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Hydrogen Transfer Reactions of Arenes in Molten Antimony Trichloride

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Abstract: The reactions of polycyclic aromatic hydrocarbons in molten antimony trichloride at temperatures from 80 to 175 °C have been studied by in situ ^{1}H NMR and quench and separation techniques. Decomposition takes place by a complex series of hydrogen redistribution reactions whose net effect is a disproportionation of a type not previously known to occur. The reaction of anthracene (I) was studied in detail. Some of the anthracene molecules lose aryl-bound hydrogen and are condensed into larger molecules with aryl-aryl bonds such as the asymmetric bianthracenes (IV, V, and VI) and anthraaceanthrylenes (VII and VIII). The hydrogen released by these reactions is quantitatively captured by other anthracene molecules to form hydroaromatic molecules such as the 9,10-dihydro- and 1,2,3,4-tetrahydroanthracenes (II and III). The catalytic role of the solvent's Lewis acidity was demonstrated by the fact that the addition of a few mol % of a strong chloride donor reduced the reaction rates by a large factor. The reaction behavior of a group of related arenes (naphthalene, phenanthrene, chrysene, pyrene, perylene, and naphthacene) of widely varying basicity and oxidizability was also surveyed.

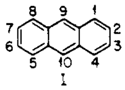
Introduction

We have briefly reported[1] that anthracene (I) dissolved in high-purity molten antimony trichloride under an inert atmosphere undergoes spontaneous hydrogen transfer reactions at temperatures as low as 100 °C with I serving as an efficient hydrogen acceptor for its own Scholl condensation reactions.[2] It has long been known that strong Lewis acids, such as molten aluminum trichloride, catalyze dehydrogenation–condensation reactions of aromatic compounds (Scholl reactions), but the fate of the hydrogen thus released had not been demonstrated. In the absence of added oxidizing agents, it has generally been assumed that hydrogen is evolved as a gas. Thus, our results are novel in two important respects: first, they demonstrate that the substrate aromatic can serve as an efficient hydrogen acceptor for its own Scholl reactions; and second, they demonstrate that Scholl reactions can be catalyzed by a mild Lewis acid, antimony trichloride. A full account of this aspect of Friedel–Crafts chemistry is reported in this article. The reaction behavior of a group of related arenes with widely varying basicity and oxidizability is also described. Most prior research on the behavior of polycyclic aromatics in liquid antimony trichloride was done at 74–99 °C[3] where we found that anthracene disproportionates quite slowly. Some research at higher temperatures[4] encountered reactions of an undetermined nature.

Results and Discussion

Solutions of anthracene in $SbCl_3$ prepared by melting together the high-purity components at 80 °C under an inert argon atmosphere were initially yellow. After about 2 h at this temperature, the solutions took on a greenish tinge. This very slow color change was greatly accelerated by increasing temperature such that at 125 °C the solutions were a very dark green almost immediately. Except for the first few minutes at 125 °C, the 100-MHz ^{1}H NMR spectrum of the melt was dominated by a pattern fully consistent in position and fine structure with that of molecular anthracene in nonreactive solvents ($CDCl_3$). The appropriateness of antimony trichloride as an NMR solvent was demonstrated by the observation of the spectrum of the triphenylmethyl cation comparable to that reported in FSO_3H.[5] The bands in the anthracene spectrum were initially broadened with the bands of $H_{9,10}$ being the broadest and those for $H_{2,3,6,7}$ being narrowest at any given instant. Since this order also corresponds to the relative magnitude of the hyperfine coupling constants in the anthracene radical cation, the broadening was attributed to exchange with traces of radical cation.[6] However, the spectrum rapidly sharpened as the radical cations decayed or as the unpaired electron was transferred to products of greater oxidizability. The presence and decay of these radical cations were confirmed by ESR at 80 °C where the decay rate was much slower. Both the color change and spectral sharpening were irreversible since they persisted when the solution was cycled between 125 and 80 °C.

Coincident with the sharpening of the anthracene spectrum, the lines for 9,10-dihydroanthracene (II) were observed and grew with time at the expense of those of anthracene. The methylene singlet at $\delta = 3.99$ ppm (referenced to $Me_4Si = 0$) and ten resolvable lines of the AA′BB′ pattern centered at $\delta = 7.33$ ppm for II were completely distinguishable from the anthracene spectrum in which no lines were further upfield than $\delta = 7.5$ ppm. After about an hour at 125 °C, bands at $\delta = 1.85$ ppm and 2.93 ppm attributable to the methylene groups in 1,2,3,4-tetrahydroanthracene (III) appeared and also continued to grow with time. Hydrogenated products II and III



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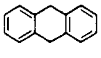
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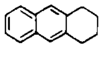
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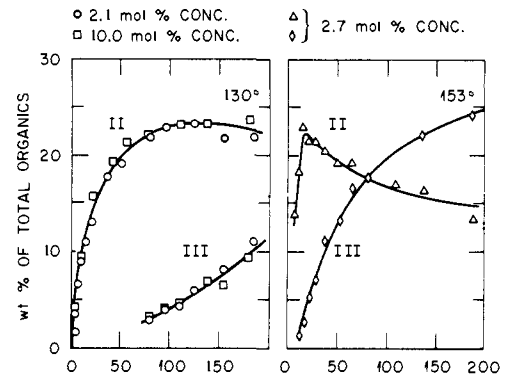


Figure 1. Effect of the initial concentration of anthracene and the temperature on the rates of formation of 9,10-dihydroanthracene (II) and 1,2,3,4-tetrahydroanthracene (III) in molten $SbCl_3$. The weight of total organics (equal to the initial weight of anthracene) remains invariant throughout the experiment.

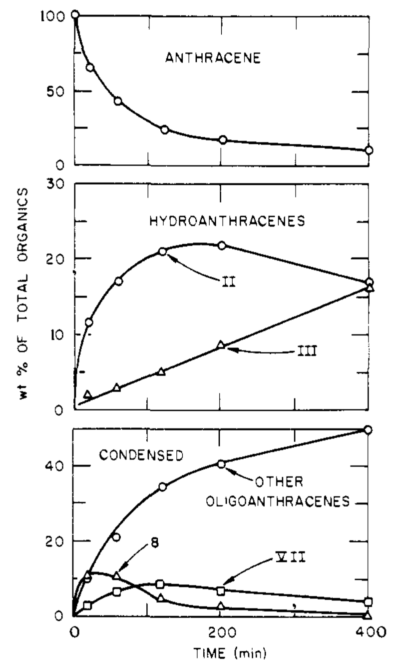
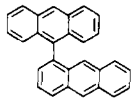


Figure 2. Rates of disappearance of anthracene and formation of the four principal products at 130 °C; initial concentration, 10 mol % anthracene in $SbCl_3$. The weight of total organics (equal to the initial weight of anthracene) remains invariant throughout the experiment.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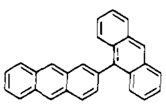
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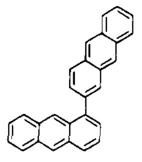
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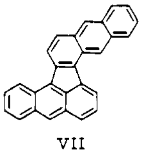
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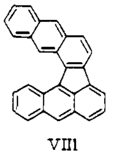
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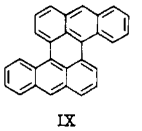

IX

were initially identified by comparison with the ^1H NMR spectra of the authentic compounds in molten $SbCl_3$. The spectra were well-resolved and very similar to the corresponding spectra for solutions in $CDCl_3$. The NMR identification was confirmed by HPLC and GC separations and UV spectra.

The reaction rates were found to be independent of the initial concentration of I over the range of approximately 2–10 mol %, whereas an increase in temperature of less than 25 °C increased the rates by a large factor. Both of these effects are illustrated in Figure 1 which is based on integration of the NMR spectra taken as the reactions proceeded. When II is dissolved in antimony trichloride at 130 °C, it disproportionated to I and III (and the products of the reaction of I) at a rate slightly less than that shown in Figure 1 for formation of II from I. The NMR spectrum of III dissolved in antimony trichloride was stable for a few hours after which some change in the spectrum was seen but not the formation of either I or II. The above reaction behavior is consistent with that shown in Figure 1; i.e., a maximum of the amount of II was reached after above 2-h of reaction time followed by its decrease and the continuous increase of the amount of III.

Under the conditions of the experiment adventitious hydrogen could not possibly have accounted for the degree of reaction described above. Since no other external hydrogen source was present, the formation of hydro derivatives of anthracene implies the formation of some coproducts containing less hydrogen than anthracene which suggests, therefore, the coupling of anthracene units. Although these condensed products were not seen as resolved entities in the NMR spectra, extra absorption appeared as a broad nondescript envelope lying under the distinct anthracene lines and grew as I decreased. In order to identify the condensed products and also to confirm the NMR integration results for the hydrogenated products, quench and separation techniques were employed.

The components of the organic phase recovered after a run were separated principally by HPLC and TLC and identified by UV, NMR, mass spec, and melting point. We found by HPLC that the condensed aromatic material was comprised of approximately 20 different compounds. However, a significant fraction of the condensed material during the first hour or two of the reaction was made up of just two of these compounds, an asymmetric bianthracene (B) which is either the 1,9′-bianthracene (IV) or the 2,9′-bianthracene (V) (see Experimental Section), and anthra[2,1-*a*]aceanthrylene (VII). Evidence from UV and mass spectra suggested that the two other asymmetric bianthracenes (VI and either IV or V), anthra[1,2-*a*]aceanthrylene (VIII), and dibenzo[*a,j*]perylene (IX) were among the minor products formed. The remainder was composed of more condensed materials (oligoanthracenes formed from two to six anthracene units have been identified by mass spec) and other unidentified substances.

There are six possible isomers of bianthracene; the preparation and properties of the three symmetrical isomers are reported in the literature[7,8] but those of the asymmetric ones have not been reported. The selectivity for asymmetric bianthracenes when I is heated at moderate temperatures for relatively short periods of time in molten $SbCl_3$ suggests that new synthetic techniques may be derived from this work.

Figure 2 summarizes the course of the reactions for the first 400 min as monitored by both NMR and separation techniques. The principal asymmetric bianthracene (B) formed rapidly coincident with II and appeared to be the precursor of VII which decayed more slowly than did B. In order to confirm that VII actually was derived from B, we studied the reactions of VII and of the principal bianthracene (B) in molten $SbCl_3$. After 1 h at 130 °C, only 5% of the bianthracene remained. The main condensation product was found to be VII (about 40% of the total organics) and the reduced products identified were I, II, and III. Again, a number of products were found which could not be identified. On the other hand, more than 90% of the original amount of VII was recovered from a solution of VII in molten $SbCl_3$ kept at 130 °C for 1 h. It is of note that authentic 9,9′-bianthracene was found to be stable for an extended period of time in molten $SbCl_3$ at 130 °C and yet we found only trace amounts of it among the condensed products of the reaction of I in $SbCl_3$.

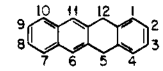
In order to ascertain the extent to which the hydrogen liberated from the condensation reactions was transferred to hydrogenated compounds in the molten reaction medium, the gas phase above the melt was also analyzed. After a typical experiment the reaction tube was cooled, connected to a mass spectrometer, and opened to the spectrometer through a break seal. No hydrogen-containing gases (H_2, HCl, or organics) in amounts greater than 0.001% of the hydrogen in the original anthracene reactant were found. This evidence, then, reconfirms the efficiency of the hydrogen transfer in the molten antimony trichloride reaction medium.

The addition of a few mole percent of a strong chloride donor, KCl, or $(CH_3)_4NCl$ greatly reduced the rate of the anthracene disproportionation reaction. For example, in the presence of 3 mol % $(CH_3)_4NCl$ after 1500 min at 130 °C, II made up 14% of the organics whereas less than 40 min were required to form an equivalent amount in the absence of $(CH_3)_4NCl$. At the same time (1500 min) with added chloride ion donor, III was not as yet discernible in the NMR spectrum. The maximum yield of II with added chloride ion donor occurred at about 2400 min as compared with about 120 min in the neat melt while III comprised about 10% of the organics at 2400 min, a concentration reached in about 180 min in the neat melt. The addition of a chloride ion donor slowed the rate of disproportionation of II in $SbCl_3$ in a like manner. This strong effect on the reaction rate suggests that the solvent's Lewis acidity is playing a catalytic role. $SbCl_3$ is very weakly ionized to $SbCl_2^+$ (a moderately strong Lewis acid) and chloride ion (solvated in some manner) with an ion product constant variously reported from 1.6 to 10^{-8} to $<3 \times 10^{-11}$ at 99 °C.[3,9] The concentration of the Lewis acid $SbCl_2^+$ is at least 2500 times greater in the neutral melt than it is in a melt with 3% $(CH_3)_4NCl$ added.

The ^1H NMR spectra of naphthalene, phenanthrene, chrysene, pyrene, perylene, and naphthacene were also measured in molten $SbCl_3$. These compounds are listed above in order of increasing basicity[10] and oxidizability,[11] anthracene taking its place between pyrene and perylene. We found that the first four compounds in the series were very stable such that the NMR spectra remained well-resolved and closely similar to the corresponding spectra for solutions in $CDCl_3$ with no extra bands appearing for periods as long as 4 days at temperatures between 125 and 175 °C. Some color changes were noted that were not reflected in the NMR spectra; naphthalene changed from pale yellow to brown red when heated at 175 °C, phenanthrene from pale yellow to amber at 150 °C, chrysene from yellow to orange at 150 °C, and pyrene from yellow to green at 175 °C. These color changes were moderated when the experiment was repeated with the addition of a few % chloride ion donor.

A solution of perylene in molten $SbCl_3$, on the other hand, was immediately deeply colored (brown to green) and gave no observable NMR signal even after heating for more than 20 h at 125 °C. The absence of NMR signal may be attributed to the presence of an appreciable concentration of perylene radical cations whose presence was confirmed by ESR. The organic extracted from this sample showed an aromatic NMR spectrum in $CDCl_3$ clearly different from perylene but we were unable to identify the products of the reaction. A solution with added chloride ion donor showed a single, unresolved aromatic band which remained constant even after heating for 16 h. The solution at this point was deep red but still less colored than the initial solution without added chloride ion donor. The organic extracted from this sample showed a clean NMR spectrum in $CDCl_3$ for perylene with no major new peaks observed. Therefore, perylene is probably more stable chemically in a solution of $SbCl_3$ with added chloride ion donor than is anthracene which showed easily detectable hydrogen transfer under the same conditions where perylene showed little or none. However, the extent of reaction of perylene in neat $SbCl_3$ appears to be at least equal to that of anthracene although whether or not the products of the reactions are similar cannot at this time be answered.

Naphthacene behaved in a still different manner. The ^1H NMR of the deep red solution of naphthacene in molten $SbCl_3$ showed three or four broad aromatic bands and possibly some even weaker aliphatic bands which showed no obvious correspondence with the spectrum of naphthacene in 1,1,2,2-tetrachloroethane at 125 °C. After heating for a few hours at 125 °C, the NMR spectrum of the naphthacene solution developed considerable fine structure in the aromatic region and a sharp methylene singlet at $\delta = 4.1$ ppm. This spectrum was identified as that of 5,12-dihydronaphthacene (X) by comparison with the spectrum of the authentic compound and comprised from 50–60% of the total organics. The remainder appeared as a broad background underneath the distinct fine structure of the aromatic region of the 5,12-dihydronaphthacene spectrum. This spectrum remained unchanged for a considerable length of time. After heating at 125 °C for 16 h, the growth of a broad band at relatively high field (centered about $\delta = 2.0$ ppm) first appeared. After another 16 h at 150 °C, this upfield band, which in analogy to the anthracene case was probably associated with methylene groups of a more hydrogenated naphthacene, was finally larger than the $\delta = 4.1$ ppm singlet. A parallel solution with added chloride ion donor was initially similar to that in the neat melt but did not show the upfield growth with extended heating. The disproportionation of naphthacene, then, resulted in a higher yield of dihydro compound than did the analogous anthracene reaction due evidently to the relative ease of further hydrogenation of the dihydroanthracene as compared to the dihydronaphthacene.



X

We have demonstrated, then, heretofore unknown spontaneous hydrogen transfer reactions in which anthracene serves as an efficient hydrogen acceptor for its own Scholl reactions. The selectivity for previously unprepared asymmetric bianthracenes and the fact that so mild a Lewis acid as $SbCl_3$ serves effectively to catalyze Scholl reactions are also noteworthy. A group of similar arenes which are less basic and oxidizable than is anthracene was found to be unreactive under similar conditions while naphthacene and possibly perylene, which are more basic and oxidizable, reacted at least similarly if not more extensively.

Mechanisms proposed for Scholl reactions[2] are of two types depending on whether or not they invoke radical cations (in addition to arenium ions) as intermediates. Both types of mechanisms can be extended to include the hydrogenation reactions in a condensation/hydrogenation type of disproportionation. While the role of the catalyst is not adequately accounted for by these mechanisms, the catalytic role of the Lewis acidity of the $SbCl_3$ solvent is evident from the strong effect of added chloride ion donor. Measurements of the half-wave potentials of a number of arenes in molten $SbCl_3$ and of the change in redox potential of the Sb^{3+}/Sb^0 couple as a function of chloride ion concentration[9,11] indicated that at appropriate chloride ion concentrations the arenes can be oxidized by the $SbCl_3$ solvent.

These results make it clear that there exists in liquid $SbCl_3$ a previously unrecognized sequence of oxidation–reduction reactions involving hydrogen transfer between aromatics. The mechanisms of these reactions are under continued investigation.

Experimental Section

Materials. $SbCl_3$ prepared from anhydrous 99.99% material obtained from three different vendors was used for most of the experiments. This material was first melted with antimony metal to reduce any $SbCl_5$ present, then sublimed under dynamic vacuum followed by a distillation in a sealed apparatus under argon. All material transfers were made in a controlled atmosphere glove box. Batches of about 50 g were prepared by this method. A variation of this method with anhydrous technical grade (99%) $SbCl_3$ as the starting material was used to prepare batches of 200–500 g. An extra final step involving zone refining was also used. In all cases, the final product melted to a clear, colorless liquid. The organic reactions followed the same course regardless of which preparation was used.

Naphthalene, phenanthrene, chrysene, pyrene, anthracene, perylene, and naphthacene were commercial reagents of the highest purity (99+ to 99.9+%). In all cases, the arenes were sublimed before use, and anthracene was also recrystallized first from acetic acid and then from toluene before sublimation. No impurities could be detected by UV, GC, or HPLC.

9,10-Dihydroanthracene was synthesized by the reduction of anthracene by Na/C_2H_5OH,[12] crystallized from ethyl alcohol and sublimed. 1,2,3,4-Tetrahydroanthracene was kindly supplied by William D. Good of the U.S. Bureau of Mines at Bartlesville, Oklahoma. Both products were found to be pure by UV, GC, and HPLC. 9,9′-Bianthracene was synthesized by reductive coupling of anthraquinone with Sn/HCl.[7a] Tetramethylammonium chloride was purified by precipitation of the commercial product from a hot methyl alcohol–acetone mixture by the addition of acetone. The precipitate was filtered and the operation repeated in Schlenk ware in a dry argon atmosphere. The product was then dried under vacuum at room temperature.

5,12-Dihydronaphthacene (X) was synthesized from tetralin and phthalic anhydride by the method of Clar.[13] The product was recrystallized from acetic acid and sublimed under vacuum. To confirm the identification, a portion of the product was converted to naphthacene as described by Clar and gave a UV-vis spectrum fully consistent with authentic naphthacene. In the previously unreported ^1H NMR spectrum of 5,12-dihydronaphthacene (X) in $CDCl_3$ solution, $H_{6,11}$ occurs as a singlet at $\delta = 7.75$ ppm superimposed on the upper part of the multiplet resulting from $H_{7,10}$, the other δ-naphthyl-type protons; the β-naphthyl-type protons $H_{8,9}$ as well as H_{1-4} of the lone aromatic ring fall in a complex multiplet at higher field ($\delta = 7.5–7.1$ ppm) and the methylene hydrogens at $H_{5,12}$ occur as a singlet at $\delta = 4.09$ ppm.

Procedure. All material transfers were performed in a controlled atmosphere glove box whose argon atmosphere was constantly circulated through a purification system and continuously monitored for moisture and oxygen content which was kept at a level of ~1 ppm.

NMR: 5 mm OD NMR tubes (1-mm wall) were filled with 0.5–1 g of $SbCl_3$ and 0.01 to 0.1 g of the organic substrate in the glove box and subsequently sealed under argon on a vacuum system. The in situ ^1H NMR runs were made at temperatures from 70 to 150 °C on a Varian XL100 which had an external ^{19}F lock. Both CW and FT modes were used. The spectra in molten $SbCl_3$ were internally referenced to $(CH_3)_4N^+$ ($\delta = 3.12$ ppm) which was itself separately referenced to Me_4Si both in the melt and in D_2O. Room temperature spectra in $CDCl_3$ were referenced to Me_4Si.

Separation and Identification. Samples for separation were prepared either in NMR tubes containing quantities of $SbCl_3$ and anthracene as described above or in larger tubes filled and sealed as with the NMR tubes but containing up to 2 g of anthracene at concentrations up to 10 mol %. At the conclusion of the appropriate heating period, the tubes were cooled and broken under a mixture of 6 N HCl and CH_2Cl_2 under argon. (In the case of the runs in NMR tubes, the ^1H NMR spectrum was measured before cooling.) The organic phase was washed with HCl until no $SbCl_3$ remained. The organics recovered after evaporation of CH_2Cl_2 were always within a few percent of the initial weight of anthracene. A ^1H NMR spectrum of the organic phase was measured in $CDCl_3$ and agreed with that obtained in the melt. One run was performed in which the $SbCl_3$ (together with some of I, II, and III) was separated by sublimation. The results for this run in which the condensed products were not exposed to HCl were in agreement with the results from the standard procedure.

The major organic products were separated utilizing open column chromatography (Al_2O_3) and preparative TLC (silica gel) followed by repetitive recrystallization, and then identified by mass, UV, and ^1H NMR spectra, and melting point. A Waters preparative liquid chromatograph was used to isolate quantities of B and VII large enough to use in the experiments in which they were the initial reactants in molten $SbCl_3$. For routine analysis the organics were extracted as described above and separated on a Waters HPLC which had a variable wavelength UV detector and a programmable gradient elution capability. A Whatman Partisil M9 ODS reverse phase column and a solvent system varied from 87% methanol–H_2O to 100% methanol (flow rate = 9 mL/min) was used. The collected fractions were characterized by their UV and mass spectra. Quantitative results were calculated from the UV spectra. A Cary 14 spectrophotometer was used for these measurements.

Compounds VII and VIII. A comparison with literature values[7b,7c,14] of the complex UV spectra and melting point of VII (mass = 352) provided identification of this product. Our melting point of 227–228 °C was in agreement with the reported value of 225–229 °C. Our measured ultraviolet spectrum of VII in methanol showed the following absorption maxima (molar absorptivity, ϵ, is given in parentheses): 238 (69 600), 245 (70 100), 264 sh (56 400), 272 (71 700), 293 (50 500), 308 (sh (26 600), 343 sh (6100), 360 sh (9300), 376 (15 000), 386 (14 200), 393 (15 300), 417 (7300), 442 (14 000), 460 sh (9900), 468 (15 700), 520 sh (1850), and 555 nm (1310).

The isomer, compound VIII, was a very minor product and was identified by comparison with literature values[7b,7c] of its complex UV spectrum.

Compounds IV, V, VI, and IX. The principal bianthracene (B) (mass = 354) was shown to be asymmetric by ^{13}C NMR. Earlier we assigned[1] its ^1H NMR spectrum as being indicative of 1,9′-bianthracene (IV). However, careful consideration of the results of several further spectral integrations does not allow us to rule out the 2,9′ isomer (V). Attempts to synthesize the authentic compounds IV and V for comparison have been unsuccessful to date. However, we have shown that the principal bianthracene (B) is the precursor for compound VII. While there is a direct route from V to VII, the formation of the latter from IV would entail a rearrangement. Therefore, compound V seems to be a more likely choice for our principal bianthracene. The isomeric assignment of VII was based on what appears to be a reliable synthetic method.[14]

The melting point of B was 229–230 °C. This is considerably lower than that reported for the symmetric isomers: 320 °C for the 1,1′,[7a] 310 °C for the 9,9′,[7c] and 369 °C for the 2,2′.[7b] Its ultraviolet absorption in methanol [249 sh (189 500), 255 (233 000), 315 sh (3930), 330 sh (6550), 347 (12 150), 364 (17 400), and 383 nm (15 100)] was very similar to but discernible from that of the 1,1′[7a] and 9,9′[7] isomers.

Two very minor fractions which were chromatographically separated close to the principal bianthracene fraction each have mass = 354 and exhibit UV spectra very similar to that of B. However, these spectra could be distinguished from that of B as well as from those of the symmetric bianthracenes. These compounds we presume to be VI and either IV or V.

Another minor fraction (less than 1%) was identified as IX by comparison with UV spectra in the literature.[15] The purple solution of IX in methanol or methylene chloride was readily photooxidizable[16] and care had to be taken to protect it from light or it was lost before its UV spectrum could be measured.

Acknowledgment. This research was sponsored by the office of Basic Energy Sciences, U.S. Department of Energy under Contract W-7405-eng-26 with the Union Carbide Corporation.

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Solvolysis of Alkyl *p*-Hydroxybenzoates in Fused Lithium–Sodium–Potassium Acetate

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Received March 9, 1979

Abstract: The Li^+,Na^+,K^+OAc^- eutectic (32, 30, 38 mol %), a molten salt in which phenolic compounds are soluble, is sufficiently basic to ionize aromatic amine indicators of pK_a = 15. Solutions of methyl *p*-hydroxybenzoate (**1**) react to form methyl acetate, carbon dioxide, methanol, phenol, and anisole. The kinetics of this $B_{Al}2$ displacement by acetate ion, at 181–220 °C in the presence of 1.3% acetic acid, shows $k\ (s^{-1}) = 1.49 \times 10^5 e^{-19900/RT}$ for **1** and successively decreasing rates for the ethyl, propyl, isopropyl, and 2-butyl esters. 2-Butyl *p*-hydroxybenzoate (**2**) undergoes both elimination and displacement; optically active **2** yields 58% inverted, 42% racemized 2-butyl acetate. Thiocyanate ion, added to the molten salt, is a nucleophile which competes with acetate ion in the displacement, accelerating the solvolysis.

Molten salts have been used as solvents for kinetic studies of a very few homogeneous organic substitution and elimination reactions.[2-10] Having reported displacements on the alkyl group of esters by thiocyanate ion, the solvent nucleophile in fused sodium–potassium thiocyanate, Na^+,K^+SCN^-,[11] we now describe solvolysis in an acetate melt, Li^+,Na^+,K^+OAc^-. We used a ternary eutectic of lithium, sodium, and potassium acetates (32, 30, 38 mol %, mp 162 °C).[12] Other lower melting but more expensive eutectics such as Na^+,Rb^+,Cs^+OAc^- (30.5, 14.0, 55.5 mol %, mp 95 °C) have been characterized.[13]

Results

Solutions in the Fused Salt. Hydroxyl groups in organic compounds cause them to be quite soluble in the fused acetate at 200 °C, just as in ammonium nitrate[14] and potassium thiocyanate[15] melts. In contrast to thiocyanate, however, we find that molten acetate is sufficiently basic to ionize the phenolic hydroxyl groups in *p*-nitrophenol, *m*-nitrophenol, and alizarin as well as the amino group in 2,4-dinitroaniline (pK_a = 15.00 in water, 25 °C)[16] but not *p*-nitroaniline (pK_a = 18.37). The medium can be made less basic by adding acetic acid, giving rise to a protic solvent system containing a preponderance of lyate ion. If the fused salt contains 0.074 M acetic acid, the ionization of 2,4-dinitroaniline is repressed so that only about 50% of it is in the anionic form, $ArNH^-$. Addition of 11 mol % acetic acid to the melt raises its acidity sufficiently to protonate the alizarin dianion to the red monoanion while a medium 62 mol % acetic acid and 38 mol % Li^+,Na^+,K^+OAc^- favors the yellow, neutral form observed in slightly acidic aqueous solution.

Of the variety of polyhydroxy compounds soluble in the acetate melt, some, such as ethylene glycol, are probably not completely ionized and dissolve by hydrogen bonding to the acetate ion.[2] Others, as demonstrated by the indicator studies, go into solution as anions. However, sodium salts such as sodium methoxide, sodium benzoate, and sodium phenoxide, unlike their conjugate acids, do not dissolve immediately in the melt. For example, sodium benzoate (2 wt %) requires at least 20 min and in some experiments several hours, to dissolve at 200 °C. Decarboxylation does not occur; the salt can be recovered as benzoic acid.[17] Immediate solution of these sodium salts can be effected by adding small quantities of acetic acid with a syringe. While this observation supports the assumption that the anions are solvated by acids in the melt,[2] we were prevented from finding a relationship between concentrations and solubility by the slow dissolution mentioned above. Solubility of the salts of oxy anions is also increased by traces of water.

Although the acetate melt is ostensibly aprotic, it is really not strictly so. Even if acetic acid is neither added directly, as in most of the kinetic studies described below, nor indirectly through the ionization of dissolved acids, traces of acetic acid as well as water are present which are difficult to remove by heating or pumping. The melt is also protic in the sense that the hydrogen atoms in the methyl group of CH_3COO^- exchange with CD_3COO^- (40% in 10 h at 250 °C).[18]

The affinity of molten acetate for acetic acid is seen in the negative deviation from ideality of the partial pressure of acetic acid vapor over solutions of it in the melt. The dotted line in Figure 1 shows the observed pressure, p, as a function of the mole fraction x of acetic acid, up to its vapor pressure, 5260 Torr at $x = 1$. The line A, drawn through the points for low x (without regard for their apparent curvature), may be expressed as $p = 0.20 p_0 x$ where 0.20 is a Henry's law constant. Curve B is $p = p_0 x$. The solubility of CH_3COOD is the same as that of CH_3COOH, within 1%, up to $x = 0.043$.

Water vapor is much less soluble in the acetate melt. It shows a positive deviation from ideality, $p = (9.5 \pm 0.1) p_0 x$, at mole fractions of water near 10^{-4}. This fact, together with

0002-7863/79/1501-5303$01.00/0