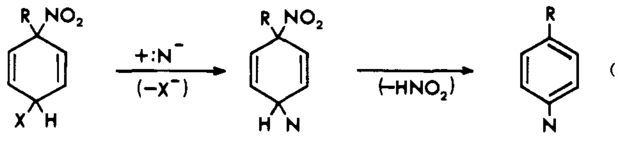
acetate to be competitive with the departure of nitrite.[9,10] The situation is clearly quite different with **2**, where the product data from aqueous solvolysis show that displacement of halogen occurs before loss of nitrite and subsequent rearomatization. With sufficiently hindered bases, such as *tert*-butoxide ion, it is possible to retain the halogen and promote what we presume to be an E2 elimination of the elements of nitrous acid. Within reasonable steric contraints, however, displacement prior to elimination may be anticipated as indicated in eq 2.



(2)

Rates of displacement are significantly enhanced by transforming the nitrodienyl chloride (**2**) to the nitrodienyl bromide in situ with the use of tetrabutylammonium bromide. The tetrabutylammonium cation also facilitates phase transfer of anions such as cyanide and nitrite, making it possible to conduct efficient displacement-elimination sequences in two-phase reaction mixtures.

It should not pass unnoticed that regiospecific nitration is now possible. One can direct the course of reaction of an ipso nitration product so that either the isomerically pure *o*-nitroalkylbenzene *or* the *p*-nitroalkylbenzene may be obtained from the same starting material. Thus treatment of 4-methyl-4-nitrocyclohexadienyl acetate with concentrated sulfuric acid yields *o*-nitrotoluene, but the sequence of displacements and elimination described above yields the para isomer. The utility of these reactions is enhanced by the development of efficient syntheses of 4-alkyl-4-nitrocyclohexadienyl acetates.[11]

The ease with which all of these transformations may be conducted and the apparent versatility of the general reaction sequence deserves stress. Ipso nitration products, curiosities uncovered by detailed mechanistic studies of aromatic nitration, appear to have significant synthetic potential.[12]

Acknowledgments. We thank the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for grants supporting this work. Initial studies in this area were conducted by Mr. A. Daniel Jones, and we are pleased to acknowledge his contributions.

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(4) The suspended sample of 1 dissolves during the addition of hydrogen chloride to yield a clear, colorless solution. The same product is obtained from either (*Z*)-**1** (mp 118–119 °C) or (*E*)-1 (mp 65–66 °C). Reconversion of **2** into 1 by treatment of **2** with silver acetate gave a mixture of (*Z*)-1 and (*E*)-1.
(5) ^{1}H NMR (DCCl$_3$): δ 1.78 (m, 9 H, methyl), 5.04 (m, 1 H, methine), 5.97 (m, 2 H, vinyl); decoupling of the methyl protons resulted in a triplet for the methine signal and a doublet for the vinyl protons, J = 4.3 Hz.
(6) The half-life of **2** in aqueous ethanol is about that found for 4-nitro-3,4,5-trimethylcyclohexadienol; see K. S. Feldman, A. McDermott, and P. C. Myhre. *J. Am. Chem. Soc.*, **101**, 505 (1979).
(7) Satisfactory analytical and spectral data were obtained for all compounds reported.
(8) In initial studies, 4-nitro-3,4,5-trimethylcyclohexadienyl bromide was prepared by reaction of 1 in methylene chloride with boron trifluoride and tetrabutylammonium bromide at −78 °C. The resulting solution was treated with nucleophilic reagents including ammonia, aqueous sodium cyanide, and the enamine of cyclohexanone to give the products indicated. Yields obtained by this more cumbersome procedure were inferior to those obtained by the methods described above.
(9) T. C. Banwell, C. S. Morse, P. C. Myhre, and A. Vollmar, *J. Am. Chem. Soc.*, **99**, 3042 (1977).
(10) H. W. Gibbs, R. B. Moodie, and K. Schofield, *J. Chem. Soc., Perkin Trans. 2*, 1145 (1978).
(11) C. E. Barnes, K. S. Feldman, H. W. H. Lee, M. W. Johnson, and P. C. Myhre, *J. Org. Chem.*, in press.
(12) It is appropriate to note that the results reported here, primarily with **2**, should be compared with an earlier report of Hahn; see ref 3b, in which a one-flask synthesis of 4-chloro-1,2-dimethylbenzene from crude 3,4-dimethyl-4-nitrocyclohexadienyl acetate is described.

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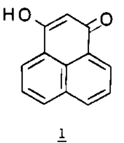
Protonation of Aromatic π Carbocations in Strong Acid. Direct Observation of Protonated Carbocations by ^{1}H NMR Spectroscopy

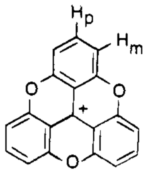
Sir:

Recently we reported evidence for a new type of electrophilic aromatic substitution which involves the reaction of H$^+$ and D$^+$ with aromatic π carbocations in strong acid media.[1,2] Although our data clearly indicated that the carbocations were being protonated directly, other mechanisms, although unlikely, could not be completely ruled out. We report at this time observations that constitute proof that the original mechanism is correct.

Our original work was done for the most part in triflic acid (CF$_3$SO$_3$H and CF$_3$SO$_3$D) where the reaction mechanism could be deduced only by inference.[1] Direct observation by ^{1}H NMR spectroscopy of a protonated carbocation, particularly if it were in equilibrium with the original carbocation, e.g., **2a** + H$^+$ $\rightleftharpoons$ **3a**, would provide overwhelming evidence that carbocations can undergo electrophilic aromatic substitution with positively charged electrophiles. In hopes of accomplishing this, the much stronger acids 1:1 FSO$_3$H/SbF$_5$ (magic acid) in SO$_2$ and SO$_2$ClF were used.



1



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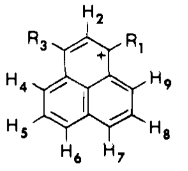
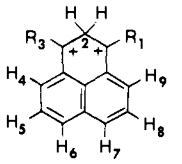


2



3

a) R$_1$ = R$_3$ = OH
b) R$_1$ = OH, R$_3$ = OEt
c) R$_1$ = R$_3$ = OEt
d) R$_1$ = OH, R$_3$ = H
e) R$_1$ = R$_3$ = H

The bottom ^{1}H NMR spectrum of Figure 1 is that of 3-hydroxyphenalenone (**1**) dissolved in magic acid/SO$_2$ at −60 °C. This spectrum,[3] which consists of δ 4.94 (br s, 2 H, H-2), 7.90 (t, J = 8 Hz, 2 H, H-5 and H-8), 8.83 (d, J = 8 Hz, 2 H, H-6 and H-7 or H-4 and H-9), and 8.97 (d, J = 8 Hz, 2 H, H-4 and H-9 or H-6 and H-7), is in complete agreement with that expected for the protonated carbocation **3a**. Barely perceptible in the NMR spectrum at −60 °C are peaks at δ 6.25 (s, 1 H, H-2), 7.47 (t, J = 8 Hz, 2 H, H-5 and H-8), 8.14 (d, J = 8 Hz, H-6 and H-7 or H-4 and H-9), and 8.42 (d, J = 8 Hz, 2 H, H-4 and H-9 or H-6 and H-7) which belong to the known monocation **2a**.[1] As seen in the top ^{1}H NMR spectrum of Figure 1, when this sample is warmed to −20 °C, there is a buildup in the monocation (**2a**) concentration and both monocation **2a**

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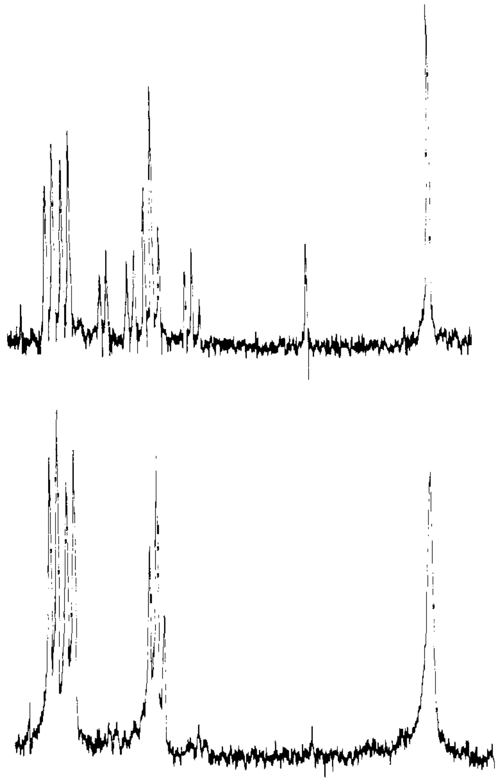

Figure 1. ^{1}H NMR spectrum of **1** in magic acid/SO_2: bottom spectrum at −60 °C; top spectrum at −20 °C.

and dication **3a** are clearly visible. Spectra taken at intermediate temperatures between −60 and −20 °C show intermediate amounts of **2a** and **3a.** Also, cooling the sample back to −60 °C regenerates the original spectrum. It is evident from the temperature-dependent spectra that the reversible protonation of **2a** is being observed under these conditions. Interestingly, when **1** is dissolved in the still stronger magic acid/SO_2ClF,[4] only the protonated carbocation **3a** can be detected at temperatures up to 0 °C.[5] It should be noted that these present results correlate very nicely with our earlier results in triflic acid.

Carbocation **2a** is not unique, for analogous results are obtained on **2c**, i.e., reversible protonation at C-2 in magic acid/SO_2 and irreversible protonation at C-2 in magic acid/SO_2ClF.[6] Surprisingly, perhaps, reversible protonation of **2b** at C-2 is observed both in magic acid/SO_2 and magic acid/SO_2ClF.[6,7] As might be expected from our original results, when there is only one electron-releasing substituent or none on the phenalenyl ring as on **2d** and **2e**, respectively, only **2d** and **2e** are observed in these highly acidic solvents.[6] Finally, the sesquixanthyl cation (**4**) is protonated irreversibly at the meta position in magic acid, both in SO_2 and SO_2ClF.[6,8]

In conclusion, it is clear that unequivocal evidence has been presented for the direct protonation of aromatic π carbocations. Furthermore, the present results in magic acid correlate very nicely (position of protonation on **2** and **4** and relative reactivity of **2a–d**) with our original results in triflic acid. Finally, it should be noted that these reversible reactions, properly calibrated, likely will represent a new method by which the acidity function (H_0) of these magic acid solvents can be measured. Studies in this area are continuing.

Acknowledgments. We thank the University of Tennessee for support and John Larsen for helpful comments.

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(3) $(CH_3)_4N^+BF_4^-$ (δ 3.10) was used in all cases as internal standard: N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **85**, 2991 (1963).

(4) This is based on the heats of ionization of alkyl halides in SbF_5/SO_2 and SbF_5/SO_2ClF: E. M. Arnett, C. Preto, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **101**, 522 (1979), and papers cited therein.

(5) The ^{1}H NMR of **1** dissolved in magic acid/SO_2ClF consists of δ 5.31 (br s, 2 H, H-2), 8.36 (t, J = 8 Hz, 2 H, H-5 and H-8), 9.26 (d, J = 8 Hz, 2 H, H-4 and H-9 or H-6 and H-7), and 9.47 (d, J = 8 Hz, 2 H, H-6 and H-7 or H-4 and H-9).

(6) NMR spectral data will be reported in our full paper.

(7) Based on substituent constants and field and resonance parameters one would expect the following order for stabilizing two positive changes: 2OH > 1OH plus $1OCH_2CH_3$ > $2OCH_2CH_3$. However, we have made no attempt to date in quantifying our data.

(8) The 2,2′,2″,6,6′,6″-hexamethoxytriphenylmethyl carbocation yields very complex temperature-dependent ^{1}H NMR spectra when dissolved in magic acid/SO_2.[6] Although the spectra have so far defied interpretation, it seems reasonable that protonation, possibly multiprotonation, of the carbocation has occurred here.

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High-Resolution ^{13}C NMR Spectra of Carbonium Ions in the Solid State

Sir:

It has recently been established[1-3] that well-resolved ^{13}C NMR spectra of solids can be obtained using a combination of pulsed NMR and "magic-angle" spinning techniques. Although initial studies have been carried out almost exclusively at ambient temperatures, full exploitation of this experiment requires variable-temperature capability.[4,5] The accessibility of low temperature, in particular, makes feasible the investigation by NMR of reactive intermediates in the solid state. Carbonium ions are classic examples of reactive intermediates and the NMR studies of Olah and co-workers[6] have led to detailed understanding of their structure in solution. Demonstration that high-resolution NMR spectra of carbonium ions can be obtained in the solid state, and particularly at low temperature, introduces the intriguing possibility of "freezing out" and observing structures which are involved in low-energy exchange processes. In this communication, we report the first high-resolution ^{13}C NMR spectra of carbonium ion salts in the solid state.

Diethoxycarbonium hexachloroantimonate (I) was chosen as representative of those carbonium ion structures in which the charge is effectively localized on a single carbon center.[7] The solid-state ^{13}C NMR spectra of this species at low (−105 °C) and ambient (27 °C) temperatures are shown in Figure 1.

At both temperatures, the resolution is sufficient to clearly identify the different carbon atoms in the system. Of particular interest is that the methylene carbons appear as two separate signals. This result is in accord with the solution proton spectrum[8] at ~30 °C, which shows two methylene-proton resonances. The inequivalence is thought to arise from restricted rotation about the C–O bonds in the preferred (Figure 1) cis,trans isomer. To compare the carbon shifts with solution values, we determined the ^{13}C spectrum of I at −45 °C in ($CDCl_3$-CD_3NO_2). The chemical-shift values (parts per million from Me_4Si) in the solid (solution) follow: C-1, 176.7 (177.1); C-2,2′, 82.6, 76.8 (81.8, 75.8); C-3,3′, 13.2 (13.9, 12.6).[9] The close agreement in chemical-shift data indicates that the preferred conformation that exists in the crystal lattice is the same as the stable conformer in solution at low temperature. In solution, the spectrum is a function of temperature with averaging of the shift inequivalence occurring at 30 °C;

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