Persistent α-CF_3-Substituted (1-Pyrenyl)dimethyl-, (1-Pyrenyl)phenylmethyl-, (4-Pyrenyl)dimethyl-, and (9-Phenanthrenyl)dimethylcarbenium Ions: Enhancing Arenium Ionic Character by Increasing Electron Demand at the Carbocation

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Received June 6, 1997[⊗]

To examine the influence of carbocation destabilization (increasing electron demand) on the magnitude of π-participation by an α-pyrene (or α-phenanthrene) moiety, a series of regioisomeric $PyC^+(CF_3)R$ (R = Me, Ph) [Py = pyrene], and $(9\text{-Phen})C^+(CF_3)Me$ [phen = phenanthrene] carbocations having a CF_3 group α to the cation center were generated from their carbinols, **1-OH** to **5-OH**, by low-temperature protonation and ionization with FSO_3H/SO_2ClF. Multinuclear (^{13}C, ^{19}F, ^1H), NOED, and 2D NMR (H/H COSY, C/H HETCOR) were used to deduce the mode and magnitude of charge delocalization and the extent of $Ar-C^+$ double-bond character in the carbocations; AM1 calculations were used to examine their energies and charges (and conformations) for comparison with NMR. Since charge delocalization into the 1-Py-, 4-Py-, and 9-Phen-substituents is quite effective, the presence of α-CF_3 greatly increased π-participation and the arenium ion character in $\mathbf{1}^+$ and $\mathbf{2}^+$ as well as in $\mathbf{3}^+$ and $\mathbf{5}^+$. On the other hand, diminished charge delocalization into a 2-Py-substituent, coupled with destabilization by α-CF_3, prevents the formation of $\mathbf{4}^+$ and ring protonation occurs to give $\mathbf{4H}^+$. It was hoped that these $(PAH)C^+(CF_3)R$ carbocations (PAH = polycyclic aromatic hydrocarbon) may serve as models of PAH-epoxide ring opening where decreased carbocation stability augments arenium ion character to an extent that nucleophilic quenching (by DNA nucleotides) at a remote site may become feasible (→PAH−DNA adduct). Model quenching reactions with pyridine, Et_3N, MeOH, and H_2O did not, however, support the occurrence of nucleophilic attack on the PAH.

Introduction

The carbocation destabilizing effect of an α-CF_3 group is well-documented in the carbocation literature both for long-lived carbocations in superacid media and for carbocations formed under solvolytic conditions.[1] Despite such destabilization, the feasibility of generating persistent (trifluoromethyl)carbenium ions from their carbinols was first demonstrated by Olah and Pittman,[2] who generated $ArC^+(R)CF_3$ type carbocations (R = phenyl, cyclopropyl, methyl) from their carbinols. With bis-(trifluoromethyl)methanols, only oxonium ions were formed and subsequent ionization did not occur.[2] The CF_3-substituted allyl cations were recently prepared by Prakash et al.[3] and found to possess unsymmetrical nature. A number of solvolytic α-CF_3-substituted carbocations have also been generated and studied by Richards and by Tidwell and their associates.[4,5]

Involvement of carbocations in the diol−epoxide activation pathway is well-documented for several classes of polycyclic aromatic hydrocarbons (PAHs) (Figure 1 is an example).[6−12] In contination of our work on charge delocalization mapping in PAH carbocations,[13−16] we recently examined the charge delocalization mode in regioisomeric pyrene-substituted carbocations PyC^+R_2.[17a] Our aim was to understand the origin of carcinogenic activity in benzo[*a*]pyrene and its absence in benzo[*e*]-pyrene by focusing directly on the intermediate carbocations.

In the present study we have utilized an α-CF_3 group as a carbocation-destabilizing substituent in order to

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1997.

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(17) (a) Laali, K. K.; Hansen, P. E. *J. Org. Chem.* **1997**, *62*, 5804. (b) An estimated average value of 129.0 ppm ($\mathbf{1}^+$) and 133.0 ppm ($\mathbf{2}^+$) were used for the two unobserved ring junction carbons.

S0022-3263(97)01014-1 CCC: $14.00

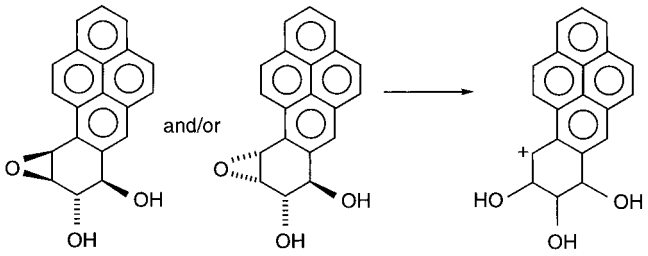

Figure 1.

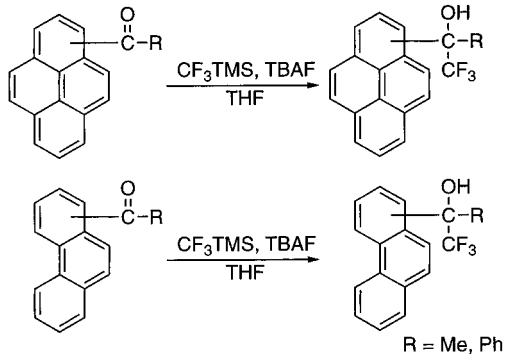

Figure 2.

modify and tune π-participation by the Py-substituent and to probe the outcome on carbocation stability in different regioisomers. In relation to our recent studies of phenanthrenium mono- and dications[15] and of isomeric (Phen)C^+R2 cations,[18] the influence of α-CF_3 on charge delocalization in (9-phen)$C^+(CF_3)$Me was also examined.

Results and Discussion

Comment on the Synthesis of the CF_3-substituted Carbinols (Figure 2). The use of CF_3-SiMe_3 ("CF_3-TMS")/TBAF system as an in situ source of "CF_3^-" and synthesis of CF_3-substituted alcohols from carbonyl compounds were pioneered by Prakash and Olah and their associates.[19] In the present study, *tert*-carbinols **1-OH** through **7-OH** were synthesized in respectable isolated yields from the isomeric ketones (see Experimental Section for details). We found that the use of a large excess of TBAF was necessary to cleave the O-TMS bond in our examples. Otherwise, the TMS ethers resisted hydrolysis and could be isolated in equally good yields. In selected cases, the same carbocations could be generated from the TMS-ethers with FSO_3H/SO_2ClF.

NMR characteristics of the CF_3-carbinols Precursors **1-OH** through **5-OH** (Figures 3 and 4): ^{1}H NMR assignments were based on the chemical shifts, multiplicities, and coupling constants (where appropriate), integrals, H/H COSY and H/C HETCOR relationships, and in selected cases via NOED spectra (see below). The ^{13}C NMR assignments were based on the chemical shifts, H/C HETCOR relationships, and C−F couplings. In all cases the assignments of several ring junction carbons remain interchangeable; these occur in a narrow chemical shift range with an average value of 130.0−131.0 ppm.

The ^{19}F NMR chemical shift in the regioisomeric PyC(OH)(CF_3)R carbinols is most upfield in the 2-isomer (**4-OH**; δ ^{19}F = −81.0) (see Figure 3). The ^2J C/F changes

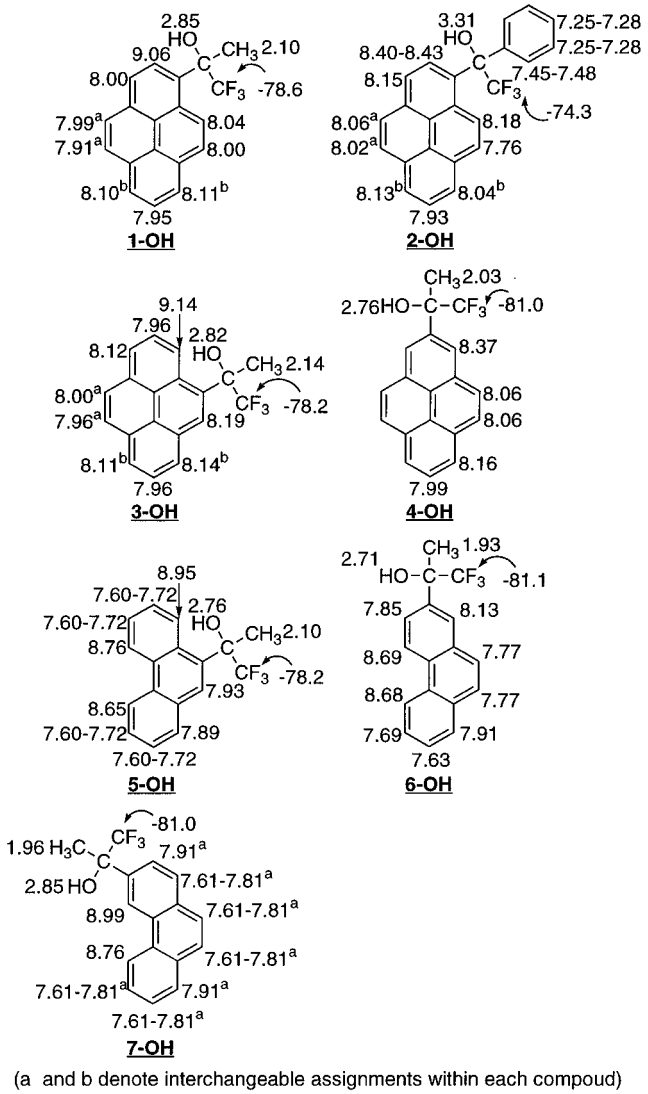

Figure 3. ^{1}H and ^{19}F NMR data for the carbinols.

from 29 Hz in **1-OH** to 33.5 Hz in the more crowded **2-OH** and 39.4 Hz in **3-OH**. For the less crowded **4-OH** this value is reduced to 18.9 Hz. A ^4J Me(H)/CF_3(F) coupling of ∼1 Hz is observable in **1-OH**.

Whereas the H-2 and H-10 protons in **1-OH** are not noticeably deshielded as compared to the nonfluorinated carbinol,[17a] for **3-OH** there is substantial deshielding for H-1 (8.94 → 9.14 ppm) and H-10 (7.91 → 8.19 ppm) protons. For **4-OH**, a ^3J C-2/F coupling of ∼14 Hz is observed. The multiplet (or two doublets!) appearance of H-2 in the crowded carbinol **2-OH** suggests restricted rotation. Relative stabilities of the two conformational isomers with interchanged Ph/CF_3 were probed by the AM1. The conformer with the CF_3 closer to H-2 (ortho) was found to be preferred by 1.2 kcal/mol. NOE enhancement was observed at room temperature on H-2 when the *o*-phenyl protons were irradiated. A similar NOE was detected on **1-OH** between the methyl protons and H-2. The peculiar appearance of H-2 is in all probability due to presence of both conformations in $CDCl_3$ at room temperature.

Comment on the EI-Mass Spectra of CF_3-Carbinols. Intense intact molecular ions were observed in all cases. No significant CF_3-substituted carbocations were formed by loss of OH. Instead, hydroxy-carbocations PAH−C^+(OH)R were formed by CF_3 loss, whose abundance decreased in the order **1-OH** > **2-OH** ∼ **5-OH**

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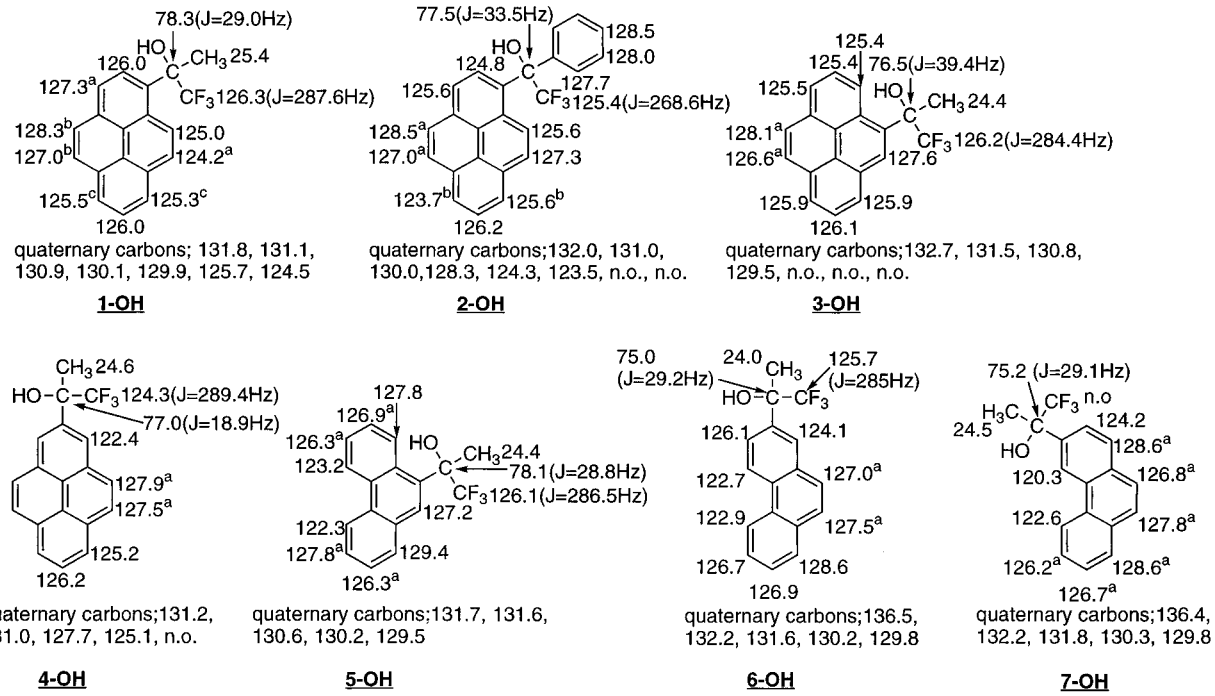


Figure 4. ^{13}C NMR data for the carbinols.

> **3-OH**. For **4-OH**, no hydroxy-carbocation was detectable. We find that the gas phase stabilities (abundances) closely parallel relative solution stabilities (ease of delocalization), as determined in our related previous work.[17a]

The CF_3-Substituted Carbocations (Figures 5 and 6). The low temperature reaction of **1-OH**, **2-OH**, and **3-OH** with FSO_3H/SO_2ClF produced "black solutions" whose NMR spectra confirmed clean generation of the corresponding carbocations. Similar low temperature reaction of **4-OH** with FSO_3H/SO_2ClF resulted in a dark-green solution whose NMR data fully agree with ring protonation to form $\mathbf{4H}^+$. Protonation of carbinol **5-OH** gave the corresponding carbocation $\mathbf{5}^+$ as a deep-red solution. The NMR data are gathered in Figures 7 and 8, and representative spectra are collected in Supporting Information.

Persistent carbocations could not be generated from **6-OH** and **7-OH** due to rapid "polymerization" on contact with the superacid at dry ice/acetone temperature to give gray precipitates which were not studied further (facile oligocondensation probably stems from reduced steric crowding in the incipient carbocations). Since $\mathbf{6}^+$ and $\mathbf{7}^+$ were inaccessible for direct NMR studies, we used AM1 calculations to obtain a qualitative idea of the relative stabilities ($\Delta\Delta H_f°$) in phenanthrene-substituted carbocations. These were roughly predicted to be $\mathbf{5}^+ \sim \mathbf{7}^+ > \mathbf{6}^+$. For each cation, two conformational isomers (CF_3/CH_3 positions) were calculated and the relative energy difference between the carbinol and the isomer with the lowest energy was considered. In $\mathbf{6}^+$ and $\mathbf{7}^+$ the difference between the two isomers was <1 kcal/mol, whereas this difference for $\mathbf{5}^+$ was 4.4 kcal/mol in favor of the conformation having the methyl group pointing toward the peri H-8.

NMR Characteristics of the Carbocations (Figures 7 and 8). The assignments of the ^1H and ^{13}C resonances were made with the aid of H/H COSY and H/C HETCOR spectra, used in conjuction with the chemical shift considerations, proton multiplicities, integrals, and C−F couplings in 1D spectra. Furthermore, comparisons were made with the NMR spectra of the

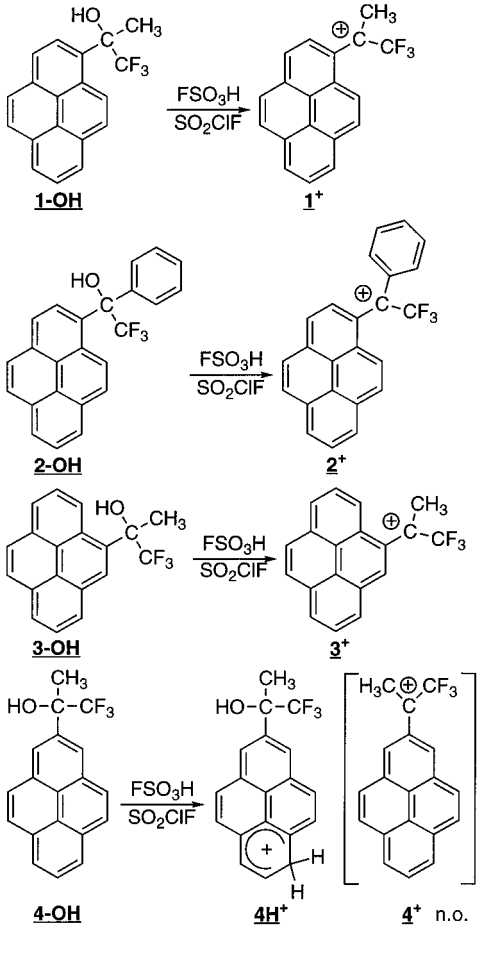
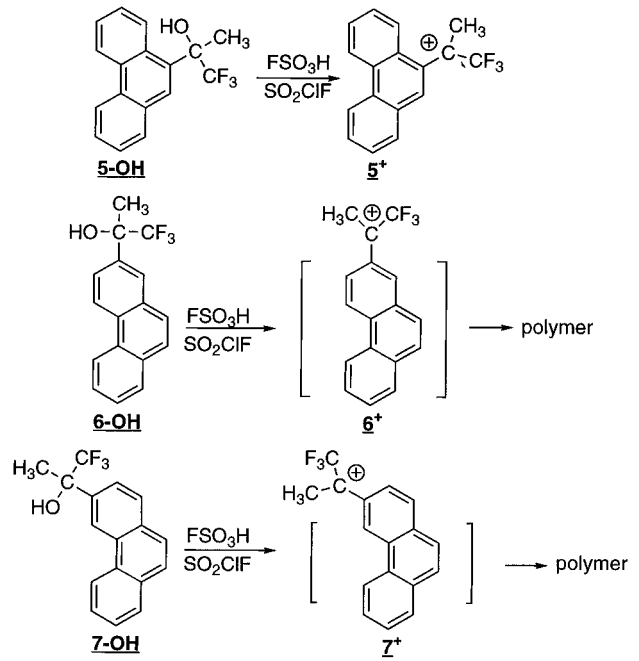


Figure 5.



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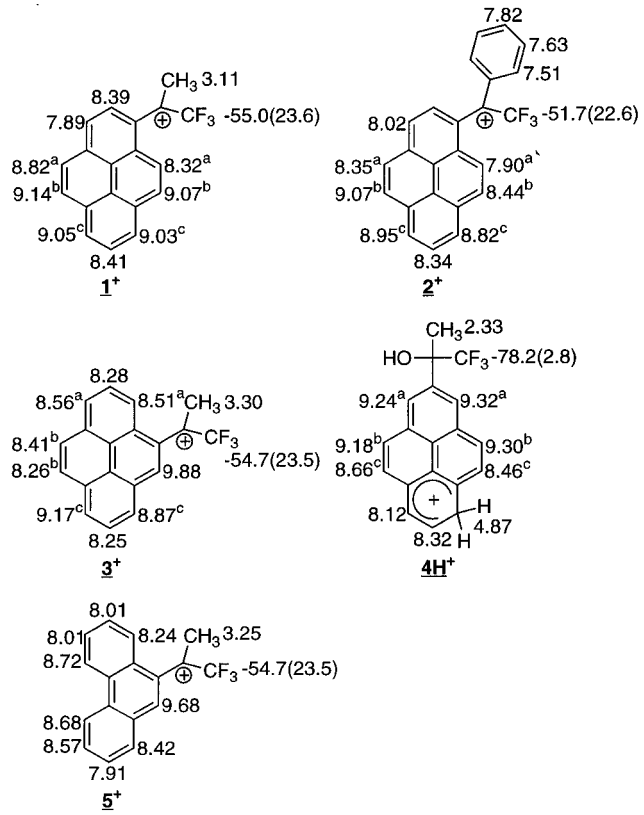

Figure 7. ^{1}H and ^{19}F NMR data for the carbocations.

nonfluorinated analogues,[17a,18] leading to a consistent trend where charge delocalization depended on the regioisomeric structure. The quaternary (ring junction) carbons which do not play a role in the charge alternation path and which occur in a narrow chemical shift range could not be specifically assigned. However, since the correlation between $\Delta\delta$ ^{13}C and Δq_c (changes in AM1-calculated Mulliken population-derived atomic charges) is quite reasonable for carbons experiencing low $\Delta\delta$ values (< ca. 10−11 ppm),[13−15] we have used the magnitude of Δq_c values to tentatively assign these. This approach, as we have shown before,[14,15] does not influence the overall pattern of charge delocalization deduced by NMR.

The chemical shift of C^+ center in $\mathbf{1}^+$ is at 159.5 ppm (quartet; with ^{2}J C/F = ∼29.0 Hz), corresponding to a shielding of 49.7 ppm relative to the C^+ in the nonfluorinated regioisomer.[17a] A $\Delta\delta$ ^{19}F of 23.6 ppm is observed and the ^{1}J C/F is reduced to 278.1 Hz from 287.6 Hz in the carbinol. Although a ^{3}J C/F is expected for the C-1 in $\mathbf{1}^+$, this quaternary carbon "quartet" is apparantly too small to be observable.

The magnitude of $\Delta\delta$ ^{13}C (hence the pyrenium ion character) in $\mathbf{1}^+$ is sigificantly higher than in the nonfluorinated analog[17a] (see also Figure 8). The Py−C^+ bond has gained increased double bond character. The calculated total deshielding $\Delta\delta^{13}C$ in the pyrenium moiety (relative to the carbinol) in $\mathbf{1}^+$ is 161.2 ppm.[17b]

The carbocation center in $\mathbf{2}^+$ is observed at 158.4 ppm (Figure 8), with the ^{2}J C/F being ∼31 Hz. No other (long-range) C/F couplings are detectable. The magnitude of the observed $\Delta\delta$ ^{19}F is similar to that in $\mathbf{1}^+$ and the positive charge is highly delocalized into the pyrene moiety. The total deshielding $\sum\Delta\delta$ ^{13}C in the pyrenium moiety amounts to 184.1 ppm,[17b] whereas the total deshielding in the phenyl group is 24.1 ppm. The observed pattern of charge delocalization is correctly predicted by AM1 calculations for both $\mathbf{1}^+$ and $\mathbf{2}^+$ based on the magnitude of Δq_c.

The carbocation center in $\mathbf{3}^+$ is more deshielded as compared to $\mathbf{1}^+$ and $\mathbf{2}^+$ (at 170.9 ppm with a ^{2}J C/F = 30.2 Hz), but the magnitude of $\Delta\delta$ ^{19}F (23.5 ppm) is similar. The C^+ chemical shift in PyC^+Me_2 is at 226.2 ppm,[17a] corresponding to ca. 55 ppm shielding in the fluorinated analogue by increased π-participation by the PAH. The H-5 protons give rise to a distinct, highly deshielded, singlet at 9.88 ppm. There is a ca. 9 Hz decrease in ^{2}J C/F coupling in going from **3** to $\mathbf{3}^+$.

Carbocation $\mathbf{3}^+$ exhibits a more limited charge alternation path in the pyrene moiety, with C-5, C-6/C-8 and C-10c experiencing maximum $\Delta\delta$ ^{13}C values. In concert with NMR-based conclusions, AM1 correctly predicts the overall mode of charge delocalization for $\mathbf{3}^+$ based on the magnitude of Δq_c values. The relative stability order $\mathbf{1}^+ > \mathbf{3}^+ > \mathbf{4}^+$ is also correctly predicted by AM1 based on the $\Delta H_f°$ values.

Under similar conditions, the formation of carbocation $\mathbf{4}^+$ becomes energetically unfavorable due to a combination of inefficiency of charge delocalization from the 2-position of pyrene and destabilization by α-CF_3. Instead, ring protonation occurred to produce $\mathbf{4H}^+$ as the major product.

The nonequivalence of H-1/H-3 protons (9.32, 9.24 ppm), taken together with significant increase in ^{2}J C/F (36.9 Hz in $\mathbf{4H}^+$ and 18.9 Hz in **4**) and a 2.2 ppm deshielding at C(CF_3)Me(OH), suggests that the OH may be protosolvated. This is in line with our finding that, among isomeric acetylpyrenes, 2-acetylpyrene is most readily diprotonated to form an oxonium−pyrenium dication.[20]

To explore the possibility that carbocations $\mathbf{2}^+$ and $\mathbf{3}^+$ may be ring protonated at higher acidities to give dications, protonation of **2-OH** and **3-OH** carbinols with $FSO_3H.SbF_5$ (1:1) "magic acid"/SO_2ClF was examined. No persistent dications could be generated. With **2-OH**, only $\mathbf{2}^+$ was formed and with **3** the NMR spectra showed very

(20) Laali, K. K.; Hansen, P. E., ongoing studies.

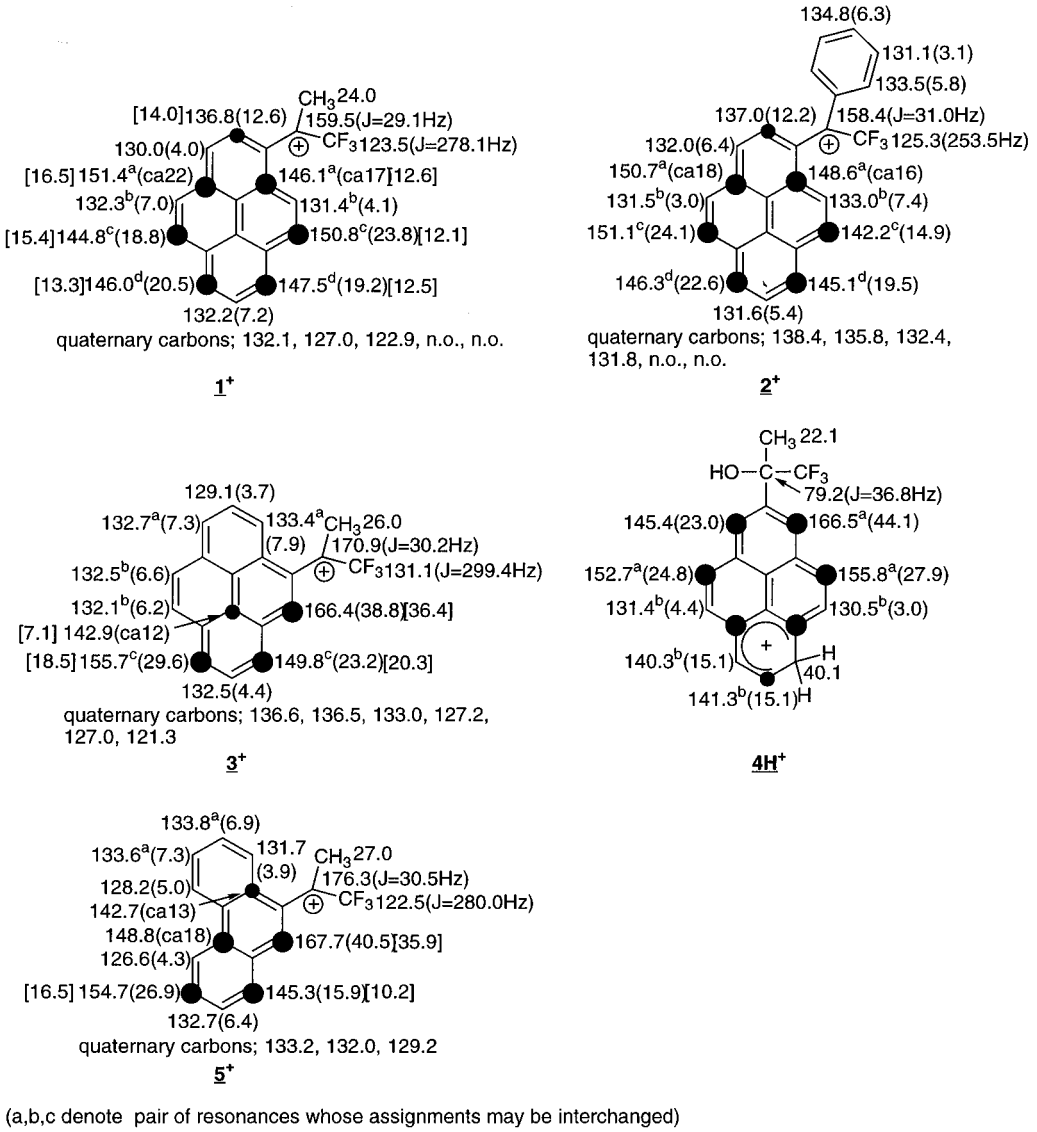

Figure 8. ^{13}C NMR data for the carbocations. $\Delta\delta^{13}C$ values: cation minus carbinol. $\Delta\delta^{13}C$ values: the CF_3-substituted minus the nonfluorinated cation; values for the nonfluorinated cations are taken from refs 17a and 18.

broad features indicative of subsequent polymerization; quenching of the "magic acid" solution gave a white solid insoluble in chloroform. We find that the charge alternation path in **4H**$^+$ is similar to other pyrenium cations of α-attack.[13]

Protonation of 5-OH. Destabilizing the α-carbenium ion attached to the meso-position of phenanthrene via CF_3 introduction has a pronounced effect on increasing the π-electron demand and participation by the 9-phenanthrenyl moiety. Thus the chemical shift of the C^+ center in **5**$^+$ is at 176.3 ppm, shielded relative to the nonfluorinated carbocation[18] by 53.8 ppm, with the corresponding $\Delta\delta$ ^{19}F being 23.5 ppm; these values are similar in magnitude to those in **3**$^+$. Upon carbocation formation, the H-1 chemical shifts in **3**$^+$ and **5**$^+$ become shielded relative to the carbinols. The ^{13}C chemical shifts of the aromatic carbons of **5**$^+$ are deshielded by 58.1 ppm as compared to the corresponding nonfluorinated carbenium ion.[18] This increased π-participation enhances the positive charge at carbon centers which are already most positive (C-4b, C-6, C-8, and C-10).

Quenching Experiments. Background. There have been several studies of quenching of chemically generated PAH radical cations as models of PAH−DNA adducts. For example, the radical cation of the potent carcinogen 7,12-dimethylbenz[*a*]anthracene (via oxidation with iodine) reacted with pyridine to give substitution products (pyridinium salts) at positions 5,7-Me_2 and 12-Me.[21] Anodic oxidation of the same PAH in the presence of deoxyribonucleosides gave several adducts which have been characterized.[22] Whereas anodic oxidation of benzo[*a*]pyrene in the presence of pyridine or 4-picoline gave the onium adducts by substitution at C-6, 1-methylimidazole apparantly reacted at C-1.[23] In a carbocation activation model, there appears to be only one published study, where a pyridinium salt was obtained from benzo[*a*]pyrene via a heterolytic process.[24] In other studies, solvolysis of 6-(chloromethyl)benzo[*a*]pyrene in the presence of added nucleosides and deoxynucleosides (containing adenine, guanine, or cytosine) gave the corresponding

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adducts by carbenium ion trapping in competition to carbinol formation.[25]

In light of sigificantly enhanced delocalization of charge into the PAH moiety in the CF_3-subsituted carbocations generated in the present study, it was of interest to explore if any adducts can be isolated that would correspond to nucleophilic attack on the PAH. Therefore, several quenching experiments on **1** and **2** were carried out using Et_3N, pyridine, MeOH, and H_2O.

Control experiments showed that SO_2ClF could be replaced by CH_2Cl_2 to generate $\mathbf{1}^+$ or $\mathbf{2}^+$ (^{1}H NMR) and that the amount of FSO_3H could be reduced to ca. 1.5−2 equiv relative to the carbinol (a necessary condition, so that minimal amounts of the ammonium or pyridinium fluorosulfate byproducts were formed on quenching).

Typically, following the formation of $\mathbf{1}^+$ or $\mathbf{2}^+$ carbocations (black solutions), addition of cold pyridine/CH_2Cl_2 turned the solution pale-brown with precipitation of pyridium fluorosulfate (see also experimental). With Et_3N there was no color change and no precipitate resulted (Et_3N^+ SO_3F^- is soluble in CH_2Cl_2).

The low temperature ^{1}H NMR spectrum of quenching of $\mathbf{2}^+$ with cold Et_3N/CH_2Cl_2 showed apart from the ammonium salt byproduct, aromatic resonances between 8.4 and 7.30 ppm and the ^{13}C NMR spectrum exhibited ca. 15 aromatic signals between 130 and 123.5 ppm. Although $\mathbf{2}^+$ was fully consumed, H/H COSY spectra argued against nucleophilic attack on the pyrene. Variable temperature NMR studies indicated that the initially formed adduct reacted further and subsequently decomposed on increasing temperature. Similar observations were made with $\mathbf{1}^+$, with the product being even less stable in this case. Whereas quenching of $\mathbf{2}^+$ with pyridine/CH_2Cl_2 gave a complex mixture with broad resonances which could not be analyzed, quenching of $\mathbf{2}^+$ with cold MeOH cleanly furnished the corresponding methyl ether. Similarly, quenching with H_2O in all cases returned the structurally intact carbinols.

These observations demonstrate that, in all cases, nucleophilic attack occurred at the carbocation; whereas quenching with H_2O and MeOH furnished the carbinols and the methyl ether cleanly, quenching with the nitrogen bases was not selective. It appears that the corresponding ammonium adducts (attack at C^+) are formed at low temperature but are unstable when the temperature is raised, leading to complex mixtures from which the onium salt (adduct) could not be isolated.

Experimental Section

1-Acetylpyrene, 2-, 3-, and 9-acetylphenanthrene, tetrabutylammonium fluoride hydrate (TBAF), and (trifluoromethyl)-trimethylsilane (CF_3TMS, 0.5 M in THF) were purchased from Aldrich and used without further purification. Samples of 1-benzoylpyrene, 2-acetylpyrene, and 4-acetylpyrene were available in our laboratory from previous studies;[17a] additional samples were prepared according to literature procedures as summarized in ref 17a. SO_2ClF was prepared via the reaction of SO_2Cl_2 with NH_4F and CF_3COOH according to a modified literature procedure.[26] SbF_5 (Fluorochem) and FSO_3H (Aldrich) were doubly distilled in an all-glass distillation unit under argon at atmospheric pressure and stored in Nalgene bottles under argon.

General Procedure for the Preparation of CF_3-Carbinols 1-OH to 4-OH. In a typical experiment, 1-acetylpyrene (244 mg, 1 mmol) was added to a THF solution of trimethyl-(trifluoromethyl)silane (4 mL, 0.5 M). Tetrabutylammonium fluoride hydrate (200 mg) was added to the solution at 0 °C, and the reaction mixture was allowed to warm to room temperature and stirred for 3 h. Subsequently, the reaction mixture was poured into ice−water and extracted with chloroform. After removing the solvent, the product was purified by column chromatography with hexane−chloroform (5:1) eluent to give **1-OH** (85% yield; mp 117−118 °C; MS: M^+ at *m*/*z* 314).

2-OH: 90% yield; mp 144−146 °C; MS: *m*/*z* 376 (M^+).

3-OH: 57% yield; mp 99−101 °C; MS: *m*/*z* 314 (M^+).

4-OH: 48% yield; mp 160−162 °C; MS: *m*/*z* 314 (M^+).

General Procedure for Preparation of Carbinols 5-, 6-, and 7-OH. In a typical experiment, to 9-acetylphenanthrene (200 mg, 0.91 mmol) was added 3 mL (1.5 mmol) of CF_3TMS (0.5 M in THF) under argon at 0 °C. Upon addition of 2−3 mg of TBAF the solution turned yellow. After stirring at room temperature for 2 h (dark-red color), excess TBAF (>300 mg) was added and the mixture was stirred for ca. 15 min. The reaction mixture was then poured into ice and extracted three times with ether. The combined organic layers were washed with ice−water and brine and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The resulting yellow oil was purified by column chromatography (pentane/ether 5:1−2:1) to give 180 mg of the carbinol as a pale yellow solid.

5-OH: 68% yield; mp 105−106 °C; MS: *m*/*z* 290 (M^+).

6-OH: 61% yield; mp 127−129 °C.

7-OH: 66% yield; mixture of **7-OH** and **6-OH** (25%).

Preparation of Carbocations. About 30 mg of the carbinol was placed in a 5 mm NMR tube and the NMR tube was connected to the high-vacuum line (ace-thread port). After several cycles of evacuation and flushing with argon, the NMR tube was kept under vacuum for ca. 5 min. About 0.3 mL of SO_2ClF was condensed into the NMR tube which was cooled to liquid nitrogen temperature. After completion of the SO_2ClF addition, the liquid nitrogen bath was replaced by a dry ice/acetone bath, and about 0.05 mL of FSO_3H was slowly added to the NMR tube under argon wherupon the color turned black (green in the case of $\mathbf{4H}^+$ and deep-red in the case of **5-OH**). After vigorous stirring at −78 °C (vortex), CD_2Cl_2 was added to the NMR tube (vortex). Attempted ionization of **6-OH** and **7-OH** yielded gray polymeric precipitates.

The FSO_3H solutions of $\mathbf{1}^+$ and $\mathbf{2}^+$ were stable for several days at dry ice temperature, and the trifluoromethyl alcohols were recovered intact after quenching with water. On the contrary, $\mathbf{3}^+$ and $\mathbf{4H}^+$ were unstable on storage and gave unidentified white solids which were insoluble in chloroform after quenching.

Quenching Experiments. FSO_3H (20 mg) was added to a CH_2Cl_2 (0.3 mL) solution containing CD_2Cl_2 (0.1 mL) with **1** (30 mg) or **4** (30 mg) in a 5 mm NMR sample tube at dry ice temperature under argon, and the solution was mixed immediately to form the carbocation. Precooled pyridine (30 mg) or triethylamine (30 mg) was quickly added to the cation solution, and the mixture was mixed (vortex) at dry ice/acetone temperature before NMR analysis. The reverse addition (the FSO_3H solution to a large excess of cold pyridine or triethylamine) was not attempted due to anticipated difficulties to isolate/identify the desired pyridium (ammonium) fluorosulfate salts.

Acknowledgment. We thank Prof. P. E. Hansen (Roskilde) for his interest and involvement. Support of our work in the area of reactive intermediates of carcinogenesis of PAHs by the NCI of NIH (R15CA63595) is gratefully acknowledged.

Supporting Information Available: Selected ^{1}H NMR, H−H COSY, ^{13}C NMR and C−H HETCOR spectra of $\mathbf{2}^+$ and $\mathbf{5}^+$ (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO971014Z