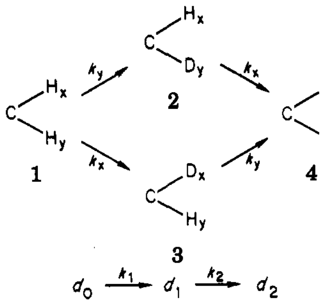
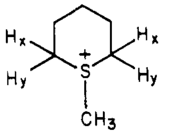
Scheme I



tested the program by using Eliel's data[6] on H/D exchange in the sulfonium salt **5** which contains two pairs of diastereotopic α-methylene hydrogens H_x and H_y. By treating the reaction according to the sequence



5

$$5 \xrightarrow{k_1} 5\text{-}d_1 \xrightarrow{k_2} 5\text{-}d_2 \xrightarrow{k_3} 5\text{-}d_3 \xrightarrow{k_4} 5\text{-}d_4$$

Eliel obtained $k_1{:}k_2{:}k_3{:}k_4 = 4.4{:}3.0{:}1.83{:}0.84$ from which he concluded that there was at best a very minor preference for abstraction of one proton pair over the other. Equation 2 for this particular case where $n = 4$ and $p = 2$ reduces to eq 3 from which we obtain rate constants of 1.83×10^{-2}

$$e^{-k_x t} + e^{-k_y t} = 4d_0 + 3d_1 + 2d_2 + d_3 \qquad (3)$$

h^{-1} and 7.95×10^{-3} h^{-1} for abstraction of the two sets of protons, i.e., a rate ratio of 2.3.

Finally we point out that the particular utility of eq 1 and 2 lies in their application to kinetics where the exchange rates differ by less than a factor of ten. In addition to examples such as the one cited above, this situation is likely to arise in isotope exchange of polycyclic homo- and heteroaromatic derivatives.

Acknowledgment. We thank the Natural Sciences and Engineering Council of Canada for financial support.

Registry No. 5, 41158-37-6.

Supplementary Material Available: A listing of the program (MULTISITE) written in BASIC (3 pages). Ordering information is given on any current masthead page.

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[6] Obtained from the Supplementary Material to ref 1.

Hydride Abstraction from 9,10-Dihydroanthracene and 5,12-Dihydronaphthacene in an Aprotic Molten Salt Medium

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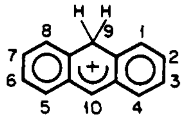
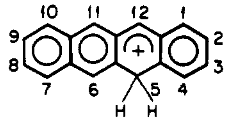
We have recently reported several novel hydrogen-transfer reactions in molten antimony trichloride.[1,2] For example, anthracene in high-purity molten antimony trichloride undergoes a spontaneous catalytic disproportionation at temperatures as low as 100 °C.[1] Some of the anthracene molecules are condensed to larger aromatics, liberating hydrogen which is quantitatively captured by unreacted anthracene molecules to form hydroanthracenes. When 9,10-dihydroanthracene (DHA) is dissolved under the same conditions, it disproportionates to anthracene and 1,2,3,4-tetrahydroanthracene (THA). If the Lewis acidity and oxidizing power of the $SbCl_3$ solvent are increased by the addition of 10 mol % $AlCl_3$, the dissolution of anthracene in this melt results instead in the prompt formation of stable solutions of the anthracenium ion (**1**) in 55–65% yields.[2] The proton source for this reaction is the condensation–dehydrogenation of a portion of the anthracene combined with a stoichiometric reduction of $SbCl_3$.

We now report that DHA dissolved in high-purity, aprotic molten $SbCl_3$–10 mol % $AlCl_3$ at temperatures from 100–130 °C also results in the prompt formation of **1**. In this case, **1** is generated by a formal hydride abstraction from some of the molecules of DHA while the hydrogen abstracted is transferred to unreacted molecules of DHA to form a mixture of THA, 1,2,3,4,5,6,7,8-octahydroanthracene (OHA), and other hydroanthracenes and/or hydroarenes. The role of the Sb^{3+} as an oxidant is again evident in the recovery of stoichiometric amounts of Sb metal in the product mixtures. We have also found a similar reaction to occur for 5,12-dihydronaphthacene (DHN), producing the naphthacenium ion (**2**).



1



2

The formation of **1** and **2** was followed by ^1H NMR measurements on the melts both with and without a $(CH_3)_4N^+$ internal standard. Their identities were confirmed by comparison of their respective integrated ^1H NMR spectra with those obtained from authentic samples measured in various molten salt solvents.[2] The prominent feature in the spectra of these ions is the presence of a midfield peak for the hydrogens on the sp^3-hybridized carbons at δ 4.9 with an integral twice that of the low-field-shifted resonance of H_9 (for **1**) and H_{12} (for **2**) at δ 9.6. The disappearance of the DHA starting material was observed by monitoring the resonance for its methylene hydrogens at δ 4.0. DHA was found to be completely reacted after 10–15 min at 100 °C and after less than 5 min at 130 °C. For DHN, the corresponding methylene resonance at δ 4.1 was not visible after the first few minutes even at 100 °C. At these times and temperatures, the arenium ions, **1** and **2**, form in 70–80% yields and remain stable for periods of at least 2 h. In each case a mixture of hydroarene products appears as broad bands in the aliphatic region δ 1.7 to 3.0. In contrast, in neat $SbCl_3$ the hydrogen-transfer reactions of both anthracene and DHA proceed at a much slower rate such that the effects of time and temperature on the rate of the reaction could be followed for many hours.[1]

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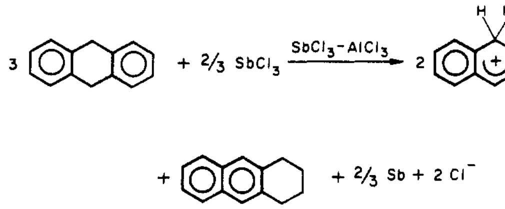
[1] Dworkin, A. S.; Poutsma, M. L.; Brynestad, J.; Brown, L. L.; Gilpatrick, L. O.; Smith, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 5299.

[2] (a) Buchanan, A. C., III; Dworkin, A. S.; Brynestad, J.; Gilpatrick, L. O.; Poutsma, M. L.; Smith G. Pedro *J. Am. Chem. Soc.* **1979**, *101*, 5430. (b) Buchanan, A. C., III; Dworkin, A. S.; Smith, G. P. *Ibid.* **1980**, *102*, 5262.

After quench and separation procedures, the organic reaction products were identified by GC, GC–MS, and high-performance LC. With DHA as the starting material, 20–25% of the product was found to be a mixture of hydroarenes about equally divided between those with mass 182 and those with mass 186. Of this 20–25%, the main products were THA (mass 182) and OHA (mass 186) with the rest made up of other isomeric hydroanthracenes and/or hydroarenes. The yield of anthracene found after hydrolysis of the reacted melt agreed with the yield of 1 in the melt determined from the NMR integration. With DHN as the starting material, essentially all of the hydrogenated product was found to be two tetrahydronaphthacenes, mass 232, and very little octahydronaphthacene or other mass 236 hydroarenes were detected.

A simplified hydride abstraction–hydrogenation reaction in $SbCl_3$–$AlCl_3$ is shown in eq 1 for DHA in terms of one



(1)

of its hydrogenation products, THA. Of course, the actual yield of 1 depends on the proportion of the various hydrogenated products formed, varying from 67% as written above to 86% if we had written a simplified equation in terms of OHA. Our finding of 75 ± 5% yield of 1 is then consistent with our finding that the main hydro products are a mixture of THA and OHA. However, the number of moles of Sb^0 produced should always be one-third that of the arenium ion generated and that is what we find within experimental error.

Holmes and Pettit[3] have reported a hydride abstraction for DHA and DHN using $SbCl_5$ in benzene. They found the reduced product to be $SbCl_3$ and the hydride abstracted was found as HCl. In most hydride-abstraction reactions for alkanes with SbF_5, HF–SbF_5, or FSO_3H–SbF_5, the reduced product is SbF_3 and the hydride eliminated has been reported as H_2 gas[4] or a mixture of H_2 and HF.[5,6] We have now demonstrated a novel hydride abstraction in the absence of either a protic superacid or a strong oxidizing agent such as $SbCl_5$. We have also demonstrated that in this molten $SbCl_3$–$AlCl_3$ medium, the hydride ultimately hydrogenates other molecules of starting material, while $SbCl_3$ is reduced. This is consistent with our previous observations of the net transfer of H^+ or $H\cdot$ between arenes in the $SbCl_3$–$AlCl_3$ medium.[2]

Several mechanisms have been proposed for hydride abstraction from hydroarenes and alkanes including direct hydride abstraction[3,4] and protolysis.[5,6] In our case, the former mechanism is unlikely since it would involve the formation of a very unstable Sb–H bond. The protolysis is also not likely since we are working in a highly purified aprotic medium.

An important point to consider in any explanation of the mechanism is that the hydride abstraction reaction reported in this work does not occur in neat $SbCl_3$ where instead a catalytic disproportionation takes place. We have previously obtained substantial evidence that the effect of added $AlCl_3$ is to enhance the oxidizing power of the Sb^{3+}/Sb couple in molten $SbCl_3$.[2] The evidence includes the observation of arene radical cations by ESR.[7] Clearly these findings plus the isolation of stoichiometric quantities of Sb metal indicate that a redox process has taken place in this hydride-abstraction reaction. Although we have no direct evidence,[8] radical cations may be important intermediates for the net hydrogen transfer between arenes in this reaction.

Furthermore, the results of our previous studies on hydrogen-transfer reactions in $SbCl_3$ melts indicate that in the presence of added $AlCl_3$ arenium ions are stabilized and further reaction is limited. For example, anthracene catalytically disproportionates in neat $SbCl_3$ to yield condensed anthracenes and hydrogenated anthracenes, but in the $SbCl_3$–$AlCl_3$ melt the formation of a stable solution of 1 from anthracene is as far as the hydrogenation path proceeds and no hydroanthracenes are formed. Also, DHA disproportionates in neat $SbCl_3$ to anthracene (and then further to condensed anthracenes) and more highly hydrogenated anthracenes, but in the $SbCl_3$–$AlCl_3$ melt the hydride abstraction from DHA to form a stable solution of 1 is as far as the dehydrogenation path proceeds and anthracene is not formed. Thus the difference in chemistry observed for arenes in neat $SbCl_3$ melts vs. $SbCl_3$–$AlCl_3$ melts may be rationalized in terms of the increased oxidizing power of the $SbCl_3$–$AlCl_3$ melt and the increased stability of arenium ions due to the higher Lewis acidity of the $SbCl_3$–$AlCl_3$ medium.

Experimental Section

All material transfers were performed in a controlled atmosphere glovebox. The argon atmosphere in this box was constantly circulated through a purification system and continuously monitored for moisture and oxygen content which amounted to ~1 ppm each.

Materials. $SbCl_3$ was further purified from anhydrous commercially available 99.99% material. The $SbCl_3$ was refluxed over 99.999% antimony metal in an argon atmosphere to reduce any $SbCl_5$ which might be present to $SbCl_3$. Sublimation under vacuum at 40 °C followed by distillation under a reduced pressure of argon at 95 °C gave a white solid which melted to a clear, colorless liquid. Spark-source mass spectrometry did not detect any inorganic oxidizing impurities above 2 ppm.

$AlCl_3$ was prepared according to a published procedure[9] from 99.9999% aluminum metal and specially prepared HCl, yielding a colorless solid.

DHA was synthesized by M. Poutsma of this laboratory by the reduction of anthracene by Na/C_2H_5OH,[10] crystallized from ethyl alcohol, and sublimed. DHN was synthesized by M. Poutsma from tetralin and phthalic anhydride by the method of Clar.[11] The product was recrystallized from acetic acid and sublimed under vacuum. Authentic samples of THA, kindly supplied by William D. Good of the U.S. Bureau of Mines at Bartlesville, OK, and commercially available OHA were used to aid in the product identification by NMR and GC. The purity of the organic reagents was confirmed by UV and GC.

Authentic samples of the protonated arenes 1 and 2 were prepared by the method of Koptyug.[12] This involved the Schlenk-ware reaction under argon of the arene with $AlCl_3$ and HCl gas in benzene as solvent. Removal of the benzene under vacuum gave the arenium ion as a chloroaluminate salt. The salts

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(3) Holmes, J.; Pettit, R. *J. Org. Chem.* **1963**, *28*, 1695.

(4) Lukas, J.; Kramer, P. A.; Kouwenhoven, A. P. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 44.

(5) Olah, G. A.; Halperin, Y.; Shen, J.; Mo, Y. K. *J. Am. Chem. Soc.* **1973**, *95*, 4960.

(6) Olah, G. A.; Lucas, J. *J. Am. Chem. Soc.* **1967**, *89*, 4738.

(7) Buchanan, A. C., III; Livingston, R.; Dworkin, A. S.; Smith, G. P. *J. Phys. Chem.* **1980**, *84*, 423.

(8) Attempts to observe the ESR spectra of the radical cations of either DHA or DHN in molten $SbCl_3$–10% $AlCl_3$ were unsuccessful.

(9) Bjerrum, N. J.; Boston, C. R.; Smith, G. P. *Inorg. Chem.* **1967**, *6*, 1162.

(10) Bass, K. C. *Org. Synth.* **1962**, *42*, 48.

(11) Clar, E. *Ber. Dtsch. Chem. Ges.* **1942**, *75*, 1271.

(12) Koptyug, V. A.; Isaev, J. S.; Rezvukhin, A. L. *Tetrahedron Lett.* **1967**, 823.

were transferred to the glovebox and NMR samples were prepared as described below. ^{1}H NMR spectra of the authentic ions were run in molten $SbCl_3$, $SbCl_3$–10% $AlCl_3$, and $AlCl_3$–NaCl–KCl (60:26:14 mol %). The spectra for each ion in the various solvents were identical[2] and were the same as those of the arenium ions formed in the hydride-abstraction reactions.

^{1}H NMR. Reactions were studied in situ in 5-mm o.d. NMR tubes (1-mm wall) filled with 0.8–1.0 g of $SbCl_3$, 0.050–0.075 g of $AlCl_3$, and 0.020 to 0.030 g of the hydroarene. A few runs were made in 10-mm o.d. NMR tubes (1-mm wall) with 4 g of $SbCl_3$, 0.25 g of $AlCl_3$, and 0.100 g of hydroarene. The tubes were filled in the glovebox and subsequently sealed under argon on a vacuum line. The ^{1}H NMR experiments were done at temperatures from 100–130 °C on either a Varian XL-100 spectrometer with a ^{19}F external lock or a Varian FT-80 spectrometer with a ^{2}H external lock. The chemical shifts were referenced internally to $(CH_3)_4N^+$ (δ 3.12) which was itself referenced to $(CH_3)_4Si$.

Separation and Identification. Products were identified from larger scale reactions (up to 0.25 g of the hydroarene in up to 9 g of $SbCl_3$–$AlCl_3$) performed in Schlenk glassware under argon. In a number of cases the reaction products were also separated from the in situ NMR experiments and found to be the same as those identified from the Schlenk-ware reactions.

The reaction mixture was hydrolyzed in 6 M HCl and the organics were dissolved in CH_2Cl_2 under argon. The mixture was filtered and the remaining solid was thoroughly washed with 6 M HCl (to remove $AlCl_3$ and unreacted $SbCl_3$) and CH_2Cl_2. The solid residue was oxidized with a 3:1 HCl–HNO_3 (v/v) mixture, and the resulting solution analyzed for antimony with an Instrumentation Laboratory atomic absorption spectrometer. The CH_2Cl_2 layer was separated from a CH_2Cl_2/HCl workup, and the solvent removed on a rotary evaporator.

The organic products were analyzed with a Bendix gas chromatograph with a flame-ionization detector and a column containing Dexsil 400 on 80/100-mesh Chromosorb G-HP. GC–MS were obtained with a Hewlett-Packard 5985 GC-mass spectrometer using a 30 m × 0.25 mm i.d. glass capillary column coated with polyimide liquid phase. Only under these high-resolution conditions was the previously discussed mixture of isomers of THA and of OHA resolved. A Waters liquid chromatograph with a Whatman Partisil M9-ODS-1 reverse-phase column and CH_3OH–H_2O and CH_3OH–CH_2Cl_2 solvent system was used principally to confirm the absence of appreciable amounts of condensed products.

Determination of Product Yield. DHA Reaction. The amount of arenium ion formed was calculated from integration of the ^{1}H NMR spectrum. For example, the spectrum of a sample starting with 0.0201 g (0.112 mmol) of DHA and 0.0047 g (0.043 mmol) of the internal standard, $(CH_3)_4NCl$, dissolved in 1.075 g of $SbCl_3$–10 mol % $AlCl_3$ was integrated after 30 min at 100 °C. An integral ratio of 3.1 was obtained for the 12 equivalent protons of $(CH_3)_4NCl$ relative to the 2 equivalent protons on the sp^3-hybridized carbon at δ 4.9 for 1. The yield of 1 is then 0.083 mmol or 74% (estimated error ±5%) based on the original arene. Results of three additional repetitive runs fell within the range of 75–77% yield.

A larger scale DHA reaction was performed at 100 °C for 30 min with 0.250 g (1.39 mmol) of DHA dissolved in 7.90 g of $SbCl_3$–10% $AlCl_3$. After quench and separation procedures, the organic products were quantitatively analyzed by GC using 9,10-dimethylanthracene as an internal standard. The yield of anthracene formed from the hydrolysis of the anthracenium ion, 1, was found to be 0.185 g (1.04 mmol) or 75% (estimated error ±4%). This value is consistent with the yields of 1 obtained from in situ ^{1}H NMR (vide supra). The yield of hydroanthracenes, primarily THA and OHA, was also determined and found to be 0.050–0.062 g or 20–25%, thus giving approximate mass balance on the organics within experimental error. Analysis for Sb by AAS gave 0.041 ± 0.001 g (0.34 ± 0.01 mmol) of Sb which is in agreement with the stoichiometric value (0.35 ± 0.02 mmol of Sb) calculated on the basis of the yield of 1 (74 ± 5%) from ^{1}H NMR (i.e., $^1/_3$ mol of Sb for every 1 mol of arenium ion).

DHN Reaction. The yield of arenium ion, 2, was also determined by ^{1}H NMR from a reaction run at 100 °C for 30 min with 0.0267 g (0.116 mmol) of DHN and 0.0024 g (0.022 mmol) of $(CH_3)_4NCl$ in 0.89 g of $SbCl_3$–10% $AlCl_3$. An integral ratio of 1.6 was obtained for the 12 protons of $(CH_3)_4NCl$ relative to the 2 protons on the sp^3-hybridized carbon at δ 4.9 for 2. Thus, the yield of 2 is 0.082 mmol or 71% (estimated error ±5%) on the basis of the original DHN.

The other product yields were determined from a larger scale reaction performed in a 10-mm NMR tube at 100 °C for 30 min with 0.099 g (0.43 mmol) of DHN dissolved in 4.019 g of $SbCl_3$–10% $AlCl_3$. The yield of 2 based on integration of the ^{1}H NMR spectrum was 70 ± 5%. After quench and separation procedures, analysis for Sb by AAS gave 11.5 ± 0.5 mg (0.094 ± 0.004 mmol) of Sb. This value is consistent with the stoichiometric value (0.100 ± 0.007 mmol of Sb) calculated on the basis of the yield of 2 from ^{1}H NMR ($^1/_3$ mol of Sb for every 1 mol of arenium ion). The remaining 30 ± 5% of the organics were not quantitatively analyzed, but GC–MS showed them to be primarily two tetrahydronaphthacenes (mol wt 232). As described in the text, the formation of all tetrahydroarene would stoichiometrically require a 67% yield of arenium ion and, thus, would be consistent with the amount of 2 (70 ± 5%) found in this reaction.

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Registry No. 1, 46300-36-1; 2, 75716-22-2; DHA, 613-31-0; OHA, 1079-71-6; DHN, 959-02-4; THA, 2141-42-6; anthracene, 120-12-7.

Unprecedented Rearrangement Products from Ultraviolet Irradiation of a Model 2,5-Cyclohexadienone[1]

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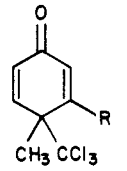
In the course of study of the photochemisty of cyclohexadienone **1b** in acidic methanol, we have observed some new and unexpected photochemical rearrangements, which provide yet additional reaction pathways in a system well-known for its diversity of behavior on electronic excitation.[2] The original goal of this study was to generate products analogous to **2a**, which is formed from the parent dienone **1a** on excitation in acidic methanol.[3] Such products preserve the stereochemistry of the zwitterion **3**, well established as an intermediate in the photochemistry of dienone **1**.[2] While only one stereoisomer of **2a** is gen-



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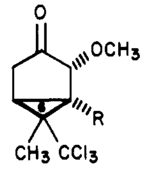

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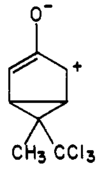

3

a, R = H; **b**, R = CH_3

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(1) Photochemistry of Ketones in Solution. 61. Part 60: Schuster, D. I.; Rao, J. M. *J. Org. Chem.*, submitted for publication.

(2) For a review, see: Schuster, D. I. *Acc. Chem. Res.* **1978,** *11,* 65.

(3) Schuster, D. I.; Abraitys, V. Y. *Chem. Commun.* **1969,** 419.