the solvent SO_2ClF is distilled into the chamber from a reservoir on the vacuum line at a rapid rate. The solvent is distilled first, since the heat generated by heats of condensation and fusion may cause unwanted rearrangements or reactions of the stable carbocations if they are sensitive to heat and if the solvent were distilled in last. Usually about 2.0–2.5 mL of solvent is added. This quantity will result in a final concentration of the solution of less than about 0.75 M. This is the maximum concentration we have been able to prepare with this technique. If it is desired that the concentration be higher, it is possible to remove some of the solvent and/or SbF_5 by distillation.

The usual practice is next to distill in some SbF_5 and then to open the needle valve so that RX distills at a slow, even rate of about 0.005 mL per min. The two reactants condense on the surface cooled by liquid nitrogen. Maintaining low pressure during the preparation is important in order that all the SbF_5 deposits as desired on the cold surface. If the pressure is too high, SbF_5 is dispersed by collisions in the gas phase into the RX nozzle. Then some of the RX reacts with this deposit and forms a layer of reactive cations and polymer in the RX nozzle where a small amount collects. This diminished the amount of RX which reaches the chamber. Polymeric material from the nozzle can also drip into the chamber upon warming and contaminate the sample.

Once the desired amounts of RX and SbF_5 are deposited, the stopcock is closed and the apparatus is removed from the vacuum manifold. The chamber is then placed in a thick slurry of 1:1 ethanol: methanol and liquid nitrogen at −125 °C and the NMR tubes are simultaneously placed in a Dewar containing an identical slurry.

The tubing which connects the NMR tubes to the chamber is wrapped in glass wool and periodically soaked with the −125 °C slurry. The slurry is slowly allowed to warm to about −120 °C at which time the SO_2ClF melts and begins to dissolve the intimate mixture of RX and SbF_5. This process can be hastened by removing the chamber from the Dewar for short periods of time and swirling the solution.

Once all of the solid has dissolved, the apparatus is tipped so that the desired amount of material pours into each NMR tube. The depth of the solution in the NMR tubes is important because the cooling system of most spectrometers only cools a limited length of the tube. Any material above this level might be subjected to higher than desired temperatures. With the desired amount of solution in each tube, the apparatus is returned to the vacuum line, where the chamber and tubes were placed in Dewars filled with liquid nitrogen. After the solution freezes, the entire apparatus is again evacuated to remove any gas which might be present. The NMR tubes are sealed off and stored at liquid nitrogen temperature.

Acknowledgments. We acknowledge support of this research by the National Science Foundation.

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1,4,5,8-Tetramethylnaphthalene Dication and Related Radical Cations

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Abstract: The oxidation of 1,4,5,8-tetramethylnaphthalene in SbF_5/SO_2ClF solution at −80 °C yields the 1,4,5,8-tetramethylnaphthalene dication. Hexahydropyrene and 1,2,3,4,-tetramethylnaphthalene, under similar conditions, give an equilibrium of the corresponding dication and radical cation, $Ar^{2+} \rightleftharpoons Ar^{+\cdot}$, whereas oxidation of dibenzopyracyclene gives only the radical cation. Study of the cations was carried out by ^{13}C NMR spectroscopy. The reasons, particularly peri-strain of the contrasting oxidation tendencies of the studied, 1,4,5,8-substituted naphthalenes, are discussed.

Introduction

The ease of oxidation of polycyclic aromatic hydrocarbons is well recognized.[3-10] In our previous work,[11] we reported the two-electron oxidation of an extensive series of arenes by SbF_5/SO_2ClF solution to dipositive ions and their study by ^{13}C NMR spectroscopy. In continuation of our work on dications, we wish to report the oxidations of 1,4,5,8-tetramethylnaphthalene (**1**), hexahydropyrene (**2**), dibenzopyracyclene (**3**), and 1,2,3,4-tetramethylnaphthalene (**4**) under similar conditions and their carbon-13 NMR spectroscopic study.

Results and Discussion

A series of 1,4,5,8-tetra-substituted naphthalenes was examined for the formation of stable dications in SbF_5/SO_2ClF solution. The dications and/or their exchanging systems with the corresponding radical cations were observed by ^{13}C NMR spectroscopy. Results are summarized in Table I. The tetra-α-substituted naphthalenes represent borderline cases for the formation of dications by oxidation with SbF_2 in SO_2ClF. The dication of octamethylnaphthalene has been reported in preceding work,[11] but neither naphthalene itself nor any of the

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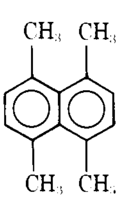

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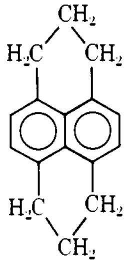

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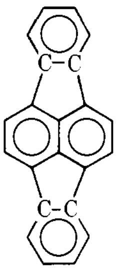

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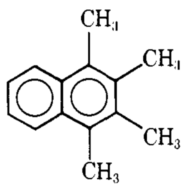


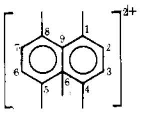
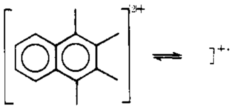
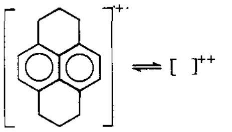
4

alkylnaphthalenes studied could be oxidized to the corresponding carbodications; only radical cations could be formed. 1,4,5,8-Tetramethylnapthalene (**1**) has now been found to be oxidized to its dication in SbF_5/SO_2ClF solution. The average *ring* carbon chemical shift for the carbodication of **1** is $\delta_{av} = 172.6$, which represents a deshielding of 38.4 from the average ring carbon resonance of the precursor (**1**). The deshielding is 192 ppm/e^- and does give a good fit with the relationship $\delta = 329-200_{av}$ determined by Forsyth and Olah for arene dications.[11] The proportionality constant of 200 ppm/e^- for these dications is significantly larger than the value of 156.3 ppm/e^- reported for monocations of cyclic and bicyclic systems. The reported deshielding of 244.7 ppm/e^- for octamethylnaphthalene is unusually large compared with the value of 192 ppm/e^- found in the present work for **1**. It should be considered, however, that steric interaction might significantly affect chemical shifts in highly crowded systems.

The hexahydropyrene **2** is a closely related tetrahydronaphthalene; yet oxidation of **2** with SbF_5/SO_2ClF, according to the ^{13}C NMR spectrum, did not result in formation of its dication. Although broad signals are observed at −80 °C, which do sharpen at higher temperatures (−30 °C), no complete two-electron oxidation to the carbodication could be achieved. Apparently, there is an equilibrium of the dication with the radical cation, $Ar^{2+} \leftrightarrows Ar^{+}\cdot$.[12] Similar cases have been reported previously for picene and 1,2,3,4-dibenzanthracene.[11] Apparently, ring closure between the α-ring carbons prevents complete oxidation to the dication, in contrast to **1**, where the α positions of the naphthalene skeleton are substituted by "free" methyl groups.

The polycyclic aromatic hydrocarbon **3**, dibenzopyracylene, is a different type of peri-substituted naphthalene and is a nonalternant hydrocarbon; it was prepared by a modification of the route of Stubbs and Tucker.[13] Oxidation with SbF_5/SO_2ClF gave no observable signals in the ^{13}C NMR spectra. We conclude that only one-electron oxidation takes place to the radical cation. Similarly, oxidation of 1,2,3,4-tetramethylnaphthalene (**4**) gave only some structural signals. In this context, the color changes of the solutions of the oxidations should also be noted. The resulting ions of **1, 2,** and octamethylnaphthalene, upon warming up of the original green solution, give red solutions. The solutions of **3** and **4**, in contrast, stay green. Apparently, the green color is that of the radical carbocations.

Table I. $^{13}C^{a}$ NMR Shifts of 1,4,5,8-Tetramethylnaphthalene Dication and Related Exchanging Ions

	$C_1, C_4, C_5, C_8 = 204.73$ $C_2, C_3, C_6, C_7 = 153.86$ $C_9, C_{10} = 146.21; CH_3 = 35.7$
	205.78, 195.79, 157.25, 142.06, 140.39, 133.72, 130.76, 129.69, 52.07, 26.98, 24.28, 22.83, and 15.65
	171.25, 153.76, 152.56, 150.54, 133.10, 131.73, 129.80, 124.01, 44.83, 33.92, and 27.05

[a] Shifts in ppm are from external capillary Me_4Si.

These contrasting oxidation tendencies are explained in the following manner. β-Methyl substitution provides less stabilization of naphthalene cation than α-methyls and **4** with its two β-methyls is fully expected to be less readily oxidized than the fully α-substituted **1**. Moreover, since naphthalene is an alternant system, removal of two electrons from its HOMO is expected to have the same direction of structural change as addition of electrons to its LUMO. The structure of naphthalene dilithium[14] has been shown to have, as expected, a substantially shorter C_2-C_3 and longer C_1-C_2 bond than naphthalene, but has also increased C_9-C_{10} bond length and a larger $C_1-C_9-C_8$ angle (124.4°) compared with naphthalene (121.75°).[15] A comparable change in forming the dication of **1** would provide relief of peri-strain[16] and provide an additional driving force for oxidation. Moreover, such structural change—a separation of peri-carbons—would be resisted in **2** and render it less oxidizable.

Despite being a hexacyclic aromatic hydrocarbon, **3** has a Hückel HOMO energy of 0.58β, substantially higher than the threshold value of 0.5β demonstrated previously to be required for formation of dication by SbF_5/SO_2ClF oxidation. The present result demonstrates that this threshold appears to apply as well to nonalternant hydrocarbons.

Experimental Section

Tetramethylnaphthalenes **1** and **4** were available from our preceding work. Arenes **3** and **4** were prepared following the published procedures.[13] Oxidation of the arenes with SbF_5/SO_2ClF were carried out by the previously published procedure.[11] The ^{13}C NMR spectra were obtained on Varian Model FT-80 NMR spectrometer equipped with a switchable variable temperature probe.

Acknowledgment. The research was assisted in part by National Science Foundation Grants No. CHE76-82170 and CHE77-10060.

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