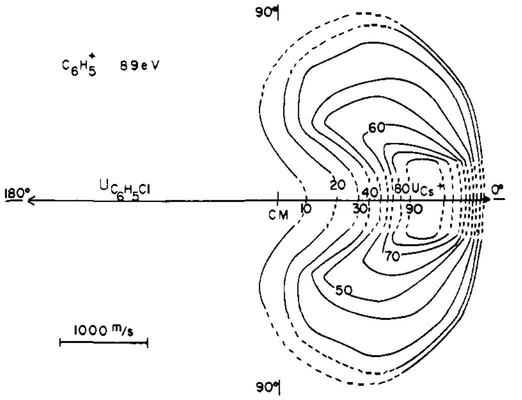

Figure 1. Contour diagram for the $C_6H_5^+$ product. The length of the double arrow represents the initial Cs^+ LAB velocity vector, which because of the small C_6H_5Cl velocities (thermal) is very nearly the relative velocity vector. The direction toward 180° is "forward" and toward 0° is "backward" for C_6H_5Cl with respect to the center-of-mass (CM) of the system. The dashed lines represent contour lines interpreted from angular distribution data alone. The contours are normalized to 100 at the maximum intensity.

which forms the lid of the scattering vacuum chamber. The beams intersect with a 90° angle directly under the center-of-rotation of the lid. Since the neutral beam is directed along the rotation axis, the plane of rotation in which the scattering is measured is perpendicular to the plane defined by the intersecting beams. The full range of the laboratory frame (LAB) scattering angles, Φ, is $-90°$ to $+90°$ with respect to the Cs^+ beam (at $\Phi = 0°$). A stopping potential technique is employed for the product ion energy analysis. The detector is a quadrupole mass spectrometer with a Channeltron electron multiplier operated in the pulse-counting mode.

Angular and recoil energy distributions were measured for reaction 1 at a collision energy of 8.9 eV. A contour diagram of scattering intensity as a function of angle and velocity was then constructed to obtain a "kinematic map" of the scattering process.[1] This is shown in Figure 1. Additional energy distributions were taken at several collision energies to see, roughly, how the map changes with energy. These are shown in Figure 2. Appearance potential measurements were also made of the $C_6H_5^+$ (5.9 ± 0.5 eV) and $C_4H_3^+$ (9.0 ± 0.5 eV) ions, which were the only species observed in this energy range. Reaction 2 appears to be analogous to $C_5H_5^+$ formation from $C_7H_7^+$ in that it is a secondary decomposition reaction from $C_6H_5^+$ and its appearance potential is in fair agreement with the calculated value from the ideal knockout model (9.6 eV).[2]

From Figure 1 one sees that the $C_6H_5^+$ is scattered exclusively backwards in the center-of-mass frame (CM) with respect to the initial direction of chlorobenzene. Evidently, in contrast to the chlorotoluenes, only the repulsive or knockout mechanism is operative in this system. Moreover, there is virtually no intensity in the immediate vicinity of the center-of-mass itself; whereas for the chlorotoluenes there was substantial intensity in this region, attributed to the formation of an ion-dipole complex for slowly recoiling products.[2] This feature and the comparatively narrow angular spread of the $C_6H_5^+$ ions indicate that the repulsive forces dominate at close range to a far greater extent than in the previous systems.

From the spectator stripping model one would predict the appearance potential for forward scattered $C_6H_5^+$ to be 9.7 eV.[1] Thus the absence of forward scattering in Figure 1 may not be unexpected. However, the LAB energy distributions in Figure 2 only show marginal evidence of forward scattering even at 13.6 eV.[7]

Recent calculations[5] of the electronic structure of the phenyl ion have found that the ground state ion is a singlet "σ-type" state, with considerable distortion of the ring. According to the arguments presented in the previous work,[1,2] the absence of complex formation here and the rather narrow backward distributions of products would seem to require such a short reaction time that the singlet reactants yield only singlet $C_6H_5^+$ and (CsCl). This is confirmed by the fact that the only secondary reaction observed also produces singlet products, $C_4H_3^+$ and C_2H_2. One can estimate the endoergicity of reaction 1 from the maximum recoil translational energy of the products. From each of the curves in Figure 2, we find an excess endoergicity of from 1 to 1.5 eV over 4.4 eV (which is computed essentially from ionization potential measurements[4]). Similarly from our appearance potential measurement we also find an excess endoergicity of ~1.5 eV. This would seem to indicate that perhaps the calculations are not correct, and the ground state phenyl ion is the "intuitively" expected triplet state, while the lowest singlet (which we observe) lies 1 to 1.5 eV higher.

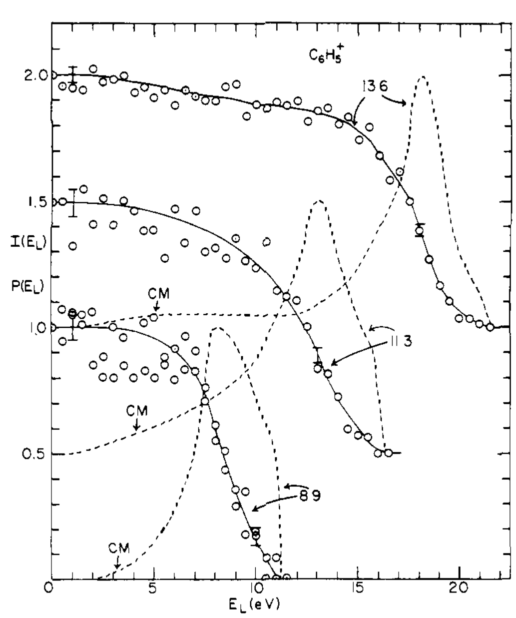

Figure 2. Laboratory energy distributions at 5° for $C_6H_5^+$ at 8.9, 11.3, and 13.6 eV collision energies. The solid line $I(E_L)$ (—) is the best curve drawn through the stopping curve data (O). The dashed line (- - -) is the LAB recoil energy distribution, $P(E_L) = -dI(E_L)/dE_L$. The curves have been shifted for display, but are normalized to unity at $I(0)$ and at the maximum of $P(E_L)$. The energy of the ion moving with the center-of-mass is labeled by arrows for each case. The error bars represent the statistical counting noise, ~(counts)$^{1/2}$.

The difference between the chlorobenzene reaction with Cs^+ and those of the chlorotoluenes appears to lie with the greater stability of the $C_7H_7^+$ system, as benzyl or tropylium. However, it is clear that better theoretical calculations of the electronic states of the $C_6H_5^+$ and $C_7H_7^+$ ions and good "correlation" schemes are required before the dynamics of these reactions can be fully understood.

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R. C. Horvat, G. D. Miller, S. A. Safron*
Department of Chemistry, Florida State University
Tallahassee, Florida 32306

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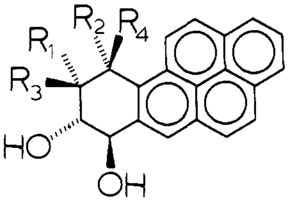
Hydrolysis of *syn*- and *anti*-Benzo[*a*]pyrene Diol Epoxides: Stereochemistry, Kinetics, and the Effect of an Intramolecular Hydrogen Bond on the Rate of *syn*-Diol Epoxide Solvolysis

Sir:

A 9,10-oxide of *trans*-7,8-dihydro-7,8-dihydroxybenzo-[*a*]pyrene has recently been implicated as a major activated metabolite in benzo[*a*]pyrene mutagenesis and carcinogenesis.[1,2] Both the *anti*-diol epoxide, **1**, and the *syn*-diol epoxide, **2**, have been synthesized.[2a,3] Although both compounds proved to be mutagenic to mammalian cells, the anti-stereoisomer, **1**, is exceptionally powerful;[2d,3] however, **2**, was more mutagenic than **1** to *Salmonella typhimurium*.[2b,c] Moreover, liver microsomal metabolism of benzo[*a*]pyrene-7,8-*trans*-dihydrodiol gave products identical on high pressure liquid chromatography with those obtained from the hydrolysis of **1**, but not of **2**.[2d]



	R_1	R_2	R_3	R_4
1:	-O-		H	H
2:	H	H	-O-	
3:	OH	OH	H	H
4:	H	H	OH	OH
5:	OH	H	H	OH
6:	H	OH	OH	H

We have investigated the aqueous solvolysis of **1** and **2** as models for the reaction of these epoxides with other weak nucleophiles in aqueous systems. We report now that ring opening of both isomers proceeds with relatively similar rates and with remarkable cis stereoselectivity at pH 5.0. In addition, oxide **2** proved more sensitive to dihydrogen phosphate general acid catalysis than **1**.

Solvolysis of both **1** and **2** was carried out at pH 5.0 in 1:1 (v/v) dioxane-water, 0.10 M in KCl at 37 °C. Acetylation of the reaction products[5] followed by thin layer chromatography[6] of the crude acetates afforded the 7,8,9,10-tetraacetoxy-7,8,9,10-tetrahydrobenzo[*a*]pyrenes in good yield.[7] NMR spectroscopy (270 MHz)[8] of the tetraacetates derived from the *anti*-diol epoxide, **1**, indicated the formation of the *trans,cis,cis*-**5**, and the *trans,cis,trans*-**3**, stereoisomers in the ratio of 3:2. These products presumably arise from addition of water at C-10 in both cis and trans directions. Regiospecific attack at C-10 is supported by the failure to detect the trans-trans-trans-isomer, **6**, expected to arise from trans-specific attack at C-9, and is consistent with the previous observations of attack of sulfur nucleophiles at C-10.[3a,b] The NMR spectrum (90 MHz) of the tetraacetates derived from the *syn* diol epoxide, **2**, showed the presence of only the 9,10-cis adduct, tetraacetyl-**4**.[10]

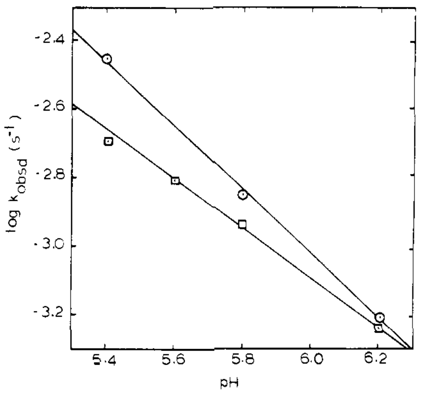


Figure 1. pH-Rate profiles of the reactions of 7α,8β-dihydroxy-9β,10-epoxy-(**1**,○) and 7α,8β-dihydroxy-9α,10α-epoxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene (**2**, ◻) in 1:1 dioxane-water at 34.8 °C, 0.0950 M in KCl and 0.0034 M in phosphate. Points are experimental; lines are theoretical.

The kinetic measurements were carried out in a solvent system of similar composition as the product studies above (1:1 (v/v) dioxane-water, 0.095 M in KCl and 0.003 42 M in phosphate).[11] The reactions were run in a spectrophotometer in order to monitor the appearance and disappearance of the characteristic λ_{max}'s of product dihydrodiols and the starting epoxide.[12]

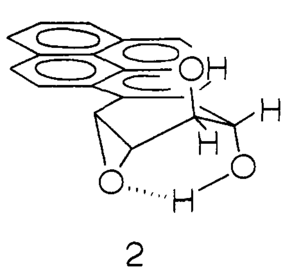
First-order rate constants were calculated from the change of absorbance at 278.8 nm.[13] The pH dependence of these reactions is illustrated in Figure 1. Diol epoxide **1** exhibits a linear log $k_{obsd,1}$ vs. pH plot with a slope = -1.0. This is normally associated with acid catalysis; i.e., $k_{obsd,1} = k_{h,1}a_H$, where a_H is the hydrogen ion activity as determined by glass electrode and $k_{H,1}$ is the specific acid catalyzed rate constant, here equal to 910 M^{-1} s^{-1}.[14]

Diol epoxide **2** failed to conform to this pattern, since the slope of the log $k_{obsd,2}$ vs. pH plot is -0.7, instead of -1.0. This deviation can be rationalized by adding a term for general acid catalysis by dihydrogen phosphate anion to the expression for $k_{obsd,2}$, i.e.,

$$k_{obsd,2} = k_{H,2}a_H + k_{H_2PO_4^-}[H_2PO_4^-] \qquad (1)$$

Substituting F_{PO_4}-$a_H/(K_a + a_H)$ for $[H_2PO_4^-]$ in eq (1), dividing through by a_H, and plotting $k_{obsd,2}/a_H$ vs. F_{PO_4}-$/a_H(K_a + a_H)$ produces a linear array of points with slope = $k_{H_2PO_4^-} = 0.32$ M^{-1} s^{-1} and intercept = $k_{H,2} = 300$ M^{-1} s.

These results are in accord with present ideas concerning the structures of diol epoxides **1** and **2** in solution.[3,15] The lower $k_{H,2}$ value may reflect a decrease in the pK_b of the oxirane oxygen caused by an internal hydrogen bond between C_7-OH and the oxirane oxygen in **2**.[3,15] *anti*-Diol epoxide, **1**, cannot form such a bond. Likewise, hydrogen bond-induced polarity in the epoxide moiety of **2** may enhance participation of the dihydrogen phosphate anion in the ring opening process.[16]



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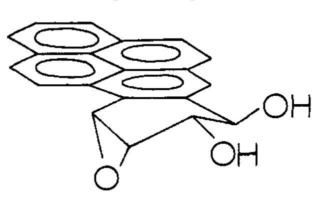

1