saturated $NaHCO_3$. The resulting material was partitioned between CH_2Cl_2 and water. Workup and chromatography (gradient of 1–3% THF in CH_2Cl_2) yielded 6.3 mg (7%) of **3** as a yellow solid: mp >360 °C; IR ν(NH) 3320, (C=O) 1690 cm^{-1}; ^1H NMR (500 MHz, Me_2SO-d_6, for assignments, see Figure 1) δ 0.97 (t, J = 7.3 Hz), 1.68 (m), ≈2.5 (obscured by solvent), 6.75 (d, J = 9.2 Hz), 6.77 (d, J = 8.3 Hz), 6.92 (d, J = 9.2 Hz), 6.99 (d, J = 8.3 Hz), 7.58 (d, J = 8.1 Hz), 7.61 (d, J = 8.6 Hz), 8.11 (d, J = 8.1 Hz), 8.12 (dd, J = 8.6 and 6.3 Hz), 8.25 (s, 2 H), 8.27 (d, J = 8.1 Hz), 8.29 (d, J = 8.6 Hz), 8.56 (d, J = 8.1 Hz), 8.58 (d, J = 6.3 Hz), 9.03 (d, J = 8.6 Hz), 10.60 (s, br); FAB-MS 906 (M^+ + 1, 100).

Acknowledgment. This work was supported by the National Institutes of Health. We thank D. R. Carcanague for assistance in the analytical characterization.

Registry No. (±)-**2**, 136805-53-3; (±)-**3**, 136827-14-0; **4**, 99073-81-1; **5**, 136805-54-4; **6**, 107027-36-1; **7**, 136805-55-5; **8**, 136805-56-6; (*Z*)-**9**, 136805-57-7; (*E*)-**9**, 136805-52-2; **10**, 136805-58-8; **11**, 136805-59-9; **12**, 136805-60-2; **13**, 136805-61-3; (±)-**14**, 136805-62-4; **15**, 136805-63-5; **16**, 69743-36-8; (*Z*)-**17**, 136805-64-6; (*E*)-**17**, 136805-72-6; **18**, 136805-65-7; **19**, 136805-66-8; **20**, 136805-67-9; **21**, 136805-68-0; **22**, 136805-69-1; (*Z*)-**23**, 136805-70-4; **24**, 136805-71-5; 2-formyl-7-methylnaphthalene, 52988-18-8; 1,4-bis(dimethylamino)-1,1,4,4-tetramethyl-1,4-disilabutane, 91166-50-6; 2-amino-6-bromopyridine, 19798-81-3.

Supplementary Material Available: ^1H NMR spectra including ^1H, ^1H COSY, and long-range ^1H, ^1H COSY's of the helices **2**, **3**, and **14**; experimental details of the X-ray crystal structure analyses of **14**, *trans*-**17**, and **22**, tables of the atomic coordinates, equivalent isotropic thermal parameters, bond angles and bond lengths, and intramolecular and intermolecular distances (**14**, *trans*-**17**, **22**); MMP2(85) structure of **14** and assigned values for missing parameters in the force field (37 pages). Ordering information is given on any current masthead page.

Protonation and Sulfinylation of Isomeric Isopropylpyrenes, 2,7-Di-*tert*-butylpyrene, and Tetracyclohexyl- and Tetracyclopentylpyrenes: Remarkably Stable, Sterically Crowded Pyrenium Cations†

Kenneth Khosrow Laali*

Department of Chemistry, Kent State University, Kent, Ohio 44242

Poul Erik Hansen

Institute 1, Roskilde University Center, P.O. Box 260, DK-4000 Roskilde, Denmark

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1-Isopropyl- (**1**), 2-isopropyl- (**2**), 4-isopropyl- (**3**), 1,3,6,8-tetraisopropyl- (**4**), and 1,3,5,7,9-pentaisopropylpyrene (**5**), 2,7-di-*tert*-butylpyrene (**6**), and 1,3,5,8-tetracyclohexyl- (**7**) and 2,4,7,9-tetracyclopentylpyrene (**8**) in FSO_3H or CF_3SO_3H (TfOH) in SO_2 or SO_2ClF solvent gave stable monopyrenium ions. In agreement with theory, exclusive α protonation occurred at low temperature (−75 → −65 °C) irrespective of the position of the substituents. The position of α-protonation is controlled by inductive stabilization of the alkyl (cycloalkyl) groups. Unlike hexahydropyrene which is diprotonated in FSO_3H-SbF_5 (1:1) Magic acid, with isopropylpyrenes stable dications could not be generated; in SO_2 solvent the Wheland intermediates of sulfinylation were observed, whereas in SO_2ClF solvent oxidation and monoprotonation were competitive. Charge distribution patterns in the sulfinylation σ-complexes are similar to those of protonated pyrenium ions. Stable pyrenium cations deprotonate or desulfinylate on quenching without dealkylation or disproportionation. At higher temperatures (ca. −40 °C), ipso-protonated **4** undergoes isomerization in FSO_3H/SO_2 solvent; other alkyl (cycloalkyl)pyrenium cations show no isomerization/disproportionation. Upon standing in Magic Acid, hexahydropyrene is oxidized to pyrene.

Introduction

Due to their carcinogenic/mutagenic activity and widespread presence in polluted environments, the synthesis, electrophilic chemistry, and spectroscopic studies of pyrene, alkylpyrenes, nitropyrenes, hydropyrenes, as well as their benzo-, indeno-, cyclopenta-annulated and methylene-bridged derivatives, are currently receiving considerable attention.[1-13]

For parent pyrene (Figure 1), simple Hückel MO[3,14] and PI-DEWAR calculations[15] predict the positions (1, 3, 6, 8) to be significantly more reactive. The Wheland intermediate of protonation at an α position is predicted to be 8.8 kcal/mol lower in energy than the σ-complex of $\alpha\beta$ attack and 20.5 kcal/mol more stable than the σ-complex of attack at a β position.[15] Since sites within 5 kcal/mol are considered possible candidates for substitution, attack at $\alpha\beta$ positions is possible but β attack is clearly not favored. Substitution of a methyl at the 1-position renders the ipso, followed by the 8, 6, and 3 positions most favored.[3] In

† Presented at the 22nd Central Regional ACS Meeting, MI, June 1990.

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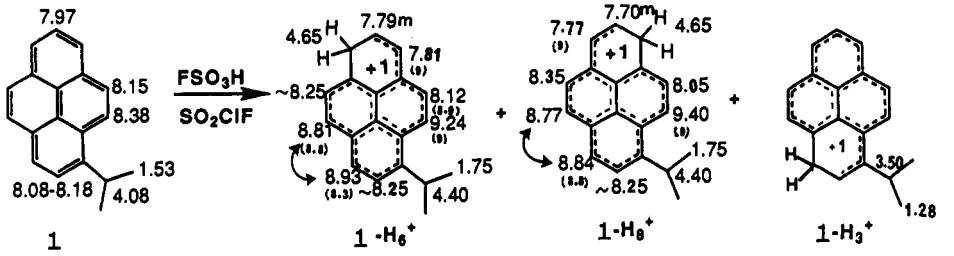
0022-3263/91/1956-6795$02.50/0

Scheme I. Monoprotonation of Alkylpyrene 1[a]



[a] Only J values for well-resolved resonances are reported (accuracy ±0.1 Hz). Chemical shifts (ppm) and coupling constants (small numbers; Hz) are given in scheme (m = multiplet). ↔ denotes interchangeable assignments within a given pyrenium ion. As two pyrenium ions are equally abundant, interchange of some resonances for hydrogens in identical relative positions in two pyrenium ions is possible.

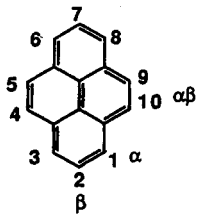


Figure 1. Parent pyrene skeleton.

agreement with theory, nitration, bromination, chlorination and acylation of pyrene give predominantly 1-substitution.[3] Aprotic sulfonation of pyrene gave 1-SO_3H and 1,3-$(SO_3H)_2$ with 0.9 equiv of SO_3, and 1,3-$(SO_3H)_2$, 1,8-$(SO_3H)_2$, and 1,6-$(SO_3H)_2$ with 3 equiv of SO_3.[3] 1-Methylpyrene gave 6,8-$(SO_3H)_2$ as the major product.[3]

In comparison with the literature data on stable arenium ions of protonation of naphthalenes,[16-19] anthracenes,[16,20,21] phenanthrenes[22] and biphenylenes,[23,24] data on stable σ-complexes of substituted pyrenes are not available.[25,26] In the early work, electronic absorption spectra and proton NMR indicated that pyrene itself is protonated at position 1.[25a] It was shown later that hexahydropyrene is monoprotonated in FSO_3H and diprotonated in Magic Acid.[27]

Synthesis and NMR studies of a range of mono-, di-, tri-, tetra-, and pentaisopropylpyrenes, as well as 2,7-di-*tert*-butyl-, tetracyclohexyl-, and tetracyclopentylpyrenes by

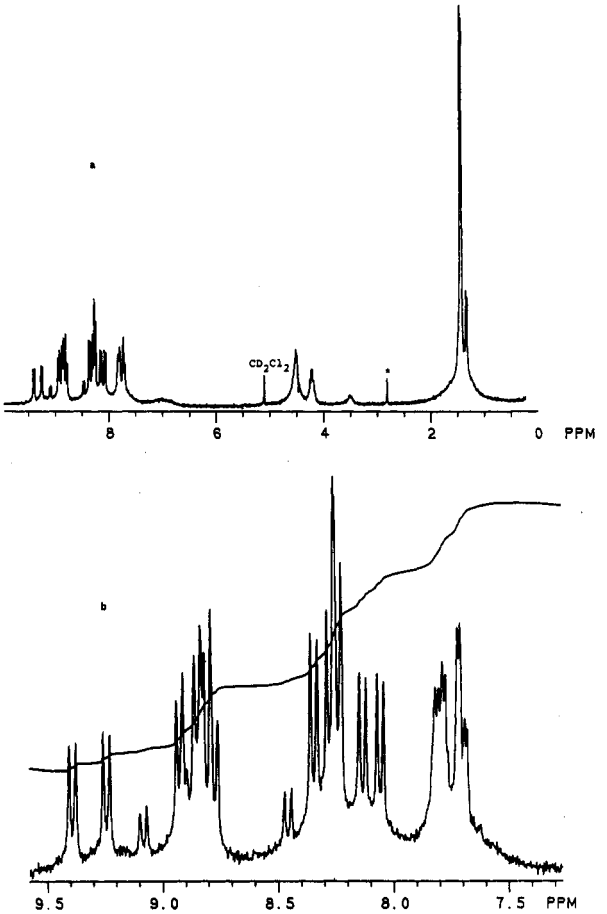


Figure 2. Protonation of 1 at −65 °C: a, full spectrum; b, expansion of aromatic region.

Friedel–Crafts alkylation and cathodic alkylation of pyrene were previously reported.[1] Preparation of these unusually crowded pyrenes through conventional Friedel–Crafts chemistry provided an impetus for the present study in which the protonation behavior of pyrenes 1–8 under persistent ion conditions was probed with the aim to address the following specific questions:

(a) Would the presence of iPr group(s) in the α position(s) lead to ipso attack and if so, is subsequent dealkylation rapid?

(b) Would the presence of an $\alpha\beta$ iPr group increase the stability of the σ-complex of $\alpha\beta$ attack relative to α attack?

(c) Would the initially formed pyrenium ion(s) of protonation undergo dealkylation/realkylation to generate functionalized pyrenes, inaccessible by conventional routes? Rearrangements and averaging of structures are easily detectable in the pyrene skeleton because of its high symmetry and presence of three NMR distinct types of protons (four H_α, two H_β, and four $H_{\alpha\beta}$).

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(25) For comprehensive reviews see: (a) Brouwer, D. M.; Mackor, E. L.; MacLean, C. In *Carbonium Ions*; Olah, G. A., Schleyer, P. V. R., Eds.; Wiley: New York, 1970; Vol. 2, Chapt. 20; (b) Surya Prakash, G. K.; Rawdah, T. N.; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 390. (c) Pagni, R. M. *Tetrahedron* **1984**, *40*, 4161. (d) Olah, G. A.; Surya Prakash, G. K.; Sommer, J. *Superacids*, Wiley: New York, 1985; pp 99–101.
(26) The oxidation dications of both pyrene and hexahydropyrene have been reported; see: (a) Forsyth, D. A.; Olah, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 4086. (b) Lammertsma, K.; Olah, G. A.; Berke, C. M.; Streitwieser, A. *J. Am. Chem. Soc.* **1979**, *101*, 6658.
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(d) Can suitably positioned substituents provide insight into conformational changes that may occur upon arene → arenium ion transformation? Isopropyl groups are interesting since their interactions with the aromatic periphery depend on the orientation of the methine protons relative to the ring system.

Results

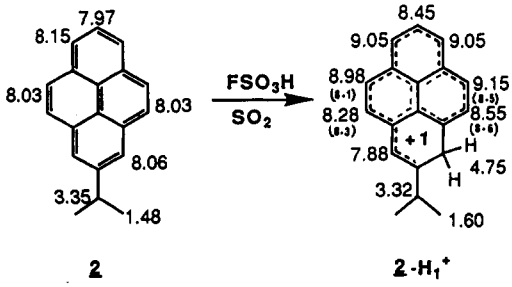
NMR Studies. Our low-temperature studies focused on ^1H NMR as opposed to ^{13}C NMR because (a) in many instances more than one pyrenium ion was formed which made ^1H NMR more diagnostic and (b) limited quantities of purified pyrene substrates were available. Assignments of the ^1H NMR spectra of pyrenium ions are based on symmetry properties of the molecules, chemical shifts, intensities, magnitude of vicinal coupling constants for well-resolved absorptions, and a consistent set of protonation effects on the chemical shifts (Scheme XIV).

Monopyrenium Ions of Protonation. Pyrenes 1–8 were cleanly monoprotonated in FSO_3H/SO_2, FSO_3H/SO_2ClF, or with CF_3SO_3H/SO_2 (Schemes I–VIII).

Monoprotonation of 1 (Scheme I). Slow addition of a homogeneous solution of FSO_3H/SO_2ClF to a slurry of 1 in SO_2ClF at dry ice–acetone temperature resulted in a green brown solution. Inspection of the aliphatic region of the low-temperature ^1H NMR spectrum at −65 °C (Figure 2a) initially indicated the formation of two monoarenium ions in 80 and 20% yield with their diagnostic CH_2 (sp^3) protons appearing as two almost overlapping broad singlets at 4.65 and 4.72 ppm. The "major ion" exhibits a considerably more downfield iPr group at 1.75 ($\Delta\delta$ = 0.22) and 4.40 ppm ($\Delta\delta$ = 0.32), indicative of the importance of hyperconjugation and inductive charge stabilization involving iPr group. The absence of low-field aromatic singlets ruled out protonation at both $\alpha\beta$ and β positions as well as at H_3. Further inspection of the expanded aromatic region (Figure 2b) confirmed that the "80% ion" was, in fact, a mixture of approximately equal amounts of two pyrenium ions (having identical iPr groups). The aromatic region showed 9 AB doublets of almost equal intensities (9 H), intense "overlapping" doublets centered around 8.25 ppm (3 H), and four upfield doublets (4 H), two of which (7.79 and 7.70 ppm) showed extra splitting due to coupling to the CH_2 hydrogens in the ortho position. The many doublets indicated that the pyrenium ions are substituted at both ends. Furthermore, the similarity of the chemical shifts for the two major species combined with the equal intensities indicated similarity in structures for the pyrenium ions as found for 1-H_6^+ and 1-H_8^+. The observed shielding of H_7 (ortho; $\Delta\delta$ = −0.18 and −0.27) and H_8 (meta; $\Delta\delta$ = −0.32 and −0.36) demonstrates that charge distribution in the pyrenium ion is quite different from alkylnaphthalenium ions[16–19] where the charge is primarily localized in the protonated ring with significant deshielding of para and ortho protons. With 1-H_6^+ and 1-H_8^+, the most deshielded protons are the H_{10}, H_3, and H_4, indicative of extensive charge delocalization into the $\alpha\beta$ and "remote" α positions.

The minor ion showed an upfield iPr at 1.28 ($\Delta\delta$ = −0.25) and 3.50 ppm ($\Delta\delta$ = −0.58), assigned to pyrenium ion 1-H_3^+.[28,29] Ipso protonation can be ruled out, as this gives rise to a methyl group ^1H chemical shift of ca. 0.8 ppm (see protonation of 4). Hence, monoprotonation of 1 gives a mixture of 1-H_6^+ (40%), 1-H_8^+ (40%), and 1-H_3^+ (20%),[30] in line with the aprotic sulfonation pattern on 1-Me-Pyrene.[3] The iPr doublets remain sharp even at −70 °C, indicative of free rotation. Raising the NMR probe temperature to −40 °C led to a reduction in the line widths of the signals, but the spectrum was essentially unchanged. 1 was recovered unchanged (^1H NMR) upon quenching of the ion solution; iPr loss, disproportionation, or fluorosulfonation was not observed.

Scheme II. Monoprotonation of Alkylpyrene 2[a]



2 2-H_1^+

[a] Only J values for well-resolved resonances are reported (accuracy ±0.1 Hz). Chemical shifts (ppm) and coupling constants (small numbers; Hz) are given in scheme.

Monoprotonation of 2 (Scheme II). Careful addition of a clear solution of FSO_3H/SO_2 to a slurry of 2 in liquid SO_2 at −70 °C resulted in a reddish brown solution, the ^1H NMR of which (−70 °C) was consistent with generation of a monopyrenium ion in which the iPr(Me) is deshielded ($\Delta\delta$ = 0.12) and somewhat broadened, but the iPr(CH) is slightly shielded ($\Delta\delta$ = −0.03) and appears almost as a broad singlet.[31] Except for reduction in line widths, the spectrum was essentially unchanged at −40 °C; a diagnostic CH_2 signal appears as a slightly broad singlet at 4.75 ppm, its integration (2 H) clearly rules out the less favored pyrenium ion of ipso attack (β). The aromatic region consists of four (1 H) doublets, a 2 H doublet, a 1 H triplet, and a 1 H singlet. Further, the presence of an aromatic triplet argues against protonation at a remote α position (6, 8), leaving C_1 protonation as the only possibility. High-field shift of iPr(CH) is indicative of anisotropic shielding by protonation at C_1. The four 1 H doublets are hence due to hydrogens (H_4, H_5, H_9, H_{10}), the 2 H doublet due to H_6 + H_8, and the 1 H triplet due to H_7. As with 1 the H_3 (meta) shows an *upfield* shift ($\Delta\delta$ = −0.18) and the positive charge is extensively delocalized into the $\alpha\beta$ and α positions. The ^3J ($H_{\alpha\beta}$–$H_{\alpha\beta}$) in the pyrenium ion is between 8.1–8.6 Hz and those of $^3J(H_\alpha–H_\beta)$ = ca. 8.2 Hz. Upon quenching of the cold ion solution intact 2 was isolated.

Monoprotonation of 3 (Scheme III). A clear reddish brown solution was obtained upon addition of a cold solution of either CF_3SO_3H/SO_2 or FSO_3H/SO_2 to a slurry of 3 in SO_2. Low-temperature ^1H NMR spectra indicated that an identical mixture of monopyrenium ions is formed in either superacid system. The aliphatic region consisted of two major deshielded iPr groups at 1.62 and 4.35 ppm ($\Delta\delta$ = 0.04 and 0.40) and at 1.58 and 4.35 ppm ($\Delta\delta$ = 0.0 and 0.40), and a minor *shielded* iPr at 1.52 and 3.52 ppm ($\Delta\delta$ = −0.06 and −0.43).[32] The iPr(Me) doublets remained sharp and showed no rotational barriers at low tempera-

(28) Only a few aromatic resonances can be observed for the minor isomer, but these fit likewise the suggested structure 1-H_3^+.

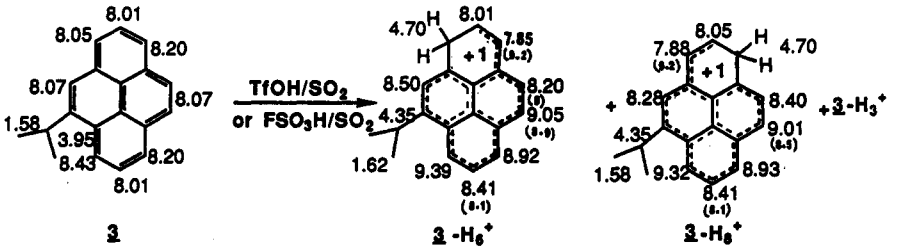
(29) The high-field shift for CH and CH_3 protons of the isopropyl group is probably caused by a conformational change upon protonation at position 3.

(30) Protonation with FSO_3H/SO_2 or CF_3SO_3H/SO_2 gave the same mixture of pyrenium ions.

(31) Presence of a tiny (overlapping) CH_2 at ca. 4.72 ppm and a small deshielded iPr doublet at 1.65 ppm are indicative of a second (minor) pyrenium ion.

(32) A less abundant upfield iPr(CH) at 3.75 ppm was also present, for which a separate iPr(Me) and discernible aromatic resonances were not observable. Based on the integral the two abundant pyrenium ions accounted for ca. 90% of the ion mixture.

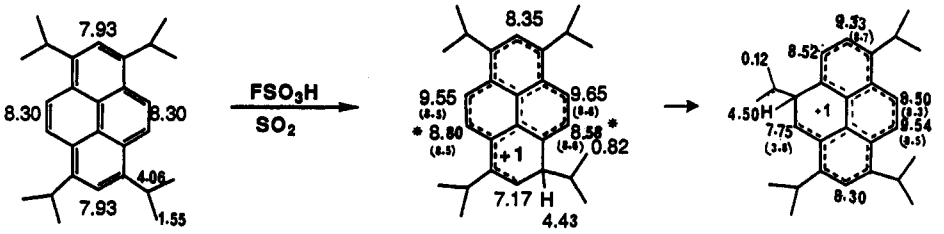
Scheme III. Monoprotonation of Alkylpyrene 3[a]



3 3-H_6^+ 3-H_8^+

[a] Only J values for well-resolved resonances are reported (accuracy ±0.1 Hz). Chemical shifts (ppm) and coupling constants (small numbers; Hz) are given in scheme.

Scheme IV. Monoprotonation of Alkylpyrene 4[a]



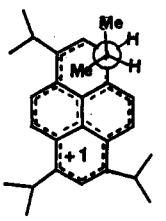
4 4-H_1^+ 4-H_5^+

[a] Only J values for well-resolved resonances are reported (accuracy ±0.1 Hz). Chemical shifts (ppm) and coupling constants (small numbers; Hz) are given in scheme. * denotes interchangeable assignments within a given pyrenium ion.

ture. The major ions are due to protonation at positions 6 and 8. The CH_2 (sp^3) protons appear as a broad singlet at 4.70 ppm for the major pyrenium ions and as a broad shoulder at 4.75 for the minor protonated cation. The aromatic region consisted of twelve $^1/_2$ABs, one doublet, two singlets, and two overlapping triplets. The resonances at 8.01 and 8.05 ppm clearly showed coupling with the CH_2 (J = 2–3 Hz). The finding that H_5 protons for the major pyrenium ions resonate at 8.50 and 8.28 ppm, respectively, showed that the monocations had to be 3-H_6^+ and 3-H_8^+, as 3-H_1^+ and 3-H_3^+ are expected to have H_5 chemical shifts >9 ppm (Scheme XIV). Mesomeric charge delocalization is evident for both 3-H_6^+ and 3-H_8^+ ions in which the ortho and meta protons are either shielded or remain relatively unchanged, whereas the corresponding α and $\alpha\beta$ protons are highly deshielded. The low-field shift of the 4-iPr group is also consistent with protonation at C_6 and C_8.

The minor pyrenium ion did not give clearly discernible resonances in the aromatic region. The high-field shift of the isopropyl protons may be explained by protonation at position 3, as ipso protonation would be expected to lead to a more extensive high field shift (see 4). Based on integrals, chemical shifts and with the aid of selective decoupling experiments,[33] the majority of absorptions for the major pyrenium could be assigned. Thus, predominant α protonation is observed leading to a mixture of 3-H_6^+ (50%) and 3-H_8^+ (40%). Intact 3 was isolated upon quenching of the cold ion solution.

Monoprotonation of 4 (Scheme IV). A clear red solution was obtained when a cold solution of FSO_3H/SO_2 was carefully added to a slurry of 4 in SO_2. The low-temperature ^1H NMR spectrum of the ion solution shows one major iPr(Me) doublet at 1.60 ppm ($\Delta\delta$ = 0.09) (4 methyls), having an overlapping doublet at 1.59 ppm ($\Delta\delta$ = 0.1) (1 methyl) and three minor *upfield* methyls at 1.44, 1.42, and 0.82 ppm ($\Delta\delta$ = −0.07, −0.09, and −0.71) (1 methyl each). The iPr(CH) multiplets are observed at 4.40 (2 H) ($\Delta\delta$ = 0.34) and 3.50–3.60 ppm (2 H) ($\Delta\delta$ = −0.51). The sp^3-hybridized CH appears as a broad singlet at 4.43 ppm (1 H) and overlaps with the iPr(CH) at 4.40 ppm. The aromatic region consists of four low-field $^1/_2$ AB's (1 H each) at 9.65 (8.6 Hz), 9.55 (8.5 Hz), 8.80 (8.5 Hz), and 8.58 (8.6 Hz) ppm and two singlets at 8.38 (1 H) and 7.17 (1 H) ppm. The NMR data support the formation of pyrenium ion of ipso attack, 4-H_1^+. Presence of a highly shielded methyl at 0.82 ppm is indicative of buttressing of the ipso iPr group and anisotropic shielding of one methyl by the ring current (Figure 3).[34] A similar effect was observed for the σ-complex of ipso protonated 9-isopropylanthracene.[20] Mesomeric delocalization leads to shielding at the ortho position, while the α and $\alpha\beta$ positions are deshielded. The intact precursor was recovered upon quenching of the cold ion solution.



4-H_1^+

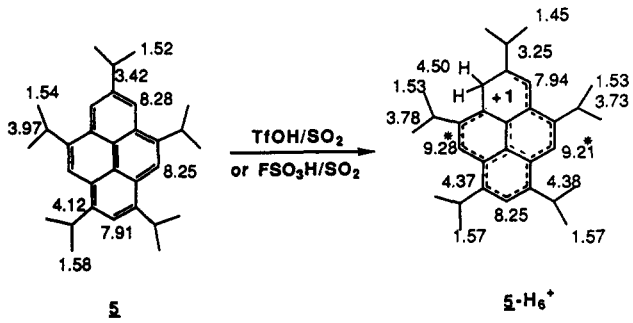
Figure 3. Anisotropic shielding of peri iPr(Me) in 4-H_1^+.

In an independent experiment, 4 was protonated in FSO_3H/SO_2 as before, but the temperature was briefly raised to ca. −40 °C. ^1H NMR spectrum showed apart from 4-H_1^+, a new pyenium ion (ca. 40%) having four aromatic $^1/_2$ AB's (1 H each) at 9.55 (overlapping), 9.33, 8.52, and 8.50 ppm, a tight doublet at 7.75 (1 H), and a singlet at 8.30 ppm. The aliphatic region showed addi-

(33) Due to the very narrow range in chemical shifts, only limited decoupling could be performed.

(34) The calculated minimum energy conformation of 4-H_1^+ showed a 52° twisting of the *ipso*-iPr (Ar–CH) bond out of the aromatic plane, with one methyl group tilted toward and the other away from the aromatic periphery.

Scheme V. Monoprotonation of Alkylpyrene 5[a]



5 5-H_6^+

[a] Chemical shifts (ppm) are given in scheme. * denotes interchangeable assignments.

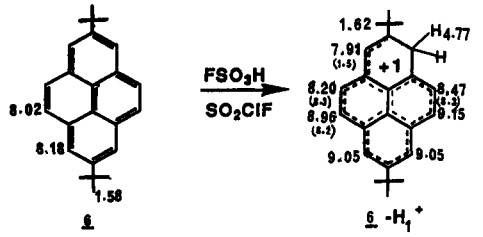
tional *shielded* iPr(CH) multiplets at 4.40, 4.35, and 3.05 ppm, iPr(Me) doublets at 1.50 and 1.26 ppm, and a characteristic *highly shielded* iPr(Me) at 0.13 ppm, indicative of ipso protonation. Prolonged reaction time (1 week at −60 → −40 °C) led to complete disappearance of 4-H_1^+ at the expense of the rearranged pyrenium ion (sample darkened). There was no overall iPr loss in the rearranged ion as confirmed by the number of iPr(CH) and iPr(Me) absorptions present, their integrals, and presence of only one sp^3 (CH) proton. Thus, an α-protonated 3,6,8-triisopropylpyrenium ion, formed by a dealkylation/aromatization/subsequent protonation sequence, was ruled out. The chemical shift for a bent α-iPr(Me) is 0.82 ppm (4-H_1^+); ipso protonation in the rearranged ion led to a greater anisotropic shielding, indicative of migration of one iPr group to an $\alpha\beta$ position and the formation of its corresponding ipso on pyrenium ion **4a**-H_5^+. The most shielded aromatic signal at 7.75 ppm (the 3.8 Hz doublet) is clearly due to H_4 (ortho), showing vicinal coupling to the ipso proton.[35] Finally, the 8.30 ppm singlet is due to H_2. The ion solution was stored for 1 additional week at −20 °C, during which time further darkening of the sample occurred. Quenching of the ion solution furnished the original all α-substituted **4**, indicative of rearrangement during exothermic quenching (see Discussion).

Monoprotonation of 5 (Scheme V). Low-temperature reaction of **5** with either CF_3SO_3H/SO_2 or FSO_3H/SO_2 gave a clear red solution, the ^1H NMR spectrum of which (−65 °C) showed a rather simple spectrum consisting of four downfield shifted aromatic singlets at 9.28 (1 H), 9.21 (1 H), 8.25 (ca. 2 H), and 7.94 ppm (1 H) and a characteristic CH_2 absorption at 4.50 ppm which appears as a relatively sharp singlet, integrating for *two* hydrogens. Four different isopropyl groups are observed, three of which are shifted *downfield* and one is *upfield*. Two of these iPr groups show overlapping CH multiplets and identical methyls. The NMR data are consistent with the formation of the pyrenium ion of attack at an α position, viz. 5-H_6^+,[36] with substantial positive charge delocalization into the α and $\alpha\beta$ positions. Quenching of the cold ion solution resulted in the recovery of intact **5**. Despite its high basicity, **5** is not monoprotonated in the much weaker TFA/SO_2 and remains totally insoluble in this medium even at −10 °C.

(35) Formation of a rearranged α, ipso-protonated pyrenium ion viz. 1,2,6,8-tetraisopropylpyrenium ion **4b**-H_1^+ was ruled out based on lack of four-bond allylic coupling between ipso and meta protons in model pyrenium ions 2-H_1^+, 5-H_6^+, 8-H_1^+, and 8-H_3^+ and unfavorable steric crowding. The alternative 1,3,6,9-tetraisopropylpyrenium ion **4c**-H_1^+ was also disregarded based on the observed position of the buttressed methyl of the ipso iPr group in comparison to that in 4-H_1^+.

(36) The calculated minimum energy structure of 5-H_6^+ indicated a 54° twisting of the *ipso*-iPr (Ar–CH) bond. **5** itself is calculated to have five planar Ar–CH bonds.

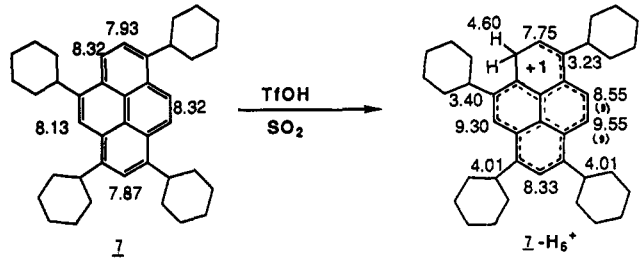
Scheme VI. Monoprotonation of Alkylpyrene 6[a]



6 6-H_1^+

[a] Only J values for well-resolved resonances are reported (accuracy ±0.1 Hz). Chemical shifts (ppm) and coupling constants (small numbers; Hz) are given in scheme.

Scheme VII. Monoprotonation of Alkylpyrene 7[a]



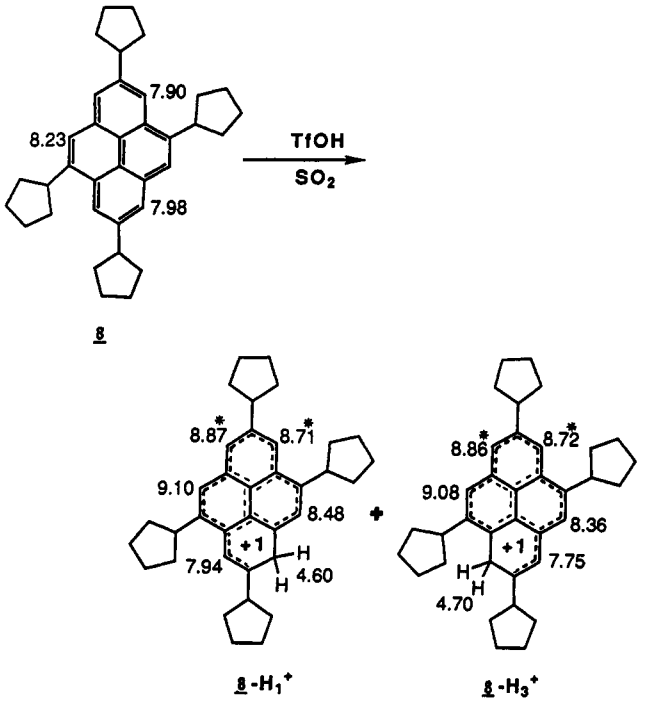
7 7-H_6^+

[a] Chemical shifts (ppm) and coupling constants (small numbers; Hz) are given in scheme.

Monoprotonation of 6 (Scheme VI). Low-temperature reaction of **6** with FSO_3H/SO_2 gave a light red solution, ^1H NMR of which (−70 °C) was consistent with the formation of a single pyrenium ion of attack at an α position viz. 6-H_1^+. The originally equivalent tBu(Me) groups become nonequivalent upon protonation, as the ortho tBu group moves downfield by 0.07 ppm. Broadening of the tBu(Me) singlets was not, however, observed indicative of their free rotation in the pyrenium ion. The diagnostic CH_2 (sp^3) was observed as a slightly broadened singlet at 4.77 ppm, integrating for two hydrogens, ruling out ipso attack. The aromatic region consisted of a diagnostic *shielded* doublet at 7.91 (1 H) assigned to H_3 (meta) with a 1.5-Hz coupling to the CH_2, four deshielded 1 H doublets (three of which showed additional splitting!), and a deshielded 2 H singlet. The most downfield doublet and the 2 H singlet were almost superimposed. Deshielding of one tBu group, the number and multiplicity of the aromatic singlets, and in particular the 7.91 doublet signal clearly ruled out protonation at an $\alpha\beta$ position. The vicinal coupling constants of the $\alpha\beta$ protons were typically 8.2–8.4 Hz. The assigned chemical shifts are consistent with the observed trend of extensive charge delocalization into the "remote" α and $\alpha\beta$ positions. Quenching of the cold ion solution gave intact **6**.

Monoprotonation of 7 (Scheme VII). Low-temperature addition of **7** diluted in SO_2 to a solution of cold $TfOH/SO_2$ gave a clear red solution, the ^1H NMR spectrum of which indicated clean formation of a single pyrenium ion of α attack viz. 7-H_6^+. The spectrum shows the diagnostic CH_2 as a broad singlet at 4.60 ppm; its coupling to H_7 (ortho) is evident by broadening of the 7.75 ppm aromatic singlet absorption assigned to H_7, which in agreement with previous assignments, shows an *upfield* shift compared to the precursor ($\Delta\delta$ = −0.18). The remaining *deshielded* aromatic absorptions, viz. two (1 H) singlets at 8.33 and 9.30 ppm, are assigned to H_2 and H_4 respectively ($\Delta\delta$ = 0.46 and 1.17), whereas the deshielded pair of doublets (9 Hz) at 9.55 ($\Delta\delta$ = 1.23) and 8.55 ($\Delta\delta$ = 0.23) are due to H_{10} and H_9 ($\alpha\beta$). The aliphatic region shows three cyclohexyl methine absorptions, one of which

Scheme VIII. Monoprotonation of Alkylpyrene 8[a]



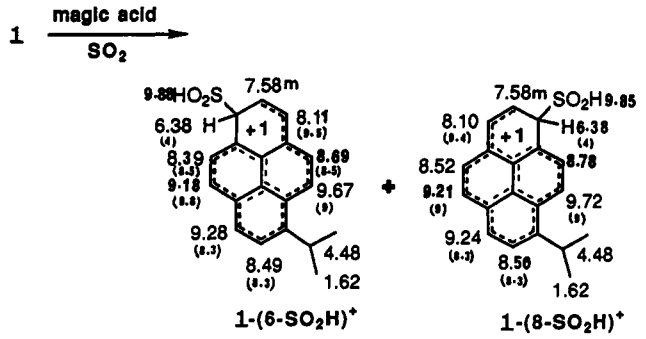
[a] Chemial shifts (ppm) are given in scheme. * denotes interchangeable assignments within a given pyrenium ion.

is *deshielded* (4.03 ppm, 2 H, multiplet), whereas the other two (3.40 and 3.23; 1 H each, broad triplets) are *shielded*. The deshielded methines are due to the cyclohexyl groups in the "remote" α positions (1 + 3), whereas the most shielded methine is for the *m*-cyclohexyl group. The cyclohexyl methylenes show restricted rotation giving rise to an unresolved envelope and a broad singlet. The intact precursor was recovered upon quenching of the cold ion solution.

Monoprotonation of 8 (Scheme VIII). The ^1H NMR spectrm of the red ion solution, obtained upon low-temperature reaction of cold TfOH/SO_2 with 8 in SO_2, shows two diagnostic CH_2 (sp^3) absorptions at 4.70 and 4.60 ppm, indicative of two pyrenium ions in a 60:40 ratio; observation of two sets of five aromatic singlet absorptions in 60:40 ratio supports this conclusion. On the basis of the relative integrals and using the already established charge distribution trends with isopropylpyrenium ions, the spectrum is analyzed as a mixture of 8-H_1^+ (40%) and 8-H_3^+ (60%). The most upfield singlets at 7.75 ($\Delta\delta$ = −0.15) and 7.94 ppm ($\Delta\delta$ = 0.04) are due to the H_3 (meta) of the ions, whereas the most deshielded singlets at 9.10 ($\Delta\delta$ = 0.87) and at 9.08 ($\Delta\delta$ = 0.85) are due to the $\alpha\beta$ protons. The cyclopentyl groups give four methine absorptions at 4.40, 3.75, 3.45, and 3.35. The most deshielded CH is for cyclopentyl groups in the $\alpha\beta$ positions, whereas the most shielded CH is for the *o*-cyclopentyl group. The cyclopentyl methylenes show restricted rotation. Upon quenching, the intact precursor was isolated.

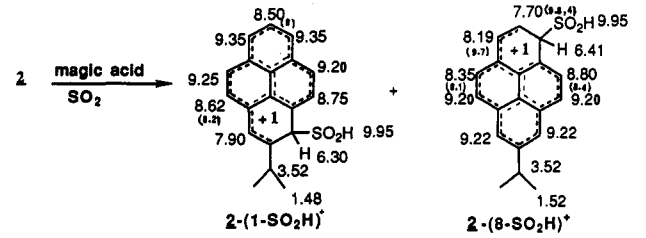
Reaction of Pyrenes 1–5 with FSO_3H-SbF_5(1:1)SO_2. Reaction with 1 (Scheme IX). The dark red ion solution formed upon addition of cold Magic Acid/SO_2 to 1 in SO_2 shows a single deshielded iPr group (δ 4.48 (CH), 1.62 (Me)) and a deshielded CH (sp^3) absorption at 6.38 ppm appearing as a 4-Hz doublet. In addition to a large number of aromatic doublets, indicative of substitution at both ends of the pyrene skeleton, two low-field absorption at δ 9.85 and 9.88 are observed (close to H_3O^+ peak), assigned to $-SO_2H$.[37] The most upfield aromatic absorption

Scheme IX. Sulfinylation σ-Complexes of 1 Formed in Magic Acid/SO_2[a]



[a] Only J values for well-resolved resonances are reported (accuracy ±0.1 Hz). Chemical shifts (ppm) and coupling constants (small numbers; Hz) are given in scheme (m = multiplet). As two pyrenium ions are equally abundant, interchange of some resonances for hydrogens in identical relative positions in two pyrenium ions is possible.

Scheme X. Sulfinylation σ-Complexes of 2 Formed in Magic Acid/SO_2[a]



[a] Only J values for well-resolved resonances are reported (accuracy ±0.1 Hz). Chemical shifts (ppm) and coupling constants (small numbers; Hz) are given in scheme.

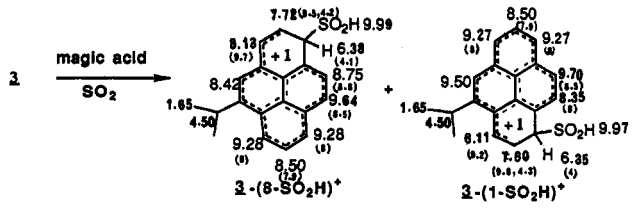
at 7.58 ppm clearly shows vicinal coupling to CH(sp^3), as was observed in the protonation σ complexes of 1 and is assigned to H_7 (ortho). The most deshielded aromatic doublets at 9.72, 9.67, 9.21 (9 Hz each), and 9.18 ppm (8.8 Hz) are due to $H_{\alpha\beta}$. The spectrum is consistent with a mixture of two Wheland intermediates of sulfinylation[38] at the "remote" α position viz. 1-(6-SO_2H)$^+$ and 1-(8-SO_2H)$^+$ in ca. 1:1 ratio. Quenching of the cold ion solution led to preferential desulfinylation to give intact 1 (85% yield).

Reaction with 2 (Scheme X). Careful addition of a cold solution of Magic Acid diluted in SO_2 to a slurry of 2 in SO_2 gave a dark red homogeneous solution, the low-temperature NMR of which was consistent with the formation of two pyrenium ions having further deshielded aromatic protons as compared to 2-H_1^+. The aliphatic region consists of three iPr groups, with unshifted methine protons. Two methyl absorptions have the same intensity (1.59 and 1.48 ppm, $\Delta\delta$ = 0.12 and 0 ppm). The third one is twice as intense (1.52 ppm, $\Delta\delta$ = 0.05 ppm). The CH (sp^3) protons have shifted further downfield and appear as a singlet at δ 6.30 and a doublet at δ 6.41 (4 Hz) integrating for ca. 1 proton. Despite further downfield shifts of the aromatic protons and the CH(sp^3) signal, the intensity of the later clearly ruled out a diprotonated pyrenium ion. The most upfield aromatic signal is a doublet

(37) The S–OH proton in "long-lived" protonated sulfinic acids is a singlet at 9.12–9.40 ppm; see: Olah, G. A.; Ku, A. T.; Olah, J. A. *J. Org. Chem.* **1970**, *35*, 3908.

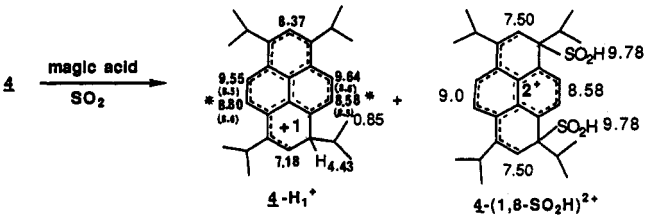
(38) For examples of competing sulfinylation in superacid media, see: Olah, G. A.; Kiovsky, T. E. *J. Org. Chem.* **1967**, *89*, 5692. Olah, G. A.; Kiovsky, T. E. *J. Org. Chem.* **1968**, *90*, 2583. Olah, G. A.; Schlosberg, R. H.; Kelly, D. P.; Mateescu, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 2546. Laali, K.; Nagvekar, D. S. *J. Org. Chem.* **1991**, *56*, 1867.

Scheme XI. Sulfinylation σ-Complexes of 3 Formed in Magic Acid/SO_2[a]



[a] Chemical shifts (ppm) and coupling constants (small numbers; Hz) are given in scheme.

Scheme XII. Sulfinylation and Protonation of 4 in Magic Acid/SO_2[a]



[a] Only J values for well-resolved resonances are reported (accuracy ±0.1 Hz). Chemical shifts (ppm) and coupling constants (small numbers; Hz) are given in scheme. * denotes interchangeable assignments within a given pyrenium ion.

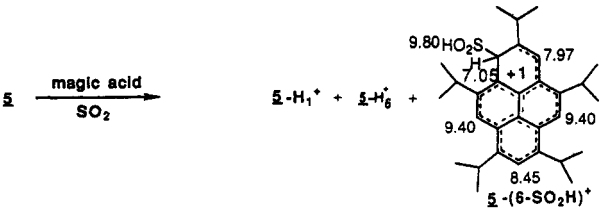
of doublet at 7.70 ppm, assigned to H_7 (ortho). The spectral data are consistent with a mixture of 2-(1-SO_2H)$^+$ and 2-(8-SO_2H)$^+$ ions (1:1 ratio). The -SO_2H signal appears as a slightly broad singlet at ca. 9.95 ppm close to H_3O^+ peak.

Reaction with 3 (Scheme XI). Careful addition of a solution of cold Magic Acid in SO_2 to a slurry of **3** in SO_2 at -75 °C gave a deep red homogeneous solution, the ^1H NMR of which indicated further downfield shifts for both aromatic and aliphatic protons. The aliphatic region shows just one major (90%) deshielded iPr group at 1.65 and 4.50 ppm ($\Delta\delta$ = 0.07, 0.55) and a minor (10%) iPr at 1.70 and 4.75 ppm ($\Delta\delta$ = 0.12 and 0.8). The diagnostic (sp^3) CH protons are at 6.35 and 6.38 ppm (1 H; each 4.0- and 4.1-Hz doublets). The aromatic absorptions at 7.72 and 7.60 ppm both show extra splittings of allylic type and appear as doublet of doublets. Two diagnostic -SO_2H absorptions are observed at 9.99 and 9.97 ppm (sharp singlets) close to H_3O^+. The spectrum is consistent with the Wheland intermediates of sulfinylation, 3-(8-SO_2H)$^+$ and 3-(1-SO_2H)$^+$ in 67:30 ratio. Intact **2** was obtained (>80%) by ion quenching.

Reaction with 4 (Scheme XII). Low-temperature reaction of **4** with a cold solution of Magic Acid in SO_2 solvent gave a deep red homogeneous solution, the ^1H NMR spectrum of which indicated the presence of two pyrenium ions (70:30 ratio). The aliphatic region shows the CH(sp^3) proton as a broad singlet at 4.41 overlapping with an iPr (CH) multiplet. Other iPr (CH) multiplets are observed at 3.89 ppm ($\Delta\delta$ = 0.17) and 3.60 ppm ($\Delta\delta$ = -0.12). The iPr(Me) doublets are at 1.65, 1.51, and 0.85 ppm ($\Delta\delta$ = 014, 0.0, and -0.66). The aromatic region shows all the absorptions for 4-H_1^+ (see monoprotonation of **4**), in addition to four singlets at 9.78 (2 H), 9.0 (2 H), 8.58 (2 H), and 7.50 (2 H). These absorptions are indicative of a symmetrical sulfinylation dication formed by ipso attack at two α positions viz. 4-(1,8-SO_2H)$^{2+}$. Quenching of the cold ion solution led to recovery of intact **4** (>90%), indicative of preferential desulfinylation.

Reaction wih 5 (Scheme XIII). Slow addition of a solution of Magic Acid/SO_2 to a slurry of **5** in SO_2 at -75

Scheme XIII. Sulfinylation and Protonation of 5 in Magic Acid/SO_2[a]



°C resulted in a deep red solution, the ^1H NMR spectrum of which indicated a complex mixture containing two pyrenium ions of α protonation, viz. 5-H_1^+ and 5-H_6^+ and the Wheland intermediate of sulfinylation at position 6 viz. 5-(6-SO_2H)$^+$, the amount of which varied in different preparations.[39] The iPr(Me) groups showed restricted rotation (an envelope of doublets from 1.75 to 1.32 ppm). The chemical shifts for the ipso-protonated species, 5-H_1^+, are in good agreement with other α protonated pyrenium ions. The aromatic region exhibited 20 absorptions between 6.5–10 ppm. Skeletally intact **5** was obtained by ion quenching.

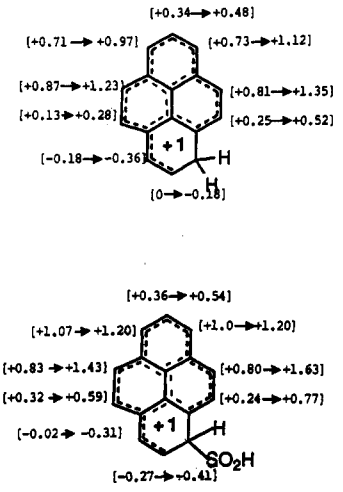
Reaction of Pyrenes 4 and 7 with FSO_3H·SbF_5 (1:1)/SO_2ClF and Comparison with 1,2,3,6,7,8-Hexahydropyrene 9. In an attempt to generate stable pyrenium dications by protonation, low-temperature reaction of **4** and **7** with Magic Acid was studied in SO_2ClF solvent to prevent sulfinylation; both pyrenes gave deep red ion solutions. The ^1H NMR spectrum of **4** showed very broad features showing resonances at 1.6 (Me), 4.2, 4.4, and 4.8 ppm, two relatively broad (small) singlets between 6–6.50 ppm and an envelope of broad (deshielded) aromatic absorptions between 7.60–9.20 ppm. That of **7** showed deshielded cyclopentyl absorptions between 2–3 ppm (CH_2) and 3.80–4.20 ppm (CH), a broad singlet at ca. 4.50 ppm and, once again, an envelope of broad aromatic absorptions. The spectra clearly indicate radical cation formation (oxidation) in competition with the protonation σ-complexes.

For comparison, we also protonated symmetrical **9** in Magic Acid/SO_2ClF and in Magic Acid/SO_2 solvent at -70 °C. In SO_2ClF, the ion solution exhibited a simple ^1H NMR spectrum consisting of one deshielded aromatic singlet at 8.75 ppm, a diagnostic CH_2(sp^3) absorption, appearing as a relatively broad singlet at 4.33 ppm (4 H) and three other aliphatic CH_2's (3.99, 3.68, and 2.51 ppm). The spectrum was essentially identical with that reported for the dication.[27] With SO_2 solvent, however, a complex spectrum was obtained with no indication for hexahydropyrene dication formation. Diagnostic CH(sp^3) absorptions were observed at 4.25, 4.40, and 5.10 ppm and a distinct -SO_2H singlet at 9.70 ppm indicative of a sulfinylation σ-complex. The aromatic region was very rich in doublets (ca. 7 Hz) between 7.4–9 ppm, in addition to eight singlets between 9.65–9 ppm. The number of aromatic resonances suggest the formation of monopyrenium ions of protonation and sulfinylation of both symmetrical **9** and asymmetrical (4,5,5a,6,7,8)-hexahydropyrene.

When the sample was stored at -40 °C for 1 week and subsequently quenched, ^1H NMR spectrum of the recovered pyrene showed apart from intact **9** (aromatic singlet at 7.20 ppm, aliphatic triplet at 3.05 ppm and aliphatic multiplet at 2.05 ppm), aromatic singlets at 8.05,

(39) (a) A fourth, as yet unidentified product was also formed in some cases. (b) A small iPr(Me) doublet was also observed at 0.85 ppm, indicative of its twisted conformation and anisotropic shielding due to ipso protonation.

Scheme XIV. Average Range of Δδ ^{1}H's for the Protonation and Sulfinylation σ-Complexes



8.15, and 8.19 ppm, indicative of oxidation to pyrene (ca. 70%).[40a]

Discussion

An Overall Comparison of Protonation Data. In agreement with PI-DEWAR calculations,[15] monoprotonation of alkylpyrenes under stable ion conditions is controlled by the greater stability of the Wheland intermediate of α attack; 8.8 kcal/mol difference in σ-complex stability (α versus αβ attack) manifests itself in the observed absence of any (major) pyrenium ions of αβ attack for pyrenes 1–8. The presence of an iPr (or a cyclohexyl) group at an α position does not lead to predominant ipso protonation; instead protonation occurs mainly at the remote α positions (6, 8). On the other hand, when an iPr (or a cyclopentyl) group is placed in the β position, exclusive monoprotonation occurs in the α position in the same ring (ortho) rather than at a remote α position, indicative of inductive stabilization of positive charge in the ortho position by the iPr group as seen with **2** and **5**. Inductive stabilization by a cyclopentyl or a tBu group similarly leads to exclusive ortho protonation. Substituent stabilization is also observed for "remote" substituents, as **3** is protonated at positions 6 and 8 rather than at positions 1 and 3. The chemical shift changes caused by protonation at an α position are very similar in all cases; the remote α and two of the αβ positions are most deshielded, whereas the ortho and meta protons are shielded (Scheme XIV).[40b]

In parent pyrene, the vicinal coupling constants (^3J) for H_α–H_β = 7.8 Hz and for $H_{\alpha\beta}$–$H_{\alpha\beta}$ = 9.0 Hz.[1] Introduction of an ortho or a peri iPr group increases the vicinal coupling by 0.4 Hz. In the pyrenium ions, an increase in $^3J(H_\alpha$–$H_\beta)$ is observed for the ortho and meta protons, indicative of decreased bond order.[41] A rather general trend of increasing $^3J(H_\alpha$–$H_\beta)$ and decreasing $^3J(H_{\alpha\beta}$–$H_{\alpha\beta})$ relative to the precursor is apparent. Whereas vicinal coupling of H (ortho) to CH(sp^3) is usually seen, four-bond coupling involving CH(sp^3) and H (meta) was rarely observed.

The ipso σ-complexes preferentially deprotonate on quenching to furnish the intact precursors.

Isomerization. With the exception of **4**, which is ipso protonated in superacid media, all other pyrenium ions of α attack were stable (at least up to −40 °C) and showed no isomerization. Absence of iPr (or tBu) rearrangement for pyrenium ions **2**-H_1^+, **5**-H_6^+, and **6**-H_1^+ is not surprising as the Wheland intermediate leading to dealkylation (the ipso σ-complex (β)) is substantially higher in energy.

Ipso-protonated **4** rearranged to **4a** upon raising the temperature to give **4a**-H_5^+. Formation of **4a**-H_5^+ cannot be adequately explained by α-dealkylation/aromatization/αβ-realkylation sequence, as the available α position is more electrophilic for realkylation. We propose the following sequence of events; nucleophilic attack by the gegenion at higher temperature (iPr–OSO_2F byproduct), followed by aromatization and rapid protonation, initially gives an α-protonated triisopropylpyrenium ion. Subsequent electrophilic attack on the monopyrenium ion by iPr–OSO_2F gives a dication. Deprotonation/aromatization at the α position leads to the observed rearranged pyrenium ion.

4a rearranges to **4** under more forcing conditions; **4a** → **4** rearrangement was previously observed in Friedel–Crafts isopropylation of pyrene (iPrBr/$AlBr_3$/60 °C) by monitoring product evolution with time. In general, iPr disproportionation is quite facile under Friedel–Crafts conditions.[42]

Attempted Diprotonation. Unlike di- and polymethylnaphthalenes,[19] phenanthrenes[22] and symmetrical hexahydropyrene,[27] which are diprotonated in Magic Acid/SO_2ClF to give stable dications, substituted pyrenes undergo oxidation in competition with monoprotonation; stable dications are not formed. Judging from the HOMO–LUMO gap (E_{HOMO}),[26a] pyrene is more susceptible to ET oxidation than phenanthrene or naphthalene; HOMO energy is further raised when electron releasing alkyl(cycloalkyl) groups are added.

Differing Nature of the Pyrenium Ions Formed in SO_2 and SO_2ClF. Role of SbF_5. In lower acidity superacids (FSO_3H or TfOH) stable monopyrenium ions of protonation were formed irrespective of solvent (SO_2 or SO_2ClF). Solvent dependency of the pyrenium ions formed was observed only at much higher acidities in the presence of SbF_5 where sulfinylation σ-complexes were observed in SO_2 and oxidation/monoprotonation occurred in SO_2ClF. We conclude that the Wheland intermediates of sulfinylation are formed by electrophilic sulfinylation of the substituted pyrenes with SO_2 → SbF_5 (a potent sulfinylating agent), rather than by nucleophilic attack of SO_2 itself on the pyrenium ion(s) of protonation.

Preference for sulfinylation in SO_2 was also seen with symmetrical hexahydropyrene, which in SO_2ClF solvent gives a stable protonation dication, suggesting that Magic Acid/SO_2 should provide a suitable medium for generation of Wheland intermediates of sulfinylation of reactive PAHs. The sulfinylation σ-complexes show the following notable features: (a) more deshielded CH(sp^3) protons (typically 6.30 to 7.05 ppm) as compared to CH(sp^3) for protonated pyrenium ions (4.30 to 4.70 ppm);[43] (b) distinct

(40) (a) **9** is usually difficult to oxidize, its facile conversion to pyrene in magic acid has synthetic merit; further studies are warrented. (b) Analysis of ^{1}H Δδ's for various positions of the pyrenium ions of protonation (e.g., **4**-H_1^+, **8**-H_1^+, **1**-H_6^+, **1**-H_3^+) (supplementary material) shows that the "out-of-range" protons are mostly in crowded positions (ortho to iPr (more shielded), peri to iPr, or peri to cycloalkyl (more deshielded)), suggesting that steric/conformational factors contribute to these deviations.

(41) For example, using $^3J = -35.10R_{\mu\nu} + 56.65$ relationship (Günther, H. *NMR Spectroscopy; An Introduction*; Wiley: New York, 1980), an increase in $^3J_{H\alpha-H\beta}$ from 7.8 Hz in the precursor to 9.20 Hz in **3**-H_6^+ corresponds to a change in the bond order from 1.3917 to 1.3518.

(42) (a) McCaulay, D. A. In *Friedel–Crafts and Related Reactions*; Olah, G. A., Ed.; Interscience Publishers: New York, 1964, Chapter 24, Vol. II, Part II. (b) Laali, K.; Sommer, J. *Nouv. J. Chim.* **1982**, *5*, 3. (c) Booth, B. L.; Haszeldine, R. N.; Laali, K. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2887.

low-field $-SO_2H$ absorptions; (c) charge distribution (and vicinal coupling) patterns very similar to those observed for pyrenium ions of protonation; and (d) preferential desulfinylation upon quenching of the Wheland intermediates.

Experimental Section

Syntheses and purification of pyrenes **1–7** are already described.[1] FSO_3H (Allied), CF_3SO_3H, and SbF_5 (both Aldrich) were distilled twice under dry nitrogen in an all-glass distillation unit prior to use. Anhydrous SO_2 (Linde) and doubly distilled SO_2ClF (Aldrich) were used as received.

Protonation Procedure. To a slurry of the pyrene (20–30 mg) in 0.5 mL of cold SO_2 or SO_2ClF inside a 10-mm NMR tube, was added a clear solution of ca. 1 mL of the superacid (FSO_3H, CF_3SO_3H or $FSO_3H.SbF_5$ (1:1)) diluted with 1 mL of SO_2 or SO_2ClF with efficient vortex mixing at dry ice–acetone temperature. A cold aliquot of the ion solution was transferred via a precooled pipet (liquid SO_2) into a cold 5-mm NMR tube, and 5 drops of cold CD_2Cl_2 was added as internal standard and lock (vortex mixing).

Ion Quenching. The cold NMR tube containing the ion solution was carefully poured into ice–bicarbonate. The organic layer was extracted (CH_2Cl_2), dried ($MgSO_4$), and evaporated to dryness. The residue was taken up in $CDCl_3$ and analyzed by ^1H NMR spectroscopy.

NMR spectra were recorded on a GN-300 wide-bore instrument. The probe was precooled to −70 °C while shimming on an acetone-d_6 sample; the cold ion solution was quickly introduced into the cold probe at −70 °C and spun for 5 min prior to data collection.

MMX force field energy calculations on **4**-H_1^+ and **5**-H_6^+ (see refs 34, 36) were carried out using the PCMODEL program (Serene Software). All pyrene carbons were assigned π atoms (SCF-π calculations were unavailable). The π system in the minimized structures was planar. The sp^3 carbon was specified C^+.

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Registry No. **1**, 78751-46-9; **1**-H_6^+, 136827-78-6; **1**-H_8^+, 136827-79-7; **1**-H_3^+, 136827-80-0; **1**-(6-SO_2H)$^+$, 136827-81-1; **1**-(8-SO_2H)$^+$, 136827-82-2; **2**, 78751-61-8; **2**-H_1^+, 136827-83-3; **2**-(1-SO_2H)$^+$, 136827-84-4; **2**-(8-SO_2H)$^+$, 136827-85-5; **3**, 74869-51-5; **3**-H_6^+, 136827-86-6; **3**-H_8^+, 136827-87-7; **3**-(8-SO_2H)$^+$, 136827-88-8; **3**-(1-SO_2H)$^+$, 136827-89-9; **4**, 24300-95-6; **4**-H_1^+, 136827-90-2; **4**-(1,8-SO_2H)$^{2+}$, 136827-99-1; **4a**-H_5^+, 136827-91-3; **5**, 78751-94-7; **5**-H_6^+, 136827-92-4; **5**-(6-SO_2H)$^+$, 136827-93-5; **5**-H_1^+, 136827-94-6; **6**, 24300-91-2; **6**-H_1^+, 136827-95-7; **7**, 78751-88-9; **7**-H_6^+, 136827-96-8; **8**, 78751-92-5; **8**-H_1^+, 136827-97-9; **8**-H_3^+, 136827-98-0; FSO_3H, 7789-21-1; SO_2ClF, 13637-84-8; Magic acid, 23854-38-8.

Supplementary Material Available: Selected NMR spectra of pyrenium ions of protonation and sulfinylation and tables of ^1H $\Delta\delta$'s (27 pages). Ordering information is given on any current masthead page.

(43) The most deshielded CH(sp^3) reported so far for an arenium ion of protonation (9-methyl-1,8-dichloroanthracenium ion) is at 5.69 ppm (see ref 20).

Selective Ortho Lithiation of (2,5-Dimethoxyphenyl)diphenylphosphine Oxide and Trapping of the Resulting Aryllithium with Electrophiles

John M. Brown* and Simon Woodward

Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY, U.K.

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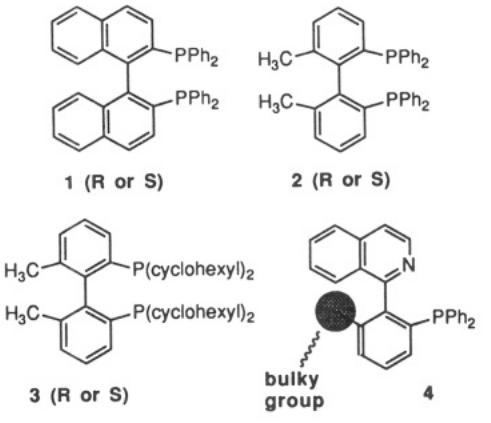
The title compound undergoes predominant 6-lithiation, ortho to the methoxy and phosphinoyl groups, on reaction with t-BuLi in THF under conditions of thermodynamic control at low temperature. The organolithium compound is stable at least to 0 °C and can be trapped by a range of electrophiles to give the corresponding tetrasubstituted (diphenylphosphinoyl)arenes in moderate to good yield. The iodide formed by this sequence undergoes Ullman coupling to the diphenyl, which exhibits a novel restricted rotation phenomenon, in good yield under mild conditions. (2,5-Dimethoxyphenyl)diphenylphosphine sulfide lithiates exclusively at the 4-position under the same conditions, whilst the corresponding phosphine is unreactive.

Introduction

Much recent catalytic asymmetric synthesis has utilized atropisomeric diphosphine ligands, among which BINAP **1** is preeminent.[1] Others of interest in this context include ligands **2**[2] and **3**,[3] and a number of related compounds have been reported recently.[4] Diphosphines are the ligands of choice for asymmetric hydrogenation with rhodium or ruthenium catalysts and also likely to be so for catalytic asymmetric hydroboration, olefin isomerization, and allylic alkylation. In many other applications in asymmetric

Chart I. Atropisomeric Ligands



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