Protonation of Stable π Carbocations. Requirements for the Reaction of Two Positively Charged Species with Each Other in Solution[1]

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The trityl ion **6** undergoes a very rapid exchange reaction ($H_m \gg H_p$) with protons in CF_3SO_3H at temperatures as low as –40 °C. Reasons are offered why this nonplanar ion is protonated so rapidly. The ^1H NMR spectra of the phenalenyl cations **8a–h** and the sesquixanthyl ion (**9**) give no indication of exchange in CF_3SO_3H. Only when CF_3SO_3D is the reaction medium do some of these planar ions give evidence of exchange via a protonation–deprotonation mechanism. In those ions that exchange, only certain sites are found to be reactive. The phenalenyl cations (**8a–d,g**) with two substituents (OH, OCH_2CH_3, and/or OCH_3) at activating positions (1, 3; 1, 9) exchange faster than the one ion (**8e**) with a single substituent (OH) at an activating position (C-1); the parent **8f**, which, of course, has no substituent, does not exchange. The position of the two activating groups on the phenalenyl ions also is critical to the rate of exchange with: **8d** (1,3-dihydroxy) $\gg$ **8g** (1,9-dihydroxy) $\gg$ **8h** (1,2-dihydroxy). The sesquixanthyl ion (**9**) is also deuterated rapidly in CF_3SO_3D. When all the above ions are generated in 1:1 FSO_3H/SbF_5 (100% magic acid) diluted with SO_2 or SO_2ClF, some of them yield dications that are observed by ^1H NMR spectroscopy. The 1,3-disubstituted phenalenyl ions (**8a,b,d**) and the sesquixanthyl ion (**9**) all yield dications, some of them reversibly and some irreversibly; none of the other species yield an observable dication in these media. Several other ions, **14a–c** and **15–17**, also undergo exchange in CF_3SO_3D. The relative reactivity and regiochemistry of these and the other exchange reactions, with the possible exception of **8h**, can be explained on the basis of classical concepts of electrophilic aromatic substitution on uncharged substrates. What is important to remember here is that these reactions involve two positively charged species.

Introduction

The concept of Coulombic charge repulsion is so pervasive in science that chemists have rarely considered the possibility that reactions between two species having the same charge can occur. This idea is, of course, quite reasonable. Clark and Weiss have shown by ab initio molecular orbital calculation, for example, that the proton affinity of the cyclopropenium ion (**1a**) is +40 kcal/mol (eq 1).[2]

a) R=H, b) R=NH$_2$
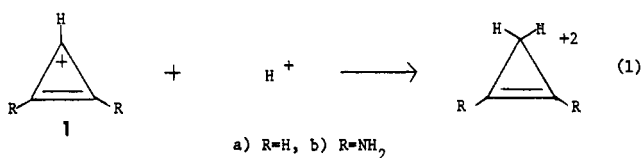
If such reactions are highly endothermic, the question is how one can reduce this endothermicity. Substituents that stabilize positive charge should reasonably lower the heat of reaction. Indeed, the calculated proton affinity of **1b**, which possesses two stabilizing amino groups, is exothermic.[2] Performing the reaction in solution should also be helpful because charge repulsion will be moderated by solvation of the carbocations and especially the proton. In acid solvent one would also expect the viability of the reaction to depend on the proton "pressure" or acidity of the medium. In other words, a stronger acid will more likely bring about a reaction, such as shown in eq 1, than a weaker acid will. One final factor that shouldn't be overlooked is the geometry of the reactant cation and product dication. If the dication is so constituted, for example, that each charge is associated with a molecular fragment that is perpendicular to the other, charge repulsion will be minimized.

One might expect that for carefully chosen systems such reactions will be observable in solution. In fact there are a few examples in the literature where the reaction of two positively charged species (one of which is H$^+$ and the other a carbocation) with each other is likely, if unproven.[3,4] To give one example, Lammertsma and Cerfontain have observed[3c] that treatment of 1,6-methano[10]annulene (**2**) with 1:1 FSO_3H–SbF_5 in SO_2ClF at ca. –120° and subsequent warming to –60 °C yielded the dication **4**, presumably by protonation of the intermediate carbocation **3**.
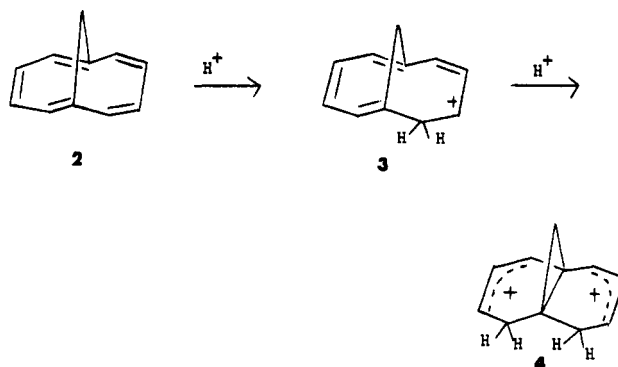
It is the purpose of this paper to discuss in detail our extensive work in this area. We hope (1) to illustrate just how general this reaction is, (2) to point out factors that appear to be important in making the reaction occur, and (3) to give unequivocal proof that one can protonate a carbocation in solution.

Results and Discussion

The first species investigated was the known hexamethoxytrityl carbocation **6**.[5] Dissolution of the carbinol

(1) Some of this work has appeared in communication form. (a) Pagni, R. M.; Smith, R. J. *J. Am. Chem. Soc.* 1979, *101*, 506. (b) Smith, R. J.; Pagni, R. M. *Ibid.* 1979, *101*, 4769.

(2) Clark, T.; Weiss, R. *J. Org. Chem.* 1980, *45*, 1790.

(3) For the protonation of a carbon atom, see (a) Weiss, R.; Priesner, C.; *Angew. Chem. Int. Ed. Engl.* 1978, *17*, 445. (b) Barltrop, J. A.; Barrett, J. C.; Carder, R. W.; Day, A. C.; Harding, J. R.; Long, W. E.; Samuel, C. J. *J. Am. Chem. Soc.* 1979, *101*, 7510, and references cited therein. (c) Lammertsma, K.; Cerfontain, H. *Ibid.* 1980, *102*, 3257. (d) Olah, G. A.; Surya Prakash, G. K.; Liang, G.; Westerman, P. W.; Kunde, K.; Chandrasekhar, J.; Schleyer, P. v. R. *Ibid.* 1980, *102*, 4485. (e) Lammertsma, K. *Ibid.* 1981, *103*, 1062.

(4) For a few examples of the protonation of a carbocation heteroatom, see (a) Sommer, J.; Schwartz, S.; Rimmelin, P.; Canivet, P. *J. Am. Chem. Soc.* 1978, *100*, 2576. (b) Bruck, D.; Minsky, A.; Dagan, A.; Rabinovitz, M. *Tetrahedron Lett.* 1981, 3545. (c) Gold, V.; Mah, T. *J. Chem. Soc., Perkin Trans. 2* 1981, 812.
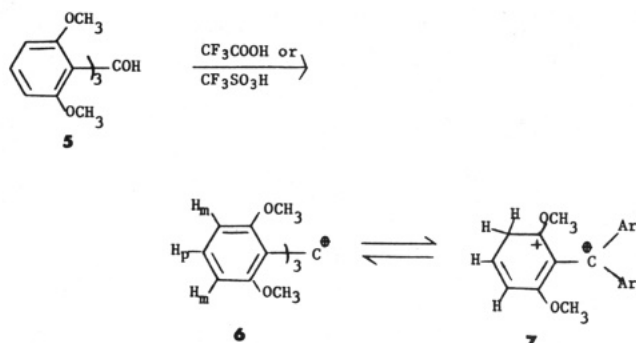
5 in CF$_3$COOH (pK_a = 0.50[6,7]) yielded a ^{1}H NMR spectrum[8] [δ 7.52 (t, *J* = 9 Hz, 3 H, H$_p$), 6.48 (d, *J* = 9 Hz, 6 H, H$_m$), 3.48 (s, 18 H, CH$_3$O)] expected for the ion **6**. Treatment of **5** with the much stronger CF$_3$SO$_3$H (H_0 = –13,[9] –14.6[10]), on the other hand, gave an entirely different ^{1}H NMR spectrum.[8] The low-field triplet (due to H$_p$) observed in CF$_3$COOH collapsed to a broad singlet [δ 8.08 (3H)] and the upfield doublet completely disappeared; the methoxy singlet [δ 4.16 (18 H)] was still present.[11a] This behavior is consistent with rapid exchange (on the ^{1}H NMR time scale) of all meta hydrogens of **6** with protons in the solvent.[11b] Even the para hydrogens of **6** will exchange. When **5** was treated with CF$_3$SO$_3$D at room temperature, the spectrum was originally identical with that in CF$_3$SO$_3$H. On heating at 125 °C for 18 h, however, the H$_p$ signal at δ 8.08 disappeared. The methoxy peak at δ 4.16 remained, and a new small peak at δ 4.13 appeared. This new methoxy peak undoubtedly arises from a slow demethylation reaction on **6**.

Three experiments were performed to demonstrate the validity of the proposed exchange mechanism, i.e., **6** + H$^+$ $\rightleftharpoons$ **7**. Could it be that **5** or its triflate ester is the vehicle of exchange? Even though this is very unlikely because of the extraordinarily low concentration of **5** in CF$_3$SO$_3$H[12] and the acid's low nucleophilicity, the above experiments were performed starting from the trityl perchlorate salt. Identical results were obtained, i.e., static ion in CF$_3$COOH and a rapidly exchanging one in CF$_3$SO$_3$H.

Could it be that the observed species in CF$_3$SO$_3$H is not **6**? The answer is no. Dilution of a CF$_3$SO$_3$H solution of **5** or **6** perchlorate with successive portions of CH$_3$CN eventually regenerated the ^{1}H NMR spectrum of **6** observed in CF$_3$COOH (Figure 1).

Finally it was possible to demonstrate that the exchange process occurred on the apparently static ion. Treatment of **5** with 5% CF$_3$SO$_3$H in CH$_3$NO$_2$ (large excess acid) yielded a ^{1}H NMR spectrum of **6** virtually identical with that of **6** in CF$_3$COOH.[13] Repeating this experiment in
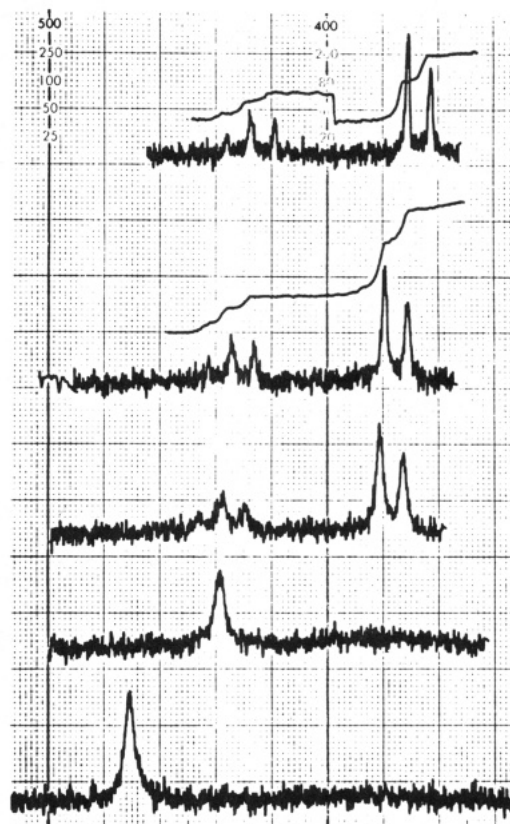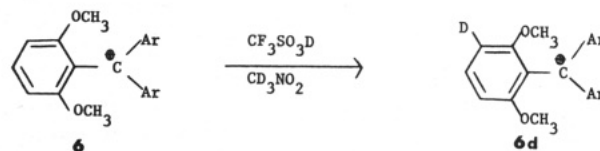

Figure 1. ^{1}H NMR spectra of **6** (aromatic region). Bottom spectrum in CF$_3$SO$_3$H; spectra above with added portions of CH$_3$CN (these spectra have been displaced somewhat upfield from the bottom spectrum).

5% CF$_3$SO$_3$D–CD$_3$NO$_2$ yielded a spectrum in which a doublet had grown into the low-field triplet. This can only be due to the incorporation of deuterium at the meta sites of **6**.[15]

Why is the reaction of two positively charged ions with each other so facile? There are three factors that are important in explaining this fact. First, the six methoxy groups help significantly in delocalizing the two positive charges in the dication **7**. Second, because trityl cations in general and this one in particular are highly twisted, little of the positive charge leaks into each of the three aryl rings of **6**. Thus, the reaction of **6** with H$^+$ might be similar in character to that between 2,6-dimethoxytoluene and H$^+$.[11b] Finally, because the aryl rings are twisted away from planarity, it is likely that the dication **7** has a geometry in which the π system associated with one unit charge is perpendicular to the other π system which is associated with the second unit charge. Charge repulsion will be minimized in this way. Based on this analysis, protonation of triarylmethyl cations may be a fairly common phenomenon.

The obvious question to ask at this point is: can a planar carbocation be protonated?[16] To explore this question

(5) Martin, J. C.; Smith, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 2252.

(6) Kurz, J. L.; Farrar, J. M. *J. Am. Chem. Soc.* **1969**, *91*, 6057.

(7) The pK_a of an acid in water should be correlated with the acidity of the neat acid.

(8) Internal standard is (CH$_3$)$_4$N$^+$BF$_4^-$ (δ 3.10). Deno, N. C.; Richey, Jr., H. G.; Friedman, N.; Hodge, J. D.; Houser, J. J.; Pittman, Jr., C. U. *J. Am. Chem. Soc.* **1963**, *85*, 2991.

(9) Howells, R. D.; McCown, J. D. *Chem. Rev.* **1977**, *77*, 69.

(10) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Science* **1979**, *206*, 13.

(11) (a) Note that the methoxy signal in CF$_3$SO$_3$H is lower field than it is in CF$_3$COOH. (b) 2,6-Dimethoxytoluene, an uncharged and planar model for **6**, is protonated irreversibly at H$_m$ in CF$_3$SO$_3$H. ^{1}H NMR: δ 7.75 (dt, *J* = 3 and 10 Hz, 1 H, H$_p$), 7.32 (d, *J* = 10 Hz, 1 H, H$_m$), 4.40 (s, 3 H, OCH$_3$), 4.27 (s, 3 H, OCH$_3$), 3.99 (d, *J* = 3 Hz, 2 H, CH$_2$) and 2.03 (s, 3 H, aryl CH$_3$; internal standard).

(12) Based on pK_{R+} = 6.5 for **5**[5] and the H_0 values for CF$_3$SO$_3$H,[9,10] [**5**] must be less than 10^{-15} M.

(13) ^{1}H NMR: δ 7.63 (t, *J* = 9 Hz, 3 H, H$_p$), 6.62 (d, *J* = 9 Hz, 6 H, H$_m$), 3.65 (s, 18 H, CH$_3$O). Internal standard CH$_3$NO$_2$: δ 4.29.[14]

(14) Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972; p 251.

(15) Treatment of **5** or **6** perchlorate with H$_2$SO$_4$, FSO$_3$H, and 1:1 FSO$_3$H–SbF$_5$ has been attempted. The resulting ^{1}H NMR spectra are complex and in some cases temperature dependent. This is undoubtedly due to multiple protonation and/or sulfonation of **6**.

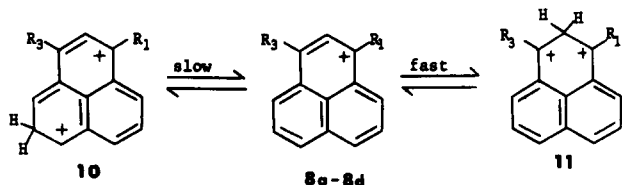in detail, we synthesized the phenalenyl cations **8a–f** and
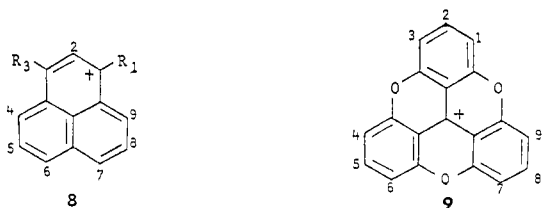
a) $R_1 = R_3 = OCH_2CH_3$ d) $R_1 = R_3 = OH$

b) $R_1 = OH, R_3 = OCH_2CH_3$ e) $R_1 = OH, R_3 = H$
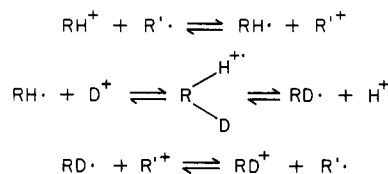
c) $R_1 = OH, R_3 = OCH_3$ f) $R_1 = R_3 = H$
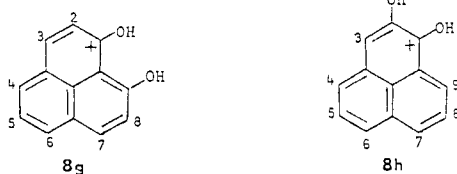
the sesquixanthyl ion **9** (See Experimental Section). These ions were chosen for study because of their ease of synthesis; their high symmetry, which makes for simple, interpretable ¹H NMR spectra; and, in the case of the phenalenyl ions, their possesing differing numbers of activating groups. The NMR spectral data for these ions are shown in Table I; the spectral data for the related phenalenyl cations **8g** and **8h**, which have been discussed in detail elsewhere,[17] are shown for comparison. The most important things to note from these NMR data are the H-2 chemical shifts for the phenalenyl cations **8a–g**. It can be seen that for those ions that possess electron-releasing substituents at both C-1 and C-3 the chemical shift is substantially lower than for those ions that have only one or no electron-releasing substituent at these sites. Of more pertinence to this study is the fact that the ¹H NMR spectra of the ions **8a–f** and **9** give no indication for rapid, reversible (or irreversible) protonation at room temperature. If the reactions are occurring, they are considerably slower than that observed for **6** under the same conditions. It was thus necessary to use deuterium-labeled acid to determine if the desired reactions were occurring. All the ions except **8f** were generated in CF₃SO₃D; **8f** was generated in FSO₃H ($H_0 = -15.6$[9,10]) and diluted 1:1 with FSO₃D. The reason why **8f** was treated in this manner can be found under Experimental Section.

All the ions that have activating groups at both C-1 and C-3, i.e., **8a–d**, exchange rapidly at C-2 at room tempera-

ture. For **8d**, for example, the signal for H-2 had almost completely disappeared within 15 min of sample preparation. This represents the slowest possible rate of reaction, as it took approximately 15 min to degas and seal each sample. In addition, there were no changes in any other signal (intensity and pattern). If these samples were then treated at 100 °C for 18 h, the ¹H NMR spectrum for each ion gave evidence for exchange at C-5/8 and no ex-

(16) In all the work described in this paper, we mean protonation of a carbon atom.

(17) Pagni, R. M.; Smith, R. J.; Moore, T.; Burnett, M. N. *Isr. J. Chem.* **1980**, *20*, 308.

Scheme I. Exchange via Neutral Radicals

change at C-4/9 and C-6/7. A singlet was seen to grow in between each of the doublets assigned to H-4/9 and H-6/7; there was also a decrease in signal intensity for the H-5/8 triplet. Interestingly, the H-2 singlet grew in intensity during this time because, as H-5/8 were replaced by deuterium, the amount of protium in the acid increased. This protium then reexchanged at C-2 in the deuterium-labeled ion. One can conclude from these experiments that for ions **8a** thru **8d** exchange at C-2 occurs much more rapidly than at C-5/8, with no exchange occurring at C-4/9 and C-6/7.

Unlike the ions **8a–d**, ion **8e** with a sole activating group did not exchange at room temperature, even if the sample was allowed to stand for several days. Only by heating the sample at 100 °C for 18 h did the ¹H NMR spectrum indicate that exchange at C-2 had occurred. The parent phenalenyl cation **8f**, which, of course, possesses no activating groups, neither exchanged at room temperature in FSO₃H/FSO₃D nor at 100 °C (18 h) in the same medium. Therefore, the number of activating groups that the ion possesses has a profound effect on its reactivity with H⁺ (D⁺). This conclusion is no different than one would make if one were dealing with electrophilic aromatic substitution reactions on uncharged aromatic substrates.

The sesquixanthyl cation (**9**) is similar in structure to the trityl cation **6** but is constrained to planarity. Thus, the planar **9** should be a good model to test how much effect the propellar conformation of **6** has on its reactivity. Treatment of the carbinol **12**, ($pK_{R^+} = 9.05$[5]) with CF₃S-
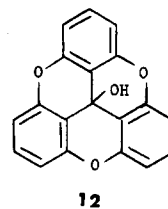
O₃H yielded a solution whose ¹H NMR spectrum is similar to that of **9** of CF₃COOH (Table I).[18] There is clearly no indication of any rapid, reversible protonation. A different spectrum was observed, however, upon treatment of **12** with CF₃SO₃D at room temperature. Within 15 min of sample preparation, the ¹H NMR spectrum showed a doublet between the triplet due to H-2/5/8; the doublet belonging to the remaining hydrogens decreased in intensity but did not change in appearance. These observations can be attributed to the incorporation of deuterium at the corner sites on **9**. Heating the sample at 100 °C resulted in additional incorporation of deuterium at the corner sites; no deuterium incorporation at C-2/5/8 was observed. It is quite certain from these results that the geometry of an ion has a large influence on its reactivity.

Before proceeding further, it is worth spending a few moments describing why other mechanisms of exchange are unlikely. One can envision, for example, that the exchange actually occurs by reversible protonation of a neutral radical present in low concentration. This mechanism, which is shown in Scheme I, can be discounted for

(18) Martin, J. C. *J. Chem. Educ.* **1961**, *38*, 286.

Table I. ^{1}H NMR Chemical-Shift Data for Phenalenyl Cations and the Sesquixanthyl Ion

	chemical shift[a] (multiplicity)[b]								
cation[c]	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9
8a[d]		6.82 (s)		8.95 (d)	8.00 (t)	8.67 (d)			
8b[d,e]		6.72 (s)		8.82 (d)	7.82 (t)	8.48 (d)			
8c[d,e]		6.75 (s)		8.78 (d)	7.83 (t)	8.50 (d)			
8d		6.70 (s)		8.85 (d)	7.87 (t)	8.53 (d)			
8e		7.50 (d)	8.80 (d)	9.33 (d)	8.15 (t)	8.72 (d)	8.72 (d)	8.07 (t)	8.92 (d)
8f	8.80 (d)	8.00 (t)							
8g		7.54 (d)	8.72 (d)	8.58 (d)	7.94 (dd)			7.54 (d)	
8h			8.17 (s)	8.50 (d)	8.00 (t)	8.57 (d)	8.90 (dd)	8.20 (t)	9.30 (dd)
9	7.62 (d)	8.23 (t)							

[a] δ units relative to internal $(CH_3)_4N^+BF_4^-$ (δ 3.10). [b] s = singlet; d = doublet; t = triplet; dd = doublet of doublet.
[c] All ions in CF_3SO_3H except 8f, which is in FSO_3H, and 9, which is in CF_3COOH. [d] The nonaromatic signals are not recorded here. [e] H-7, H-8, and H-9 are not identical with H-6, H-5, and H-4, respectively. The chemical shifts were very close to being identical, however.
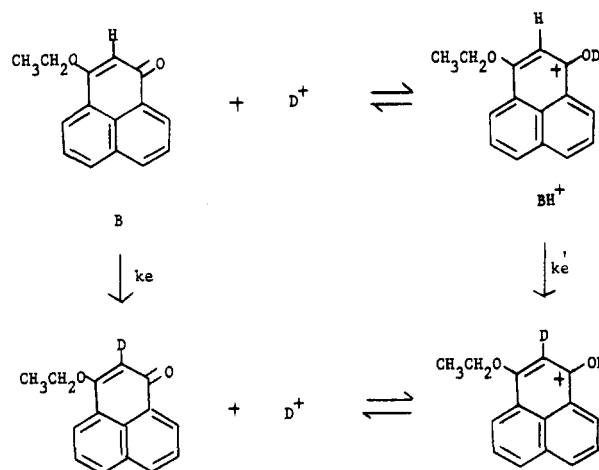
Scheme II. Deprotonation–Protonation
Mechanism of Exchange

Scheme III. Exchange Involving a Neutral Species
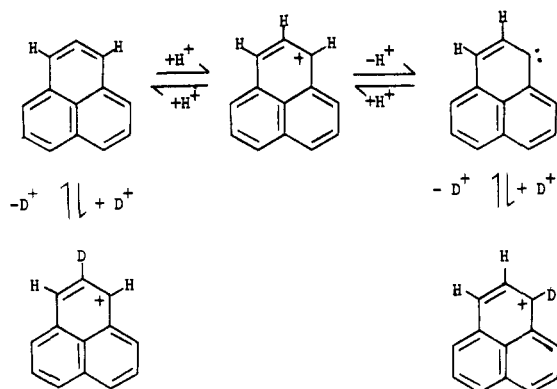
several reasons: (1) The ^{1}H NMR peaks are sharp; electron exchange should broaden the peaks. The phenalenyl cation (8f), for instance, in the presence of a small amount of the phenalenyl radical yields no ^{1}H NMR signal at all.[19] (2) Frontier orbital theory[20] and the more quantitative superdelocalizabilities (S_r)[20-22] predict that an electrophile will attack the neutral radicals having the molecular frameworks of 8d–f at the *corner* positions (1, 3, 4, 6, 7, and 9).[23] (3) When carbocations such as 8b are generated in FSO_3D, where radicals are very rapidly oxidized, the exchange reaction still occurs.

Loss of a proton from a corner (1, 3, 4, 6, 7, 9) or central (2, 5, 8) position of the phenalenyl and sesquixanthyl cations will generate a carbene and highly strained allene,[25]

(19) Pagni, R. M.; Easley, P.; Smith, R. J., unpublished results.
(20) Salem, L. "The Molecular Orbital Theory of Conjugated Systems"; W. A. Benjamin: New York, 1966; pp 326–332, and references cited therein.
(21) Fukui, K.; Yonezawa, T.; Nagata, C. *Bull. Chem. Soc. Jpn.* 1954, 27, 423. Fukui, K.; Yonezawa, Y.; Nagata, C. *J. Chem. Phys.* 1957, 27, 1247.
(22) The superdelocalizability at atom r was calculated from Hückel MO's (see Experimental Section) with the formula:

$$S_r = 2\sum_{j=1}^{m} \frac{c_{jr}^2}{\epsilon_j} + \frac{c_{(m+1)r}^2}{\epsilon_{(m+1)}}$$

where 1, 2, ... m are the doubly occupied MO's and m + 1 is the singly occupied MO. This formula is an extension of Fukui's formula[21] for electrophilic attack on aromatic compounds, such as benzene and naphthalene.
(23) The phenalenyl radical on treatment with D_2SO_4 yields 1-deuteriophenalenyl cation.[19] This result can be explained by electrophilic deuteration at C-1 of the radical followed by oxidation. This interpretation is less than conclusive because the radical is in equilibrium with a dimer.[24] The dimer could be the vehicle of exchange.
(24) Gerson, F. *Helv. Chim. Acta* 1966, 49, 1463.

respectively. Addition of D^+ to either of these reactive species will regenerate a carbocation that is now deuterated (Scheme II). If this mechanism were operating, it is difficult to see why only the central sites are reactive. If anything, the corner sites, which yield carbenes on deprotonation, should be more reactive. Ab initio MO calculations also discount this deprotonation mechanism.[2]

Another mechanism that must be considered is one in which the exchange occurs on a neutral species present in low concentration and in equilibrium with the aryl cation (Scheme III). This is quite plausible, as all of the carbocations containing hydroxy groups are generated by protonation of the corresponding ketone, and several others were generated from a carbinol. This and similar schemes can be discredited on several grounds. First of all, of those cases where the cation was originally generated from a carbinol, identical results were obtained when the ion was generated from the corresponding perchlorate salt. Secondly, no matter how rapidly the neutral molecules react with H^+ or D^+, even if at the rate of diffusion, their concentrations are so small that their overall rate of exchange is far too little to account for the observed rates. One can estimate the concentration of a neutral species from the equation $H_0 = pK_a + \log [B]/[BH^+]$, which is ordinarily

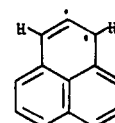(25) Loss of a proton from a central carbon can also yield a carbene which cannot adequately be drawn.

Table II. Relative Reactivity and Regiochemistry of Exchange for
Three Dihydroxyphenalenyl Cations in CF₃SO₃H; Experiment and Theory

dihydroxyphenalenyl cation	regiochemistry		reactivity	
	exptl[a]	prediction[b]	exptl[c]	prediction[b]
1, 3 (8d)	2 > 5/8	2 > 5/8	$\tau_{1/2}$ < 3 min, RT[d]	8d > 8g > 8h
1, 9 (8g)[e]	2/8 ~ 5	2/8 > 5	$\tau_{1/2}$ ≈ 1-2 days, RT[d]	8d > 8g > 8h
1, 2 (8h)[e]	3 >> 5 > 4 ~ 6	5 ~ 8 > 3	$\tau_{1/2}$ ≈ 1.5 days, 100 °C	8d > 8g > 8h

[a] Only the sites that exchange are shown. [b] Based on superdelocalizabilities. [c] The $\tau_{1/2}$ is for the most reactive site.
[d] RT = room temperature (20-25 °C). [e] Reference 17.

used to determine acidity functions. For the reaction shown in Scheme III, the pK_a of protonated 3-ethoxyphenalenone (BH⁺) is approximately 1[26] and H_0 for CF₃-SO₃H is -13 to -14.6.[9,10] Thus, the concentration of the neutral ketone (B) must be 10⁻¹⁴th or less that of BH⁺. One can now use these numbers to compare the rate of exchange for B and BH⁺. The total rate of exchange will be k_e[B][D⁺] + k_e'[BH⁺][D⁺], where the first term represents the phenomenological rate of exchange for the ketone and the second for the carbocation. Note that [D⁺] is common to both terms. It can be seen that even if k_e be close to the rate of diffusion, 10⁹ L M⁻¹ s⁻¹, and k_e' be 10⁻⁹th of that value, the second term will still be larger than the first by 10⁵. In other words, the rate of exchange on the carbocation overwhelms the rate of exchange on the ketone. Similar arguments can be put forth to show that exchange on a neutral substance formed by reaction of the aryl cation with solvent is very small when compared to exchange on the cation itself.[1a,28,29]

Now that the protonation–deprotonation exchange mechanism seems secure, it is worth looking at the effect that the positions of the hydroxy groups have on the regiochemistry and relative reactivity of exchange for the phenalenyl cations 8d,g,h. These three ions all have the same carbon skeleton and two hydroxy groups. Ions 8d and 8g have the substituents in positions where they can stabilize positive charge; 8h has only one in a stabilizing position, while the other one at C-2 is deactivating because of the electronegativity of the group's oxygen atom. Thus, one would expect 8d and 8g to exchange more rapidly than 8h does and for each of these ions to exchange at the central 2, 5, and 8 positions more rapidly than at the corner positions. It is difficult to predict intuitively where 8h might exchange. As summarized in Table II, our expectations for the relative reactivity of the three ions and the regiochemistry of exchange for 8d and 8g were born out. The unusual behavior of 8h has not been adequately explained but is discussed at length (and that of 8g) in a previous paper.[17] Also of interest to note is the fact that 8d exchanges so much more rapidly than 8g, even though they both have two stabilizing substituents. These experimental data, with the exception of the regiochemistry of exchange for the 1,2-dihydroxyphenalenyl cation (8h), are in excellent agreement with the predictions of the Hückel theory (superdelocalizabilities) (Table II).

The rapid exchange observed, especially for the sesquixanthyl and 1,3-disubstituted phenalenyl carbocations, suggests that the dication is not appreciably higher in energy than the monocation (plus H⁺) precursor. If the acidity and solvating power of the medium are increased,
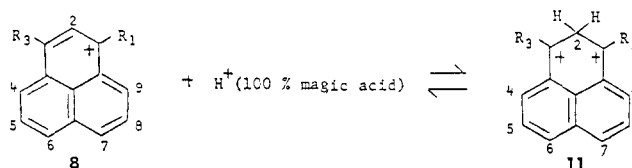
Table III. Ions Observed in Magic Acid[a]

ion initially generated	ions obsd in magic acid		
	25%[b]	100%[c]	
		SO₂[d]	SO₂ClF[d]
8a	C[e]	D ⇌ C[e,f]	D
8d	C	D ⇌ C	D
8b	g	D ⇌ C	D ⇌ C
8g	g	C	C
8h	g	C	C
8e	g	C	C
8f	g	C	C
9	g	D	D
14a	g	C	g
17[h]	g	C	C

[a] Magic acid = mixture of SbF₅ and FSO₃H. [b] 1:4 SbF₅/FSO₃H. [c] 1:1 SbF₅/FSO₃H. [d] Diluent. [e] C = monocation, D = dication. [f] Monocation in equilibrium with dication. [g] Not run. [h] The NMR of the monocation 17 was temperature dependent.

then it should be possible to lower the energy of the dication relative to the monocation and observe the dication directly by ¹H NMR. Fluorosulfonic acid (FSO₃H)–antimony pentafluoride (SbF₅) combinations (magic acid) diluted with SO₂ or SO₂ClF to reduce the viscosity of the medium seemed ideal for this purpose.[10] Ultimately, this approach was successful in several cases.

Because the 1,3-disubstituted phenalenyl cations exchange most rapidly in CF₃SO₃D, they were investigated first. Generation of 1,3-diethoxyphenanlenyl cation (8a) in 25% magic acid (1:4 SbF₅–FSO₃H)/SO₂ yielded a ¹H NMR spectrum that showed only this species; no peaks attributable to a dication were observed (Table III). Identical behavior was observed for the 1,3-dihydroxyphenalenyl cation (8d) in 25% magic acid (Table III). The results were strikingly different when these ions were generated in the much stronger 100% magic acid (1:1 SbF₅/FSO₃H). At -60 °C in SO₂, each solution yielded ¹H NMR peaks whose chemical shifts were not appreciably different from those observed in CF₃SO₃H for the monocation. These peaks were thus assigned to 8a and 8d, respectively. In addition, each solution gave peaks that were assigned to the dications 11a and 11d. As shown for

(26) Carbocation 8e has pK_a = -1.4.[27] Carbocations 8b–d should be less acidic because they all possess electron-releasing substituents.
(27) Culbertson, G.; Pettit, R. *J. Am. Chem. Soc.* **1963**, *85*, 741.
(28) Smith, R. J. Ph.D. Dissertation, University of Tennessee, 1980.
(29) Another mechanism of exchange is plausible,[30] but it requires the presence of good nucleophiles, which are not present in CF₃SO₃H.
(30) El-Anani, A. A.; Greig, C. C.; Johnson, C. D. *J. Chem. Soc., Chem. Commun.* **1974**, *1024*.

a) R₁ = R₃ = OCH₂CH₃
b) R₁ = OH, R₃ = OCH₂CH₃
d) R₁ = R₃ = OH

the case of the 1,3-dihydroxy system (Table IV), H-2 of the dication (CH₂) is higher field than H-2 of the monocation (aryl H), and, as expected, all the remaining peaks of the dication are lower field than the corresponding peaks

Table IV. NMR Data for Carbocations in 1:1 FSO₃H/SbF₅, SO₂ at −60 °C

	chemical shift[a] (multiplicity,[b] J^c)					
carbocation	H-1	H-2	H-3	H-4/9	H-5/8	H-6/7
11a[d]		5.39 (s)		9.42 (d, 8)	8.34 (t, 8)	9.26 (d, 8)
8a		6.78 (s)		8.97 (d, 8)	8.00 (t, 8)	8.68 (d, 8)
11d		5.32 (s)		9.48 (d, 8)	8.38 (t, 8)	9.26 (d, 8)
11b[d,e]					8.30 (t, 8)	
		5.03 (d, 2)		8.90–9.50 (m)	8.35 (t, 8)	8.90–9.50 (m)
13	5.25 (s)	8.51–8.95 (m)	7.88 (d, 10)	8.12 (d, 9)	8.51–8.95 (m)	8.08 (d, 9)

[a] δ units relative to internal $(CH_3)_4N^+BF_4^-$ (δ 3.10). [b] s = singlet; d = doublet; t = triplet; m = multiplet. [c] In hertz. [d] The ethoxy resonances are not recorded here. [e] H-4, H-5 and H-6 are not equivalent to H-9, H-8, and H-7, respectively, for this ion.
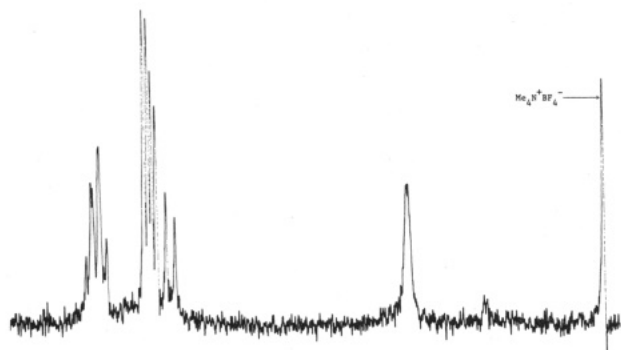

Figure 2. ¹H NMR spectrum of **13** in 100% magic acid/SO₂ at −60 °C.

of the monocation. Similar NMR behavior was observed for the 1,3-diethoxy, as well as the 1-hydroxy-3-ethoxy, system (Tables III and IV).[31]

When each of these solutions was warmed, the monocation peaks increased in intensity at the expense of the dication peaks. Reversal of the temperature returned the spectrum to its original appearance. Thus, these experiments not only demonstrate that one can observe a dication (a protonated carbocation) but also that the monocation and dication are in equilibrium with each other. It is hard to imagine a better proof for the protonation of a carbocation.[32]

13
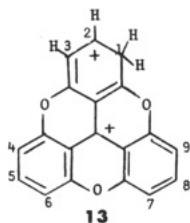
Of the remaining ions that were generated in 100% magic acid/SO₂, which included the 1,2-dihydroxy, 1,9-dihydroxy, 1-hydroxy, and unsubstituted phenalenyl cations (**8h,g,e,f**, respectively) and the sesquixanthyl ion (**9**), only **9** was protonated (Tables III and IV), and it irreversibly (to yield **13**) (Figure 2).[31,33] When all the ions were generated in the still stronger 100% magic acid/SO₂ClF,[34] only the systems that yielded dications in SO₂, i.e., **8a,d,b** and **9**, yielded dications in SO₂ClF. These results are summarized in Table III.

Chart I. Exchange Behavior of Miscellaneous Ions in CF₃SO₃D
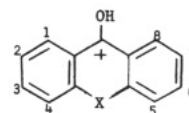
14a, X=NH; **14b**, X=S; **14c**, X=O

Regiochemistry: In all cases 2/7 ∿ 4/5

Relative Reactivity: **14a** ≫ **14b** ∿ **14c**
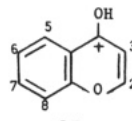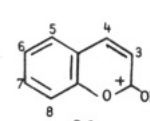
15   **16**

Regiochemistry: **15**: Unknown
16 3 > 6, 8 > 4, 5, 7

Relative Reactivity: **16** > **15**
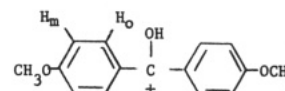
17

Regiochemistry: Hₘ > > H₀

Several other ions were also generated and investigated in CF₃SO₃H(D). A detailed analysis of the solutions' ¹H NMR spectra and mass spectral and ¹H NMR analysis (with shift reagents) of the quenched solutions yielded the results shown below (Chart I). (See Experimental Section for details). The two most reactive ions, **14a** and **17**, were also generated in magic acid; neither of them yielded a dication in magic acid (Table III). These results are exactly what one would expect by analogy with electrophilic aromatic substitution on "ordinary" substrates.[35]

Concluding Remarks

It has been shown in this work that aromatic carbocations are not immune to reaction with positively charged electrophiles, as one might think intuitively, but can undergo electrophilic aromatic substitution, sometimes very

(31) The peaks for the dications integrated correctly.
(32) We also looked for the dications in CF₃SO₃H. Even at 160 °C, they were not observed in the ¹H NMR spectra.
(33) There is a very small peak at δ 4.39 that might be attributed to a multiply protonated ion. We have no concrete evidence that this is so, however.
(34) Arnett, E. M.; Preto, C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 522.

(35) These ions have the following pKₐ values: **14a**, −0.16;[36] **14b**, −3.95;[37] **14c**, −4.1;[38] **15**, −2.00;[39] **16**, −4.8;[38] **17**, −4.4.[38]
(36) Kokubun, Z. *Z. Electrochem.* **1958**, *62*, 599.
(37) Degani, I.; Fochi, R.; Spanta, G. *Boll. Sci. Fac. Chim. Ind. Bologna*, **1968**, *26*, 3; *Chem. Abstr.* **1969**, *70*, 3131z.
(38) Arnett, E. M.; Quirk, R. P.; Larsen, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 3977.
(39) Ellis, G. P. In "Chromenes, Chromanones, and Chromones"; Ellis, G. P., Ed.; Wiley, New York, 1977, p. 561.

rapidly, with H^{+} and D[+].[40] That these reactions proceed by the protonation of a carbocation has been most convincingly demonstrated by the ^{1}H NMR observation, in several cases, of a cation–dication equilibrium in super acid medium. The observed relative reactivity, regiochemistry, and substituent effects are quite predictable, based upon classical concepts concerning electrophilic aromatic substitution reactions. It will be interesting to see what the limits are (strength of acid and nature of the carbocations) for this new type of chemistry.

Experimental Section

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on Varian A-60, T-60A, and HA-100 and Nicolet TT-14 spectrometers. All variable-temperature spectra were recorded on the HA-100 instrument.

Samples treated with deuterated acid solvents were prepared by the following general technique. The acid (0.5 mL) was placed in a test tube and cooled in an ice bath with vigorous stirring, while under an Ar or N₂ atmosphere. The compound to be treated was slowly added to the cold, stirred solution. About 50–75 mg was required, depending upon the molecular weight and the number of hydrogens. About 10 mg of tetramethylammonium tetrafluoroborate (Me₄N^{+}BF₄^{-}) was added as an internal integral and chemical-shift standard.[8] The solution was transferred to a thick-walled NMR tube, degassed by the standard freeze–pump–thaw technique, and sealed under high vacuum. The tubes were immersed in a thermostatted oil bath when heating was required.

Samples for low-temperature spectra with SO₂ or SO₂ClF cosolvents were treated differently. A test tube fitted with a glass-coated magnetic stirrer was cooled, under a flow of Ar or N₂, to -78 °C. Sealed ampules of SO₂ClF were cooled and then opened, and the solvent (ca. 0.3 mL) was quickly transferred by chilled Pasteur pipet. SO₂ (ca. 0.3 mL) was condensed directly into the cooled test tube from a gas cylinder. The acid (ca. 0.3 mL) was added and allowed to cool. The sample compound (50–75 mg) and Me₄N^{+}BF₄^{-} (10 mg) were added slowly. The resulting solution was quickly transferred by chilled pipet to an NMR tube precooled to -78 °C. The tube was flushed with Ar or N₂ and covered with the standard cap. At no point until disposal was the temperature of the solution allowed to exceed the boiling point of the cosolvent.

Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer. Mass spectra were recorded with a Hewlett-Packard 5980A GC/mass spectrometer with the 5934A data system. Melting points were determined with a Hoover melting point apparatus and are uncorrected.

Reagents. Solvents (ether, pentane, chloroform, etc.) were obtained from Fisher. Unless noted otherwise, they were of certified ACS grade and were used without further purification. Ligroin (30–60 °C) was technical grade and was distilled prior to use.

Trifluoroacetic acid and magic acid (25 and 100%) were obtained from Aldrich Chemical Co. and used as received. Fluorosulfonic acid from Allied Chemical Co. was distilled prior to use. Trifluoromethanesulfonic acid (Fluorad FC-24) was obtained from 3M Company and distilled prior to use. Trifluoromethanesulfonic acid-d₁ was prepared by a method described elsewhere.[41]

Deuterium oxide (99.9% D) and tetramethylammonium tetrafluoroborate were purchased from Aldrich Chemical Co. Alumina (Brockmann activity I) was purchased from Fisher Scientific Co. Deactivated alumina (Activity II) was prepared by adding ca. 20 mL of distilled water to 1 lb of Brockmann activity I alumina.

Synthesis of Ion Precursors and Ion Salts. 2,2′,2″,6,6′,6″-Hexamethoxytriphenylmethanol (5), the precursor to 6, and sesquixanthol (12), the precursor to 9, were prepared

by the method of Martin and Smith.[5]

2,2′2″,6,6′,6″-Hexamethoxytriphenylmethyl perchlorate was prepared as follows. Alcohol 5 (0.9 g) was dissolved in 10 mL of ether and cooled to -78 °C. Addition of 1.7 mL of 70% perchloric acid resulted in the immediate formation of an intense purple color. After some time the reaction mixture solidified, and enough nitromethane was added to allow the mixture to be stirred. Upon warming to room temperature, the solution was filtered, and the residue was washed with ether and air-dried. The reaction yielded 0.93 g (83%) of the dark purple salt.

Phenalenone, the precursor to **8e**, was prepared by the method of Pagni and co-workers,[42] and phenalene, the precursor to **8f**, was synthesized from phenalenone by the method of Pagni and Watson.[43] 3-Hydroxyphenalenone, the precursor to **8d**, was prepared by the method of Eistert, Eifler, and Goth.[44] 3-Methoxyphenalenone, the precursor of **8c**, was prepared from 3-hydroxyphenalenone by a modification of the procedure described by Hunig and co-workers[45] in which triethylamine was substituted for ethyldiisopropylamine. 1,3-Diethoxyphenalenium tetrafluoroborate (source of **8a**) was prepared from 3-hydroxyphenalenone as described by Hunig and co-workers.[45] 3-Ethoxyphenalenone, the precursor of **8b**, was a side product in the preparation of 1,3-diethoxyphenalenyl tetrafluoroborate and was isolated by chromatography of the crystallization mother liquors. 2-Hydroxyphenalenone, the precursor to **8h**, was prepared from phenalenone according to the procedure of Fieser and Newton[46] and 9-hydroxyphenalenone, the precursor to **8g**, was synthesized by the method of Haddon and co-workers.[47] Acridone (9-hydroxyacridine), thioxanthone, xanthone, chromone, coumarin, and 4,4′-dimethoxybenzophenone, the precursors to **14a**, **14b**, **14c**, **15**, **16**, and **17**, respectively, were commercial materials (Fisher and Aldrich) and were chromatographed and/or sublimed in vacuo prior to use.

Generation of the Phenalenyl Carbocation (8f) in FSO₃D. The phenalenyl carbocation (**8f**) can be prepared cleanly by addition of phenalene to FSO₃H at low temperature as described elsewhere.[48,49] When phenalene is added to FSO₃D, the resulting phenalenyl ion contains deuterium.[50] Thus, in order to prepare the nondeuterated ion in FSO₃D, it was necessary to prepare it first in FSO₃H and then dilute (1:1) with FSO₃D.

Studies Concerning the Behavior of 9-Hydroxyacridinium (14a), 9-Hydroxythioxanthylium (14b), and 9-Hydroxyxanthylium (14c) Ions in CF₃SO₃H(D). (a) Ion 14c. Dissolution of xanthone, the precursor of **14c**, in CF₃SO₃D produced a solution whose ^{1}H NMR spectrum initially was no different than that in CF₃SO₃H: δ 8.13 (dd, H-1/8), 7.42 (td, H-2/7), 7.87 (dt, H-3/6), and 7.58 (d, H-4/5). After 96 h at room temperature, there was still no change. When the sample was heated for 20 h at 100 °C, a visible change in the spectrum was produced. A doublet (J = 2 Hz) was seen to grow into the doublet of doublets (J = 8 Hz, 2 H) at δ 8.13 (H-1/8), and a triplet was seen to grow into the doublet of triplets (J = 8 and 1 Hz) at δ 7.87 (H-3/6). This result is due to the incorporation of deuterium at sites 2,7 and 4,5. The integrals for these hydrogens had decreased by 40 and 30%, respectively. Heating for a total of 67 h raised the amount of deuterium incorporation at sites 2/7 to 65% and at sites 4/5 to 63%. The patterns of the peaks at δ 7.42 (H-2/7) and 7.58 (H-4/5) did not change, indicating that there was no deuterium incorporation at sites 1/8 and 3/6. The solution was quenched with aqueous sodium bicarbonate, and the neutral

(40) We have attempted to react aryl carbocations with NO₂^{+} and have obtained ambiguous results so far.[28]

(41) Smith, R. J.; Pagni, R. M. *J. Org. Chem.* **1981**, *46*, 4307.

(42) Pagni, R. M.; Burnett, M. N.; Hassaneen, H. M. *Tetrahedron* **1982**, *38*, 843.

(43) Pagni, R. M.; Watson, C. R., Jr. *Tetrahedron* **1973**, *29*, 3807.

(44) Eistert, B.; Eifler, W.; Goth, H. *Chem. Ber.* **1968**, *101*, 2162.

(45) Hunig, S.; Wolff, E. *Liebigs Ann. Chem.* **1970**, *732*, 7.

(46) Fieser, L. F.; Newton, L. W. *J. Am. Chem. Soc.* **1942**, *64*, 917.

(47) Haddon, R. C.; Wudl, F.; Kaplan, M. L.; Marshall, J. H.; Cais, R. E.; Bramwell, F. B. *J. Am. Chem. Soc.* **1978**, *100*, 7629.

(48) (a) Larsen, J. W.; Bouis, P. A.; Watson, C. R., Jr.; Pagni, R. M. *J. Am. Chem. Soc.* **1974**, *96*, 2284. (b) Pagni, R. M.; Bouis, P. A.; Easley, P. *Tetrahedron Lett.* **1975**, 2671.

(49) For reasons described elsewhere,[28,50] the ion cannot be generated cleanly in CF₃SO₃H(D) starting with phenalene or phenalenium perchlorate.

(50) Easley, P. E. M.S. Thesis, University of Tennessee, 1976.

material was extracted into CH_2Cl_2. Mass spectral analysis yielded the following amounts of deuterium in the recovered xanthone: d_0, 1.9%; d_1, 12.5%; d_2, 32.2%; d_3, 37.5%; d_4, 15.5%; d_5, 0.2%; d_6 0.1%.[51]

(b) Ion 14b. Thioxanthone, the precursor of **14b**, had a more complex spectrum in CF_3SO_3D than **14a**; only the doublet at δ 8.87 could be assigned (to H-1/8). The remaining six protons yield a multiplet of overlapping peaks at δ 7.83–8.33. After standing at room temperature for 48 h, the CF_3SO_3D solution showed no change in the ^1H NMR spectrum. When the solution was heated at 100 °C, a singlet was observed to grow into the H-1/8 doublet. There was also an observable change in the remaining portion of the spectrum. After 90 h at 100 °C, the doublet at δ 8.87 was almost entirely replaced by the new singlet, and all that remained of the complex multiplet was a large singlet superimposed on a small multiplet. The intensity of the δ 7.83–8.33 region (H-2/7, H-3/6, H-4/5) was reduced by about 50%. If the exchange in the δ 7.83–8.33 region is due to incorporation at the 4/5 sites, the rate of exchange at the 2/7 and 4/5 sites must be comparable.

The reaction mixture was quenched, and the recovered material was subjected to analysis by an NMR shift reagent and by mass spectrometry.

Thioxanthone responded favorably to the shift reagent tris-(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione)europium [Eu(FOD)₃]. A control experiment of thioxanthone and Eu(FOD)₃ in CDCl₃ produced a cleanly separated spectrum consisting of two low-field doublets and two higher-field triplets. These were assigned (on the basis of splitting patterns and correlation of chemical shifts to distances of hydrogens from thioxanthone's carbonyl group) as, from low to high field, H-1/8, H-4/5, H-3/6, and H-2/7. After the thioxanthone sample had been heated with CF_3SO_3D, as described above, it was quenched and extracted into CH_2Cl_2, and the solvent was removed. Upon treatment with Eu(FOD)₃ in CDCl₃, in a manner identical with the control, the spectrum revealed that large peaks had grown into the H-1/8 doublet and the H 3/6 triplet. The H-4/5 doublet and the H-2/7 triplet retained the appearance of the control but were greatly diminished in intensity. This is an indication that the H-4/5 and H-2/7 sites are exchanging at comparable rates and that there is little or no exchange at 1/8 and 3/6.

The mass spectrum of the recovered thioxanthone indicated the following amounts of deuterium incorporation: d_0, 0%; d_1, 2.7%; d_2, 14.8%; d_3, 34.3%; d_4, 35.8%; d_5, 11.1%; d_6, 1.1%; d_7, 0.2%. Based on these numbers there must be a small amount of deuterium incorporation at sites 1/8 and 3/6.

(c) Ion 14a. Acridone, the precursor of **14a**, yielded an NMR, spectrum in $CF_3SO_3H(D)$ very similar to that of thioxanthone; only the H-1/8 protons are assigned [δ 8.48 (d)], with the remainder comprising a complex multiplet (δ 7.57–8.20). Unfortunately, no product was recovered on quenching. Thus, neither shift data nor mass data are available.

The behavior of **14a** in CF_3SO_3D was like that of **14c** and **14b**, only the exchange was faster. In this case, the singlet grew into the H-1/8 doublet (δ 8.48) at room temperature, indicating exchange at H-2/7. Exchange at other sites, presumably H-4/5, was evidenced by changes in the patterns of the complex multiplet. After 96 h at room temperature, the intensity of the δ 7.57–8.20

multiplet had decreased by 40%.

Studies Concerning the Behavior of Ions 15 and 16 in $CF_3SO_3H(D)$. (a) Ion 15. Chromone, the precursor of **15**, yielded the ^1H NMR spectrum in CF_3SO_3H: δ 7.13 (d, J = 6 Hz, H-3), 7.43–8.07 (m, H-6, H-7, H-8), 8.20 (d, J = 8 Hz, H-5), 6.45 (d, J = 6 Hz, H-2).

After **15** was heated in CF_3SO_3D for 13 days at 100 °C, its nmr spectrum showed no change. The sample was quenched, and the mass spectrum of the recovered chromone yielded d_0, 81.5%; d_1, 17.5%; d_2, 0.9%; d_3, 0.1%,[51] indicating a small amount of exchange.

(b) Ion 16. Coumarin, the precursor of **16**, yielded the ^1H NMR spectrum in $CF_3SO_3H(D)$: δ 6.45 (d, J = 9 Hz, H-3), 6.93–7.40 (m, H-5, H-6, H-7, H-8), and 8.50 (d, J = 9 Hz, H-4).

Ion **16** showed no NMR spectral changes after 5 days in CF_3SO_3D at room temperature but did undergo exchange at 100 °C. After the sample was heated for 20 h, a singlet was seen growing into the doublet at δ 8.50 (H-4), and the doublet at δ 6.45 (H-3) had begun to decrease in intensity. After heating for 3 days at 100 °C, integration of the H-3 doublet revealed 25% deuterium incorporation at this site. The aromatic multiplet had also decreased in intensity by 25%. After 9 days, the H-3 site was 80% deuterated, and the aromatic sites were 30% deuterated. Coumarin, recovered in the usual way, yielded the following deuterium distribution: d_0, 0%; d_1, 7.8%; d_2, 33.3%; d_3, 48.5%; d_4, 10.5%.[51]

Studies Concerning the Behavior of the Carbocation 17 in $CF_3SO_3H(D)$. 4,4'-Dimethoxybenzophenone, the precursor of **17**, yielded in $CF_3SO_3H(D)$ the ^1H NMR spectrum: δ 4.05 (s, OCH₃), 7.23 (d, J = 9 Hz, H_m), 8.03 (d, J = 9 Hz, H_o).

On standing in CF_3SO_3D at room temperature a singlet grew into the H_o doublet, and the H_m signal remained a doublet but its signal decreased in intensity. This is due to deuterium incorporation into the H_m sites. There is no incorporation into the H_o sites.

Calculation of Superdelocalizabilities. This was accomplished by methods described elsewhere.[17]

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(51) The numbers are accurate to ±1%.