Anal. Calcd for $C_{11}H_{13}NO_6S$: C, 45.99; H, 4.56; N, 4.87; S, 11.16. Found: C, 46.08; H, 4.54; N, 4.88; S, 11.07.

Registry No. $CH_3CH(NO_2)CH_2OCH_3$, 95798-39-3; $C_2H_5O(CH_2)_2NO_2$, 31890-52-5; $CH_3C(NO_2)_2CH_2OCH_3$, 5917-65-7; $C_2H_5OCH_2CH(NO_2)_2$, 5946-60-1; $(C_2H_5OCH_2)_2CHNO_2$, 95798-42-8; $(HOCH_2)_3CNO_2$, 126-11-4; $C_2H_5OCH_2CH(CH_2OH)NO_2$, 95798-43-9; $C_2H_5CH(NO_2)CO_2CH_3$, 59906-50-2; $(C_2H_5OCH_2)_2C(NO_2)_2$, 95798-44-0; $CH_3C(NO_2)_2CH_2OH$, 918-52-5; $(HOCH_2)_2C(NO_2)_2$, 2736-80-3; $C_2H_5OCH_2C(NO_2)_2CH_2OH$, 95798-45-1; $C_2H_5C(NO_2)_2CO_2CH_3$, 95798-46-2; $(CH_3)_2C(NO_2)CN$, 18992-13-7; $(CH_3)_2C(NO_2)SO_2Ph$, 41774-06-5; $C_2H_5C(NO_2)(SO_2Ph)CO_2CH_3$, 95798-47-3; $(CH_3)_2CHNO_2$, 79-46-9; $CH_3CH_2NO_2$, 79-24-3; $CH_3(CH_2)_3NO_2$, 627-05-4; $CH_2{=}CHCH_2CH_2NO_2$, 32349-29-4; $(CH_3)_2C(NO_2)_2$, 595-49-3; $CH_3CH(NO_2)_2$, 600-40-8; $CH_3(CH_2)_2CH(NO_2)_2$, 3759-55-5; $CH_2{=}CHCH_2CH(NO_2)_2$, 10229-09-1; nitrocyclohexane, 1122-60-7; nitrocyclopentane, 2562-38-1; 2,2-dimethyl-5-nitro-1,3-dioxane, 4064-87-3; 1,1-dinitrocyclohexane, 4028-15-3; 1,1-dinitrocyclopentane, 10515-17-0; 3,3-dinitrooxetane, 81764-66-1; sodium nitrite, 7632-00-0; potassium ferricyanide, 13746-66-2; triethyl orthoacetate, 78-39-7; formalin, 50-00-0; nitromethane, 75-52-5; sodium cyanide, 143-33-9; 3-nitrooxetane, 86632-92-0; 2-methyl-2-ethoxy-5-nitro-5-(hydroxymethyl)-1,3-dioxane, 95798-40-6; 2,2-dimethyl-5,5-dinitro-1,3-dioxane, 5086-75-9; 2-ethoxy-2-methyl-5,5-dinitro-1,3-dioxane, 95798-41-7; 1-nitro-1-cyanocyclohexane, 58102-55-9; 1-nitro-1-(phenylsulfonyl)cyclohexane, 41774-11-2; dimethyl 2,3-diethyl-2,3-dinitrosuccinate, 95798-48-4; sodium persulfate, 7775-27-1; 3-ethoxy-2-nitro-1-propene, 95798-49-5; 2,2-dimethyl-5-nitro-5-(hydroxymethyl)-1,3-dioxane, 4728-14-7; benzenesulfinic acid sodium salt, 873-55-2.

Redox vs. Lewis Acid Catalysis. The Chemistry of 1,2-Diarylethanes in $SbCl_3$-Rich Molten Salt Media

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The product selectivity for the reactions of 1,2-diarylethanes, $ArCH_2CH_2Ar$ [Ar = phenyl (DPE), 1-naphthyl (DNE), and 9-anthryl (DAE)], in $SbCl_3$-rich molten salt media at 80–150 °C is found to be highly dependent on the nature of the aryl group. This chemistry, which has been examined primarily by in situ ^1H NMR and by quench and separation techniques, is interpreted in terms of a change in mechanism from Lewis acid catalysis to redox catalysis as the aryl group becomes more oxidizable. DPE is activated solely by the Lewis acid function of the melt, which generates a benzylic carbenium ion, ArC^+HCH_2Ar, as a reactive intermediate by hydride abstraction by $SbCl_2^+{\cdot}nSbCl_3$. This intermediate leads to transalkylation products resulting from the selective cleavage of the benzylic (sp^2–sp^3) carbon–carbon bond. DAE, on the other hand, is activated by the redox function of the melt, which generates a radical cation intermediate, $ArCH_2CH_2Ar^{+\cdot}$, by oxidation by Sb^{3+}. At 80 °C, the primary reaction pathway for the DAE radical cation is an intramolecular aryl–aryl coupling with internal hydrogen transfer to produce an unusual spiro isomer (1) of DAE in high yield. At higher temperatures (150 °C) cleavage of the ethylenic (sp^3–sp^3) carbon–carbon bond in the radical cation becomes an important process in competition with the intramolecular coupling. For DNE, combined Lewis acid catalysis (positional isomerization and transalkylation) and redox catalysis (intramolecular coupling) generates a complex product mixture. The reactions observed for $DAE^{+\cdot}$ and $DNE^{+\cdot}$ in these highly purified anhydrous $SbCl_3$-rich melts are discussed in relation to reaction pathways for alkylbenzene and diarylethane radical cations in other media.

Molecular antimony trichloride is an extremely weak Lewis acid with little ability to catalyze organic reactions when dissolved in an inert solvent.[1] However, if $SbCl_3$ is present as a continuous molten phase, it is reported to be an active catalytic medium for hydrocracking coal with a high specificity for distillate hydrocarbons.[2] In our research on molten salt catalysis with coal model compounds, we have also found $SbCl_3$-rich melts to be active catalytic media for inducing selective organic reactions.[3] These melts have been found to possess two active catalytic functions: a Lewis acid function and, perhaps more surprisingly, a redox function. Moreover, the strength of these catalytic functions can be tuned by controlled additions of chloride donors or acceptors, which produce a flexible catalyst with reproducible control over reaction rates and product selectivities.

The Lewis acid function of the melt results from the fact that in the molten state $SbCl_3$ is weakly ionized, as modeled in eq 1, with a reported ionization constant, K_i, at 99

$$SbCl_3 \rightleftarrows SbCl_2^+{}_{(solv)} + Cl^-{}_{(solv)} \qquad (1)$$

°C ranging from 3×10^{-11} to 2×10^{-8} M^2.[4] As indicated in eq 1, the ions are not present in the melt as discrete entities, but instead are complexed to neutral $SbCl_3$ molecules (or chains of $SbCl_3$ molecules) through chlorine bridge bonds as indicated from Raman[5] and electrical conductivity[6] studies. There is currently no objective ev-

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idence as to specific formulae for the ions involved; therefore, the ion $SbCl_2^+{\cdot}nSbCl_3$ is probably the best representation of the Lewis acid entity in the melt. However, for the purpose of the present discussion, $SbCl_2^+$ will be used as a symbol to represent the chloride deficient antimony species that is acting as the Lewis acid in the melts.

The Lewis acidity of the melt can be tuned by controlling the concentration of $SbCl_2^+$ in the melts. Basic melts are formed by adding a few mol % of a chloride donor such as KCl (eq 2), while acidic melts are generated by adding a strong chloride acceptor such as $AlCl_3$ (eq 3). The degree to which the Lewis acidity can be altered is indicated from the calculation that in an $SbCl_3$–10 mol % $AlCl_3$ melt the concentration of $SbCl_2^+$ is increased by a factor of 10^4–10^5 compared to that in a neat $SbCl_3$ melt (as estimated from the range of K_i values at 99 °C).

$$KCl \xrightarrow{SbCl_3} K^+ + Cl^- \quad (2)$$

$$SbCl_3 + AlCl_3 \xrightarrow{SbCl_3} SbCl_2^+ + AlCl_4^- \quad (3)$$

We have also observed that $SbCl_3$ melts have a redox function in which Sb^{3+} can act as an oxidant. As shown in eq 4, the concomitant reduction of Sb^{3+} in the melt liberates chloride and, thus, the oxidizing power of the melt will depend on the melt acidity. The effect of added chloride donor or acceptor on the formal potential of the Sb^{3+}/Sb couple was measured by electrochemical methods.[7] As expected, the addition of a few mol % of the chloride donor (KCl) decreased the oxidizing power of $SbCl_3$, while the addition of a few mol % of the chloride acceptor ($AlCl_3$) increased the oxidizing power. In going from an $SbCl_3$–5 mol % KCl melt to an $SbCl_3$–5 mol % $AlCl_3$ melt, the formal potential of the Sb^{3+}/Sb couple and the resulting oxidizing strength can be tuned over ~0.5 V.[4b,7]

$$^1/_3SbCl_3 + e^- \rightleftarrows {}^1/_3Sb + Cl^- \quad (4)$$

It should be noted that antimony can exist in oxidation states between 3+ and the metal, with the nature of these soluble lower oxidation-state species depending on the melt acidity.[8] Thus, any single electron oxidation of organic substrates by Sb^{3+} can take place homogeneously in the melt with these lower oxidation-state species acting as electron carriers. When $SbCl_3$ is reduced in significant quantities, Sb metal may be isolated from the reaction products after hydrolysis of the melt as a consequence of a disproportionation reaction of the lower oxidation-state species.[9]

In earlier research on the chemistry of polycyclic aromatic hydrocarbons (arenes) in $SbCl_3$-rich melts, we observed a variety of unusual hydrogen redistribution reactions at surprisingly low temperatures, 80–130 °C.[9-12] These reactions were driven by the redox function of the melt and involved $SbCl_3$ as an oxidant in both a catalytic[10-12] and stoichiometric[9] fashion. Arene radical cations were found to be key intermediates,[13] and tuning the strength of the redox function of the melt as described above was found to dramatically alter reaction rates and product selectivities. Only recently have we observed reaction chemistry in which the Lewis acid function of the melt acts as the dominant catalytic function.[14] Toluene and several diphenylalkanes were found to undergo intermolecular or intramolecular transalkylation reactions in $SbCl_3$-rich melts in which benzylic carbenium ions were indicated as the key intermediates.

The 1,2-diarylethanes, $ArCH_2CH_2Ar$ [Ar = phenyl (DPE), 1-naphthyl (DNE), and 9-anthryl (DAE)] have been used as model compounds for some of the structural units present in coal. Most of the previous research has focused on bond cleavage reactions for DPE by various thermochemical,[15] reductive,[16] and oxidative[17] methods. The DPE, DNE, DAE series has been studied by alkali metal reduction in THF, and selective cleavage of the central sp^3–sp^3 bond was observed.[16b]

We have briefly described the chemistry of DPE in $SbCl_3$ melts as a part of the study on toluene and diphenylalkanes.[14] The DPE chemistry has now been more thoroughly investigated in relationship to the present research on 1,2-diarylethanes. The first ionization potential of DPE is comparable to that of toluene[18] placing it beyond the range of the oxidizing power of $SbCl_3$. On the other hand, anthracene and substituted anthracenes have been found to be readily oxidized to radical cations by $SbCl_3$-based melts.[9,10,13] Thus, the diarylethane series provides us the possibility of distinguishing the effects of the Lewis acid and redox functions of $SbCl_3$-based melts on the reaction product selectivity for this class of substrates. Furthermore if radical cations of $ArCH_2CH_2Ar$ are produced in the melts, a number of reaction channels are possible including intermolecular and intramolecular coupling,[9-11,19,20] carbon–carbon bond cleavage,[17,21] and carbon–hydrogen bond cleavage (deprotonation).[17b,d,22]

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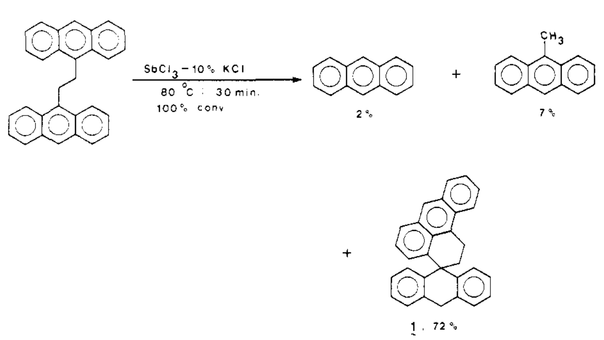
The reaction pathways for alkyl-substituted aromatic radical cations are highly dependent on reaction conditions, and comparisons will be made with the reaction pathways observed in these highly purified, aprotic metal halide melts.

Results

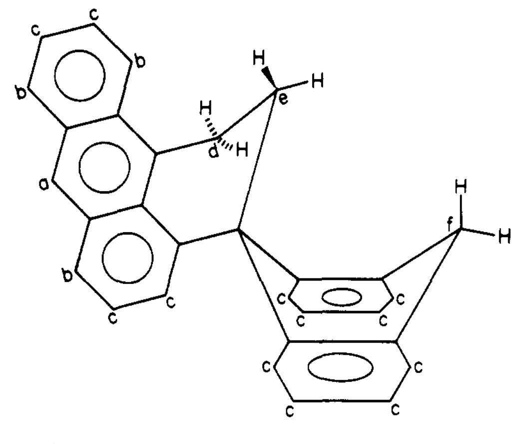
1,2-Di-9-anthrylethane [DAE]. DAE is observed to be extremely reactive even in a basic $SbCl_3$–10 mol % KCl melt. An initial ^{1}H NMR spectrum of an aprotic $SbCl_3$–10% KCl melt containing 0.7 mol % DAE shows that greater than 50% of the DAE reacts within the first 5 min at 80 °C. The DAE is completely reacted within 30 min at 80 °C, and the resulting product mixture was analyzed by GC, GC–MS, HPLC, and UV. Equation 5 presents the simple product mixture along with yields given in weight %. The balance of the organics does not elute from the GC but is observed upon washing the HPLC column with CH_2Cl_2 as high molecular weight material. The product mixture is the same whether the reaction is run in Schlenk glassware under argon or in a sealed tube under argon.



(5)

DAE undergoes some fragmentation as indicated by the formation of anthracene and 9-methylanthracene. However, the major product has been identified as 1′,2′-dihydrospiro[anthracene-9(10*H*),3′-[3*H*]benz[*de*]anthracene] (1),[23] which is formed in high yield (72%). This isomer of DAE results from an intramolecular coupling reaction that is accompanied by internal capture of hydrogen. In addition to MS and UV data, the structure of 1 was further elucidated by ^{1}H and ^{13}C NMR spectra obtained following isolation of 1 by either HPLC or column chromatography.

A perspective structure of 1 is shown in Figure 1 along with the ^{1}H NMR data measured in CD_2Cl_2. Compound 1 was synthesized previously by an independent route beginning with 10-methyleneanthrone,[23] and the reported ^{1}H NMR data for the aliphatic protons of 1, measured at 270 MHz, are in accord with our results. In addition, the ^{13}C NMR spectrum recorded for 1 exhibits the required four aliphatic carbon signals at 50.2 (spiro), 37.6 (d), 23.6 (e), and 35.7 (f) ppm. The signal at 35.7 ppm is assigned to carbon f based on a comparison with ^{13}C NMR data for other similarly substituted dihydroanthracenes.[24] Although the ethano bridge in 1 is conformationally flexible, the boat conformation for the dihydroanthracene-type ring shown in Figure 1 with the ethano bridge in a pseudoaxial position is highly favored. This conformation alleviates the severe steric interaction between the peri hydrogens on the ring and the hydrogens of the ethano bridge that occurs when the ethano bridge is in a pseudoequitorial position.[25]



	^{1}H NMR (90 MHz)	ppm
a	(s)	8.50
b	(m)	8.0 – 8.3
c	(m)	6.7 – 7.6
d	(t ; J = 6.3 Hz)	3.40
e	(t ; J = 6.3 Hz)	2.31
f	(AB; $\Delta\nu_{AB}$ = 13.8 Hz J_{AB} = 19.4 Hz)	4.30

Figure 1. Perspective structure of 1 with ^{1}H NMR data measured in CD_2Cl_2.

The DAE reaction described in eq 5 is found to be independent of the initial DAE concentration. Neither the DAE conversion nor the reaction product selectivity is altered by varying the initial DAE concentration over the range of 0.038–1.4 mol % (~5–180 mM). However, the product selectivity is dependent on the reaction temperature. At higher temperatures the proportion of cleavage products to the cyclization product, 1, increases substantially. For example, at 150 °C, a quantitative conversion of DAE is obtained within 5 min, and the yields of anthracene and 9-methylanthracene increase to 5% and 20%, respectively, while the yield of 1 decreases to 45%.

Increasing the activity of the molten salt catalyst by controlled changes in melt composition (as described in the introductory section) decreases the product selectivity for this reaction. For 100% DAE conversion at 80 °C the yields of 1 in $SbCl_3$–10 mol % KCl, $SbCl_3$, and $SbCl_3$–10 mol % $AlCl_3$ melts are 72%, 52%, and 11%, respectively. The progressive decrease in the yield of 1 is associated with a corresponding increase in the quantities of high molecular weight condensation products (up to 80 wt % for the $SbCl_3$–$AlCl_3$ melt). This resulting decrease in the yield of 1 with increased catalyst activity is attributed to the onset of Scholl condensation reactions for 1 in the more active melts.[9,10]

It should be noted that $SbCl_3$ is inactive when employed as a homogeneous catalyst in an inert solvent. If DAE (2.0 mM) and $SbCl_3$ (0.5 mM) are dissolved in THF and refluxed for 2 h, no reaction takes place. Furthermore if HCl is added as a cocatalyst and the solution is refluxed for an additional hour, DAE remains inert. Therefore, as we have observed previously, $SbCl_3$ must be present as a continuous molten phase in order to be catalytically active.[3,12,14]

ESR and CV Studies of DAE. Anthracene and alkyl-substituted anthracenes are readily oxidized to radical cations in $SbCl_3$-rich melts, and subsequently undergo intermolecular coupling reactions.[9,10] In dilute solutions (≤1 mM) steady-state concentrations of these radical

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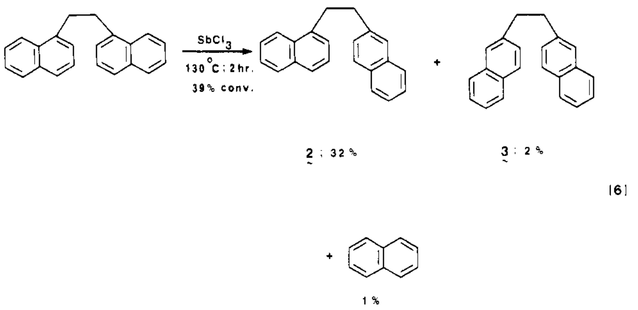
cations can be observed in situ by ESR.[13] However an examination of $SbCl_3$-rich melts containing DAE by ESR provided no evidence for any detectable steady-state concentration of the DAE radical cation.

We have also probed the oxidation of DAE to its radical cation by means of cyclic voltammetry (CV). The CV was performed on DAE solutions in an $SbCl_3$–$AlCl_3$–BPCl [BP = *N*-1-butylpyridinium] basic melt of 60:19:21 mol % composition. This melt has the advantage that it is molten at 25 °C,[26] and DAE reacts more slowly in it at 25 °C than in the $SbCl_3$–10 mol % KCl melt at 80 °C. After 10 min at 27 °C, DAE undergoes only a 1% conversion in the $SbCl_3$–$AlCl_3$–BPCl melt.[27] A disadvantage to the melt is that DAE is only slightly soluble (≤1 mM) in it.

The voltammogram (available as supplementary material) obtained 7 min after adding DAE to the melt at 27 °C exhibits a well-defined anodic peak before the onset of solvent oxidation (Sb(III) → Sb(V)). However the oxidation of DAE to its radical cation at the glassy carbon electrode is quite irreversible at the highest sweep rates employed (0.2 V s^{-1}). The anodic peak potential, E_{pa}, for a saturated solution of DAE measured at a sweep rate of 0.1 V s^{-1} is 0.56 V vs. the $SbCl_3$–BPCl (liquid), $SbCl_3$ (solid)/Sb reference electrode. The irreversible oxidation reaction for DAE is in contrast to the behavior observed for 9,10-dimethylanthracene, which undergoes a reversible oxidation ($E_{1/2}$ = 0.47 V, E_{pa} = 0.50 V) in the same melt.[26] The instability of the DAE radical cation has been noted by other investigators who have also observed an irreversible oxidation process in benzene–acetonitrile (1:1 v/v).[28]

1,2-Di-1-naphthylethane [DNE]. DNE is much less reactive than DAE and reacts only slowly even in neat $SbCl_3$. A 2 mol % solution of DNE in $SbCl_3$ was examined in situ by ^{1}H NMR. Initial spectra at low temperatures (80 °C) are those of the molecular DNE and provide no evidence for reaction or complexation with the Lewis acid solvent. At 130 °C a slow reaction can be observed, and the most distinctive change in the NMR spectrum is a band at 3.24 ppm that gradually grows in near the peak for the methylene protons of DNE at 3.51 ppm. This upfield shifted band is consistent with the formation of a dinaphthylethane in which one or both of the methylene groups is bonded to the 2-position of the naphthalene ring rather than the 1-position. For comparison the methylene resonances for DNE and isomer **3** are at 3.33 and 3.18 ppm, respectively, in $CDCl_3$.[29] Increasing the acidity of the melt greatly enhances the rate of this reaction. NMR of an $SbCl_3$–10 mol % $AlCl_3$ melt containing DNE shows substantially more reaction occurring within 2 min at 80 °C than in 2 h at 130 °C in neat $SbCl_3$.

Analysis of the products from the NMR experiment in $SbCl_3$ at 130 °C after a 2-h reaction period shows that 39% of the DNE has reacted, and that the primary reaction is an isomerization to form **2** and **3** (eq 6) as suggested by the ^{1}H NMR results. This finding was confirmed from larger scale reactions of DNE in $SbCl_3$ also performed in sealed tubes under an argon atmosphere. DNE, **2**, and **3** exhibit essentially identical electron impact mass spectra at 70 eV. The assignments for **2** and **3** are based on GC coelution with an authentic sample of **3**.

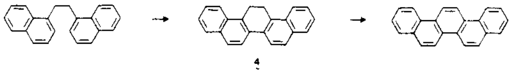


(6)

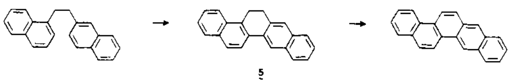
The melt catalyzed isomerization of DNE appears to be accompanied by a transalkylation reaction, which produces the naphthalene product. The unidentified 4 weight % of organics in eq 6 probably consists of higher oligomers of DNE by analogy with the transalkylation chemistry observed for DPE (vide infra). Analogous isomerization of methylnaphthalenes in an $AlCl_3$–NaCl–KCl (60:26:14 mol %) molten salt at 100 °C has also been reported to be accompanied by a small amount of transalkylation.[30]

At longer reaction times the DNE product mixture becomes much more complex. After 24 h at 130 °C in $SbCl_3$ an 80% conversion of DNE is observed, but **2** (28%), **3** (15%), naphthalene (2%), and unreacted DNE (20%) account for only 65% of the organics. Unlike the DAE reaction, little fragmentation at the central sp^3–sp^3 bond is observed as evidenced by the presence of only trace quantities (~0.1%) of methylnaphthalenes. GC and GC/MS show that the majority (~25 wt %) of the remaining material consists of 16 compounds with molecular weights (M_r) in the 278–286 range.

It appears that the mixture of dinaphthylethane isomers are undergoing intramolecular Scholl condensation reactions to produce a variety of dibenzophenanthrene and hydrogenated dibenzophenanthrene isomers. There are seven possible dibenzophenanthrene isomers (M_r = 278) that can form from the intramolecular condensation of the three dinaphthylethane isomers. Two of the three major peaks in the GC–MS with M_r = 278 were identified from their mass spectra and from GC coelution with authentic standards as picene (or dibenzo[*a,i*]phenanthrene) and benzo[*b*]chrysene (or dibenzo[*b,i*]phenanthrene). Picene is formed from the Scholl condensation of DNE (eq 7), while the benzo[*b*]chrysene is a condensation product of **2** (eq 8). Picene has been previously reported to be the Scholl condensation product of DNE in CS_2 with $AlCl_3$ as catalyst.[31]



(7)



(8)

These intramolecular coupling reactions are expected to proceed through dihydrophenanthrene-type intermediates such as **4** and **5**, and three principal products with M_r = 280 indeed are observed by GC–MS. While the condensation reactions such as those shown in eq 7 and 8 liberate hydrogen, it appears that this hydrogen is pri-

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[26] For a description of the physical and electrochemical properties of these ambient temperature molten salts and the behavior of some arene solutes, see: Chapman, D. M.; Smith, G. P.; Sørlie, M.; Petrovic, C.; Mamantov, G. *J. Electrochem. Soc.* **1984**, *131*, 1609.

[27] For conversions up to ~10% in this melt, 1 is the only product detected by HPLC.

[28] Itaya, K.; Bard, A. J.; Szwarc, M. *Z. Physik. Chem. (Munich)* **1978**, *112*, 1.

[29] Caubère, P.; Moreau, J. *Bull. Soc. Chim. Fr.* **1970**, *5*, 1986.

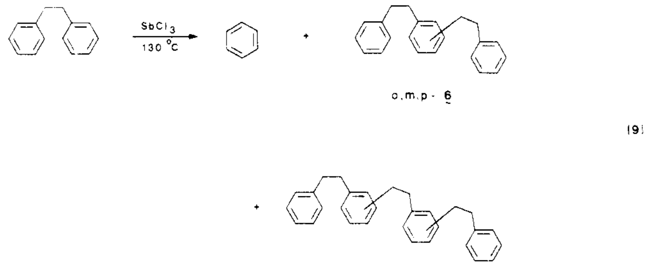
[30] English translation of Ota, E., Inoue, S.; Domae, M.; Otani, S. *Nippon Kagaku Kaishi* **1979**, *9*, 1210.

[31] Ruzieka, L.; Hösli, H. *Helv. Chim. Acta* **1934**, *17*, 470.

marily shuttled internally to form more hydrogenated dibenzophenanthrenes. For example, there are four major products with M_r = 284 as well as several smaller products with M_r = 284 and 286.

This type of condensation–hydrogen-transfer chemistry is consistent with our earlier studies of arene chemistry in $SbCl_3$-rich melts.[9-12] For example anthracene disproportionates in $SbCl_3$ to form 9,10-dihydroanthracene (DHA) and primarily 2,9′-bianthryl, while DHA in $SbCl_3$ disproportionates to produce 1,2,3,4-tetrahydroanthracene and anthracene.[10] Thus, the complex product mixture obtained for the DNE reaction in $SbCl_3$ melts is the result of melt-catalyzed condensation–hydrogen-transfer chemistry for the initially produced isomeric mixture of dinaphthylethanes.

1,2-Diphenylethane [DPE]. DPE is found to be even less reactive than DNE in $SbCl_3$-based melts. In neat $SbCl_3$ DPE reacts extremely slowly at 130 °C, and only a 12% conversion is observed after 168 h. Product analysis reveals than DPE has undergone a selective transalkylation reaction, as shown in eq 9, to produce benzene, 1-[*o*-, 1-[*m*-, and 1-[*p*-(2-phenylethyl)phenyl]-2-phenylethane (**6**), and three major isomers of the next higher oligomer (**7**).[14] Benzene, **6**, and **7** account for all the reacted DPE and are formed in a 6:4:1 mol ratio. The isomer distribution for *o*-, *m*-, and *p*- **6** obtained under these conditions is 14:39:47.



o,m,p- 6

(9)

7

The rate of the DPE transalkylation reaction in this highly purified aprotic melt is not substantially enhanced by an added proton donor. The addition of 0.25 mol % HCl to an $SbCl_3$ melt containing 3.4 mol % DPE increases the rate of the reaction described by eq 9 by a factor of only 2–3 at 130 °C. On the other hand, we have found that increasing the Lewis acidity of the melt has a dramatic effect on the reaction rate while maintaining the selectivity for transalkylation products. If DPE is added to an $SbCl_3$ melt containing 1 mol % $AlCl_3$, a 30% DPE conversion is observed after 10 min at a lower reaction temperature of 100 °C. This conversion is compared with a 12% conversion for DPE in $SbCl_3$ at 130 °C after 168 h. Thus, the rate of transalkylation upon addition of 1 mol % $AlCl_3$ to the melt is increased by a factor of at least 1×10^3 and would probably be larger if measured at a common temperature.

The selectivity for transalkylation chemistry is maintained at high DPE conversions, even in a highly active $SbCl_3$–10 mol % $AlCl_3$ molten salt catalyst where a 70% conversion of DPE is obtained after 10 min at 100 °C. Unlike the DAE and DNE reactions, no products are detected resulting from an aryl–aryl coupling that would produce condensation–hydrogen-transfer chemistry. Furthermore, no products are observed that would indicate cleavage of the central sp^3–sp^3 bond (e.g., toluene). The selectivity for benzylic bond cleavage is supported by the ^1H NMR spectrum measured in the melt, which showed the additional aromatic peak at 7.5 ppm for the formation of benzene as a major product. In addition the methylene proton singlet for DPE at 3.05 ppm was split into at least four peaks in the 3.02–3.09 ppm range, providing further evidence that the other reaction products are structurally similar to DPE.

Product analysis at this 70% conversion level indicates that the **6**:**7** ratio has decreased to a value of 3.0, and the *o*-, *m*-, and *p*- **6** ratio has become 2:71:27.[32] The transalkylation reaction at high conversions is producing more of the larger DPE oligomers such as **7**. This finding is further amplified by the fact that 16% of the products are in the form of oligomers larger than **7**, and three compounds have been detected by GC–MS that correspond to the next higher oligomer (M_r = 494).

Discussion

Lewis Acid Catalysis: Transalkylation and Isomerization. In $SbCl_3$-rich melts, DPE exclusively undergoes a transalkylation reaction as shown in eq 9, in which unreacted DPE acts as the receptor for the aryl-substituted alkyl group being transferred. Transalkylation chemistry for alkylbenzenes has been extensively studied employing strong protonic acid catalysts such as $AlBr_3$–HBr,[33] $GaBr_3$–HBr,[34] BF_3–HF,[35] and CF_3SO_3H.[36] The present investigation demonstrates that, for DPE, transalkylation proceeds smoothly under anhydrous conditions in a highly purified, aprotic $SbCl_3$ melt.

Previous investigations into the mechanism of the transalkylation reaction revealed that, in contrast to secondary and tertiary alkylbenzenes, primary alkylbenzenes do not react by a protonation–dealkylation mechanism as illustrated in eq 10 and 11 even with the strong protonic

$$C_6H_5R + H^+ \rightarrow C_6H_6 + R^+ \qquad (10)$$

$$R^+ + C_6H_5R \rightarrow RC_6H_4R + H^+ \qquad (11)$$

acid catalyst normally employed. This pathway is apparently unfavorable because a primary alkyl cation would be generated as an intermediate. Instead substantial evidence has been accumulated indicating that transalkylation for primary alkylbenzenes occurs by a mechanism in which the formation of a benzylic cation through hydride abstraction is rate determining.[33c,34,37,38] An analogous benzylic cation mechanism is summarized in eq 12–14 for the case of DPE in $SbCl_3$-rich melts. The method by which the benzylic cation is generated (eq 12) will be discussed below. Equation 13 is a composite of several steps that includes the electrophilic attack of the benzylic cation on another DPE molecule, an internal proton transfer to the vicinal phenyl ring, and generation of benzene as one product. The remaining benzylic cation then hydride abstracts as shown in eq 14 or hydride abstracts from DPE to form the other transalkylation product.

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[32] In transalkylation reactions for alkylbenzenes, production of the meta isomer is generally favored. For examples, see: (a) Brown, H. C.; Smoot, C. R. *J. Am. Chem. Soc.* **1955**, *78*, 2176. (b) McCauley, D. A.; Lien, A. P. *J. Am. Chem. Soc.* **1957**, *79*, 5953. (c) Schriesheim, A. *J. Org. Chem.* **1961**, *26*, 3530.

[33] (a) Brown, H. C.; Smoot, C. R. *J. Am. Chem. Soc.* **1955**, *78*, 2176. (b) Schriescheim, A. *J. Org. Chem.* **1961**, *26*, 3530. (c) Roberts, R. M.; Roengsumran, S. *J. Org. Chem.* **1981**, *46*, 3689.

[34] (a) Streitwieser, A.; Rief, L. *J. Am. Chem. Soc.* **1960**, *82*, 5003. (b) *Ibid.* **1964**, *86*, 1988.

[35] McCaulay, D. A.; Lien, A. P. *J. Am. Chem. Soc.* **1957**, *79*, 5953.

[36] Bakoss, H. J.; Roberts, R. M. G.; Sadri, A. R. *J. Org. Chem.* **1982**, *47*, 4053.

[37] (a) Pines, H.; Arrigo, J. T. *J. Am. Chem. Soc.* **1958**, *80*, 4369. (b) Pines, H. "The Chemistry of Catalytic Hydrocarbon Conversions"; Academic Press: New York, 1981; p 71 ff.

[38] Roberts, R. M.; Khalaf, A. A.; Greene, R. N. *J. Am. Chem. Soc.* **1964**, *86*, 2846.

$$C_6H_5CH_2CH_2C_6H_5 + SbCl_2{}^+{\cdot}nSbCl_3 \rightarrow C_6H_5C^+HCH_2C_6H_5 + HSbCl_2{\cdot}nSbCl_3 \quad (12)$$

$$C_6H_5C^+HCH_2C_6H_5 + C_6H_5CH_2CH_2C_6H_5 \rightarrow C_6H_6 + C_6H_5CH_2C^+HC_6H_4CH_2CH_2C_6H_5 \quad (13)$$

$$C_6H_5CH_2C^+HC_6H_4CH_2CH_2C_6H_5 + HSbCl_2{\cdot}nSbCl_3 \rightarrow C_6H_5CH_2CH_2C_6H_4CH_2CH_2C_6H_5 + SbCl_2{}^+{\cdot}nSbCl_3 \quad (14)$$

Additional support for the benzylic cation mechanism comes from our recent findings that 1,3-diphenylpropane in $SbCl_3$-rich melts reacts selectively to produce benzene and indan, while 1,4-diphenylbutane yields benzene and tetralin.[14] Although both these reactions are intramolecular transalkylations and the DPE reaction is an intermolecular transalkylation, all of these reactions occur at the same rate. These data are consistent with the similar stabilities expected for the corresponding benzylic cations. Furthermore, in all of these cases the absence of any alkylbenzene or isomerized products is strong evidence against the formation of primary phenylalkyl cations as intermediates.[33-35] Therefore, the benzylic cation mechanism does appear to be applicable to the transalkylation reaction for DPE in $SbCl_3$-rich melts.

An important catalytic question is how the benzylic cations are generated. For the transalkylation of alkylbenzenes in protonic acid catalysts, it is generally believed that protonation of an alkene impurity gives a carbenium ion that can abstract a hydride from the alkylbenzene and initiate a cationic chain reaction.[34,37,38] This does not appear to be the source of the benzylic cations for the DPE chemistry since this reaction was not performed with a protonic acid catalyst but instead was performed in an aprotic, metal halide melt. Furthermore the effect of an added proton donor was examined, and the results showed that the addition of 0.25 mol % HCl to an $SbCl_3$ melt had only a modest effect (factor of 2–3) on increasing the DPE transalkylation rate at 130 °C. This suggests that protons do not play an important role in the rate-determining generation of benzylic cations.

Another possibility suggested from the literature is that if a radical cation were formed, it could deprotonate and form a benzylic cation by the sequence shown in eq 15.[17b,d,22] This pathway was found to be important in the

$$PhCH_2CH_2Ph^{+\cdot} \xrightarrow{-H^+} Ph\dot{C}HCH_2Ph \xrightarrow{-e} PhC^+HCH_2Ph \quad (15)$$

side chain oxidation of alkylbenzenes using a variety of oxidants and will be discussed later in relation to the radical cation chemistry of DAE. As pointed out in the introduction, the oxidation potential of DPE is similar to that of toluene. This means that the potential required for oxidation of DPE to its radical cation is beyond the potential (by ~0.3 V) that would oxidize the $SbCl_3$ solvent (Sb(III) → Sb(V)).[7] Therefore DPE cannot be oxidized to a radical cation by neat $SbCl_3$. Furthermore, even at the highest DPE conversions observed (70% in $SbCl_3$–10 mol % $AlCl_3$), no products resulting from aryl–aryl coupling or cleavage of the central carbon–carbon bond were observed that would be indicative of the presence of radical cation intermediates (unlike the $DAE^{+\cdot}$ and $DNE^{+\cdot}$ chemistry described below).

The formation of the benzylic cation in the melt is attributed to hydride abstraction by the Lewis acid species in the melt, $SbCl_2{}^+{\cdot}nSbCl_3$, as shown in eq 12. As opposed to the small enhancement in the DPE reaction rate in $SbCl_3$ due to added HCl, we have found that increasing the Lewis acidity of the melt by the addition of only 1 mol % $AlCl_3$ results in an increase in reaction rate of at least 10^3 at 100 °C compared with that in neat $SbCl_3$ at 130 °C. This rate enhancement, which would be larger if measured at a common temperature, corresponds roughly with the calculated increase in $SbCl_2{}^+{\cdot}nSbCl_3$ concentration (~ 10^3–10^4) upon changing the melt composition from neat $SbCl_3$ to $SbCl_3$–1 mol % $AlCl_3$. Additional evidence for the ability of the melt to hydride abstract comes from earlier studies of 9,10-dihydroanthracene and 5,12-dihydronaphthacene in an acidic $SbCl_3$–10 mol % $AlCl_3$ melt.[39] Stoichiometric (rather than catalytic) hydride abstraction from these hydroaromatics produced stable benzylic cations that were identified by ^1H NMR. The sum of these results strongly implicates the Lewis acid function of the melt as performing the dominant catalytic role by generating catalytic amounts of benzylic cations by hydride abstraction. The formation of benzylic cations leads to the selective cleavage of the benzylic sp^2–sp^3 bond of DPE and results in transalkylation products.

The initial chemistry observed for DNE also appears to be the result of Lewis acid catalysis. DNE reacts more rapidly than DPE, and the isomerization and transalkylation products observed are shown in eq 6. The isomerization of DNE to its positional isomers **2** and **3** is not a rapid process in $SbCl_3$ at 130 °C, but the rate of this process can be enhanced greatly by increasing the Lewis acidity of the melt (e.g., $SbCl_3$–10 mol % $AlCl_3$). Equilibration among the isomers is not observed due primarily to the onset of aryl–aryl coupling reactions (vide infra). For comparison, the isomerization of 1-methylnaphthalene to 2-methylnaphthalene in the more acidic $AlCl_3$–NaCl–KCl (60:26:14 mol %) melt was reported to be rapid at 100 °C, and within 2 min an apparent equilibrium mixture was obtained (ratio of 2-methyl to 1-methyl was 4.4).[30] However, a $ZnCl_2$–NaCl–KCl (60:20:20 mol %) melt was found to be inactive as a catalyst even at 400 °C.[30]

Roberts and Roengsumran investigated the mechanism for isomerization of related alkylbenzenes with C-13 ring-labeled compounds and by monitoring the isomerization of the alkyl group relative to the ring label in $AlBr_3$–HBr at 35 °C.[33c] While toluene-*1*-^{13}C isomerized intramolecularly, presumably by successive 1,2-shifts, isomerization of ethylbenzene-*1*-^{13}C occurred only after diethylbenzenes were formed. This and additional results from rate measurements of labeled compounds lead to the conclusion that the positional isomerization of ethylbenzene proceeded through an intermolecular transalkylation route with benzylic cations as reactive intermediates.[40]

A similar intermolecular transalkylation pathway could apply to the isomerization of DNE in $SbCl_3$-rich melts as typified by eq 16 and 17 where eq 16 is the analogous step to eq 13 for the DPE case. The isomeric cations **8** are formed in eq 17 by the reverse of eq 16 and are the precursors to a mixture of DNE and **2**. As discussed above for the case of DPE, benzylic cations are readily generated by $SbCl_2{}^+{\cdot}nSbCl_3$ in the melts, and the DNE isomerization reaction is observed to be accompanied by transalkylation. Furthermore, the rate of isomerization of DNE is greatly increased by increasing the Lewis acidity of the melt, analogous to the transalkylation reaction for DPE.

Redox Catalysis: Radical Cation Chemistry. DAE is much more reactive than DPE and gives a 100% conversion to products within 30 min at 80 °C in a basic $SbCl_3$–10 mol % KCl melt. The simple product mixture

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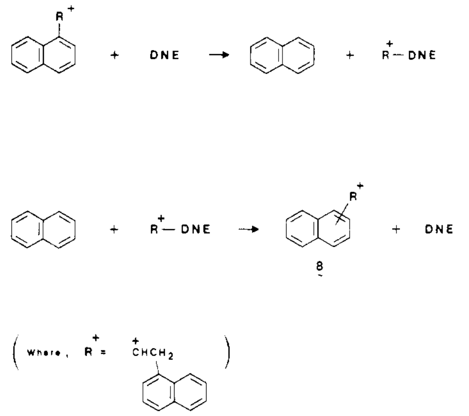
(39) Buchanan, A. C., III; Dworkin, A. S.; Smith, G. P. *J. Org. Chem.* **1981**, *46*, 471.

(40) Toluene transalkylates at a much slower rate than ethylbenzene,[33a] presumably a result of the lower stability of its benzylic cation.



(16)

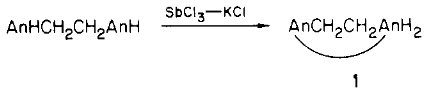
(17)

obtained (eq 5) is quite different from that obtained for DPE in $SbCl_3$-rich melts, and very little fragmentation of the benzylic sp^2–sp^3 bond is observed. Instead the major reactions involve an aryl–aryl coupling to form **1** and a cleavage of the central carbon–carbon bond to form 9-methylanthracene. Both of these reaction channels can be understood by invoking radical cations, rather than benzylic carbenium ions, as the reactive intermediates that are produced by the redox function of the $SbCl_3$-rich molten salt catalyst.

Polycyclic arenes such as anthracene are readily oxidized to radical cations by $SbCl_3$-rich melts.[3,13,41] In $SbCl_3$ or $SbCl_3$–$AlCl_3$ melts the arene radical cations produced undergo intermolecular coupling reactions (Scholl condensation) at 100–130 °C[9–11] and, in the cases in which $SbCl_3$ acts as a catalytic oxidant, the hydrogen released is captured by unreacted arenes to form hydroarenes[10,11] as represented by the simplified eq 18. In basic melts like $SbCl_3$–3 mol % $(CH_3)_4NCl$ the reaction rates for this condensation–hydrogen transfer are much slower for arenes like anthracene even at 130 °C, but are relatively unaffected for the much more easily oxidized arenes like naphthacene.[10]

$$3ArH \xrightarrow{SbCl_3} ArH_3 + Ar\text{–}Ar \qquad (18)$$

The reaction of DAE in $SbCl_3$–10 % KCl is very rapid at only 80 °C, but no condensed or hydrogenated products are observed resulting from an intermolecular coupling reaction analogous to the one shown in eq 18. Instead the DAE radical cation appears to be very reactive because it can undergo an intramolecular coupling reaction with internal capture of hydrogen to form the spiro isomer **1** as summarized by eq 19 (where AnH is $C_{14}H_9$). The selectivity for the formation of **1** is greatest in an $SbCl_3$–KCl melt at 80 °C because **1** (like anthracene) appears to be resistant to further reaction by intermolecular aryl–aryl coupling in this basic melt. In $SbCl_3$ and $SbCl_3$–$AlCl_3$ melts **1** is more readily oxidized to its radical cation and is able to undergo further condensation reactions.



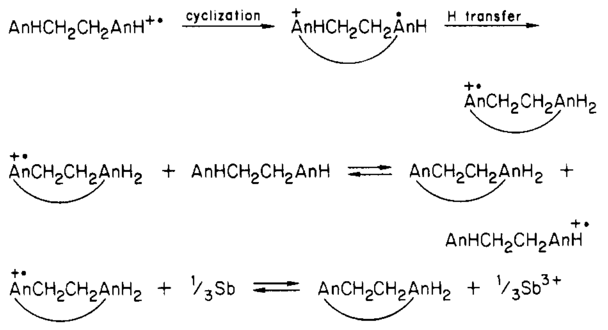
$$AnHCH_2CH_2AnH \xrightarrow{SbCl_3\text{—}KCl} AnCH_2CH_2AnH_2 \qquad (19)$$

1

Normally polycyclic arene radical cations that react via intermolecular condensation reactions can be stabilized in dilute solutions such that they can be observed in the melts by ESR and optical spectroscopies.[3,13,41] However, the reaction rate of DAE in $SbCl_3$–KCl at 80 °C is not affected by changes in the initial DAE concentration from 0.038–1.4 mol % (~5–180 mM), and no steady-state concentration of DAE radical cations is observed for ~1 mM solutions by ESR. The apparent high reactivity of the DAE radical cation is substantiated by the CV results. The electrochemical oxidation of DAE to its radical cation in a basic $SbCl_3$–$AlCl_3$–BPCl (60:19:21 mol %) melt is irreversible even at 25 °C, in contrast to the reversible oxidation observed for the related 9,10-dimethylanthracene in the same melt.[26] This behavior is contrary to that reported for the reduction chemistry of DAE for which stable radical anions and dianions can be prepared both electrochemically[28] and chemically.[42] However, the instability of the DAE radical cation has been noted previously and has precluded electrochemical investigations.[28]

Therefore, the high reactivity observed for DAE in the $SbCl_3$-rich melts is ascribed to a very reactive radical cation intermediate that primarily undergoes a facile intramolecular coupling as outlined in the scheme below. The $SbCl_3$ must be present as a continuous molten phase, not as a homogeneous catalyst in an inert solvent, in order to be catalytically active. In the oxidation step (eq 20) the

$$AnHCH_2CH_2AnH + {}^1\!/_3Sb^{3+} \rightleftharpoons AnHCH_2CH_2AnH^{+\bullet} + {}^1\!/_3Sb \qquad (20)$$



$$AnHCH_2CH_2AnH^{+\bullet} \xrightarrow{\text{cyclization}} \overset{+}{A}nHCH_2CH_2\overset{\bullet}{A}nH \xrightarrow{\text{H transfer}} \overset{+\bullet}{A}nCH_2CH_2AnH_2 \qquad (21)$$

$$\overset{+\bullet}{A}nCH_2CH_2AnH_2 + AnHCH_2CH_2AnH \rightleftharpoons AnCH_2CH_2AnH_2 + AnHCH_2CH_2AnH^{+\bullet} \qquad (22)$$

$$\overset{+\bullet}{A}nCH_2CH_2AnH_2 + {}^1\!/_3Sb \rightleftharpoons AnCH_2CH_2AnH_2 + {}^1\!/_3Sb^{3+} \qquad (23)$$

reduced form of antimony in the melt is shown to be the metal for convenience. However, as was discussed in the introduction, the reduction of Sb^{3+} proceeds through several lower oxidation-state species between Sb^{3+} and the metal.[8] Since these reduced forms are soluble in the melt, they can act as electron-transfer agents in the melt and contribute to product formation as shown in eq 23. Once $DAE^{+\cdot}$ is formed it can undergo an intramolecular cyclization as indicated in the first step of eq 21. This type of cyclization has been reported for the radical cations of other 1,2-diarylethanes, such as 1,2-bis(3,4-dimethoxyphenyl)ethane generated electrochemically in CH_3CN or in CH_2Cl_2–CF_3COOH.[20b–d] However, other diarylethane radical cations under similar conditions can also give intermolecular coupling products.[20b,c] The unusual feature of the $DAE^{+\cdot}$ reaction is that following cyclization hydrogen is not lost externally as H_2 or HCl but is captured internally such that the product is actually an isomer of DAE. This hydrogen-transfer step cannot occur in a concerted fashion and must be mediated by the $SbCl_3$ melt. As pointed out earlier, products can be formed by reacting with the reduced forms of Sb in the melt (eq 23), or they can be formed by reacting with DAE as shown in eq 22 to set up a chain mechanism.

The other identifiable reaction pathway for the DAE radical cation is cleavage at the central carbon–carbon bond leading to the formation of 9-methylanthracene. Carbon–carbon bond cleavage has been observed in radical cations of 1,2-diarylethanes and alkylbenzenes that have been produced either chemically[17(a,b),43] or photochemically

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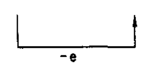
[41] Sørlie, M.; Smith, G. P.; Norvell, V. E.; Mamantov, G.; Klatt, L. N. *J. Electrochem. Soc.* **1981**, *128*, 333.

[42] (a) Huber, W.; Unterberg, H.; Müller, K. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 242. (b) Williams, D. J.; Pearson, J. M.; Levy, M. *J. Am. Chem. Soc.* **1971**, *93*, 5483.

[43] Walling, C.; El-Taliawi, G. M.; Zhao, C. *J. Org. Chem.* **1983**, *48*, 4914.

in the presence of an electron acceptor.[17c,21] For example, cleavage of the ethylenic bond of the photochemically generated radical cations of substituted 1,2-diphenylethanes in the presence of oxygen produced the corresponding benzaldehyde products.[17c] Oxidation of C_6H_5CHOHR [R = Me, Et, *i*-Pr, *t*-Bu, benzyl] by $S_2O_8^{2-}$–Cu^{2+} in acetonitrile gave both carbon–carbon and carbon–hydrogen bond cleavage for the radical cations with the amount of carbon–carbon cleavage increasing as the stability of the radical R· increased.[43] In the gas phase, mass spectral studies show that the major reaction path for DNE radical cation is cleavage at the central carbon–carbon bond,[44] and we have also observed this to be the case for DAE (see Experimental Section), which has little intensity associated with the molecular ion.

A likely pathway for the formation of 9-methylanthracene is from the fragmentation of $DAE^{+\cdot}$ as shown in eq 24–26. In eq 26 the cation is shown as abstracting



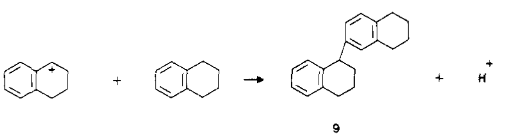
$$AnHCH_2CH_2AnH^{+\cdot} \longrightarrow AnH\dot{C}H_2 + AnH\overset{+}{C}H_2 \quad (24)$$

$$AnH\dot{C}H_2 + AnHCH_2CH_2AnH \longrightarrow AnHCH_3 + AnH\dot{C}HCH_2AnH \quad (25)$$

$$AnH\overset{+}{C}H_2 + AnHCH_2CH_2AnH \longrightarrow AnHCH_3 + AnH\overset{+}{C}HCH_2AnH \quad (26)$$

hydride from unreacted DAE, but it could also abstract hydride from the DAE oligomers produced from the transalkylation reaction of $AnHC^+HCH_2AnH$ (vide infra). In an effort to intercept the benzylic radical and cation formed by the cleavage of $DAE^{+\cdot}$ (eq 24), a DAE reaction was performed in $SbCl_3$–KCl at 150 °C in the presence of tetralin, which can act as both a hydride ion[12] and hydrogen atom donor.[45] Using a tetralin–DAE mol ratio of 15, the only new product observed was 1,2,3,4,5′,6′,7′,8′-octahydro-1,2′-binaphthalene (**9**), which is a product resulting from tetralin acting as a hydride donor (eq 27 and 28).[12] No naphthalene or other products indicative of tetralin acting as a hydrogen atom donor were observed.[45] This means that the benzylic radical reacts preferentially with DAE even in the presence of excess tetralin as in eq 25 and the resulting radical leads to nonvolatile products, or perhaps more likely the benzylic radical is further oxidized to the benzylic cation in the presence of excess oxidant as shown in eq 24.[46]

(27)



(28)

9

The radical cation chemistry for DAE is accompanied by a small amount of transalkylation, which generates the anthracene as a product as well as some oligomers of DAE (in analogy with eq 9) that have not been identified. In the basic $SbCl_3$–10 mol % KCl melt it is highly unlikely that the required benzylic cation intermediate, $AnHC^+HCH_2AnH$, is produced by hydride abstraction by the melt because of the extremely low concentration of $SbCl_2^+\cdot nSbCl_3$. The radical cation cleavage pathway is the most probable source of this cation (eq 24 and 26) that produces the transalkylation chemistry.

The relative rates of the cleavage pathway (eq 24–26) and the coupling pathway (eq 20–23) for the DAE radical cation are independent of the initial DAE concentration in the melt over the range studied (5–180 mM) as determined from the relative product yields of 9-methylanthracene and 1. Therefore, these two processes appear to have the same kinetic order with respect to DAE. However, the relative rates of these two reaction pathways are sensitive to reaction temperature with carbon–carbon bond cleavage becoming more competitive with aryl–aryl coupling at higher temperatures (e.g., the weight ratio of 1:9-methylanthracene is ~10 at 80 °C and ~2 at 150 °C).[47]

Other reaction pathways available for $DAE^{+\cdot}$ include carbon–hydrogen bond cleavage (deprotonation) and reaction with nucleophiles. Thermochemical calculations suggest that alkylaromatic radical cations can be very acidic[48] and, if an appropriate base is present, benzylic carbon–hydrogen bond cleavage via proton loss can be an important process. This reaction pathway has been found to be operative for the side chain oxidation of alkylbenzenes, e.g., by (1) $S_2O_8^{2-}$–Cu^{2+} in acetic acid or acetonitrile,[22b,e] (2) Ce^{IV} in acetic acid,[17b,22a] and (3) Co^{III} in acetic acid–water.[22c] However, deprotonation has not been observed in our studies of alkylaromatic radical cations in anhydrous $SbCl_3$-rich melts.[3,9,13,26] Apparently no good bases are present to allow for radical cation deprotonation and, therefore, it is probable that this pathway does not contribute to the formation of the transalkylation reaction intermediate $AnHC^+HCH_2AnH$ (by deprotonation and oxidation of the resulting radical), whose formation can be readily explained by eq 24 and 26.

Arene radical cations are also known to react with nucleophiles giving substitution products.[20a,49] Neat $SbCl_3$ and $SbCl_3$–$AlCl_3$ melts are media of low nucleophilicity, but in $SbCl_3$–KCl melts the excess chloride ion could potentially be an active nucleophile. Although this type of reaction pathway has never been detected for arene radical cations in $SbCl_3$ and $SbCl_3$–$AlCl_3$ melts, we have recently observed that anthracene radical cation (produced by oxidation with the stronger oxidant $SbCl_5$) in an $SbCl_3$–KCl melt does react with chloride to produce 9-chloroanthracene in addition to products from aryl–aryl coupling.[50] However, for the DAE chemistry in $SbCl_3$–KCl melts we find no evidence for the reaction of $DAE^{+\cdot}$ with chloride. Therefore, the DAE radical cation in $SbCl_3$-rich melts reacts by only two pathways: (1) intramolecular aryl–aryl coupling and (2) cleavage at the central carbon–carbon bond, with a high specificity for the intramolecular coupling at low temperatures.

DNE and its positional isomers 2 and 3 are also able to undergo redox reactions in $SbCl_3$-rich melts to produce radical cation intermediates. Unsubstituted naphthalene

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(44) Caluwe, P.; Shimada, K.; Szwarc, M. *J. Am. Chem. Soc.* **1973**, *95*, 1433.

(45) (a) Collins, C. J.; Raaen, V. F.; Benjamin, B. M.; Kabalka, G. W. *Fuel* **1977**, *56*, 107. (b) Benjamin, B. M. *Fuel*, **1978**, *57*, 378.

(46) The possibility of production of $AnHC^+H_2$ through the cleavage of a diradical dication, $An^{+\cdot}HCH_2CH_2An^{+\cdot}$, cannot be exluded. The analogous dianion is the intermediate currently being invoked in the alkali metal reductive cleavage of 1,2-diarylethanes at the central carbon–carbon bond.[16b,d] Also, see: Lagendijk, A.; Szwarc, M. *J. Am. Chem. Soc.* **1971**, *93*, 5359.

(47) The increase in the formation of 9-methylanthracene is accompanied by an increase in the formation of transalkylation products because of the production of larger amounts of the $AnHC^+HCH_2AnH$ intermediate (eq 24 and 26).

(48) (a) De P. Nicholas, A. M.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165. (b) Green, M. M.; Mielke, S. L.; Mukhopadhyay, T. *J. Org. Chem.* **1984**, *49*, 1276.

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(50) Unpublished results from this laboratory.

is not very reactive in $SbCl_3$, but in the more oxidizing $SbCl_3$–10 mol % $AlCl_3$ melt, naphthalene is oxidized by the melt and gives products resulting from intermolecular aryl–aryl coupling (binaphthyls and perylene).[11]

The radical cations of DNE and its isomers are also capable of undergoing the many reaction pathways described above. However, the sole reaction pathway observed for these radical cations in $SbCl_3$ and $SbCl_3$–$AlCl_3$ melts is the intramolecular aryl–aryl coupling, which ultimately produces dibenzophenanthrenes as illustrated in eq 7 and 8. This type of reaction is also known for methoxy-substituted 1,2-diphenylethane radical cations produced electrochemically in acetonitrile, which react in a similar fashion to DNE to form substituted dihydrophenanthrenes and then the corresponding phenanthrenes.[20b–d]

Unlike the DAE radical cation chemistry, DNE exhibits no cleavage of the ethylenic bond in $SbCl_3$-rich melts (<0.1% methylnaphthalenes). The $DNE^{+\cdot}$ would be expected to have a larger bond dissociation energy for the central carbon–carbon bond than $DAE^{+\cdot}$ because of the lower resonance stabilization energy for the reactive intermediates produced.[51] This apparently makes the carbon–carbon bond cleavage pathway for $DNE^{+\cdot}$ in $SbCl_3$ at 130 °C very unfavorable in competition with intramolecular aryl–aryl coupling.

Conclusions

Molten salt media based on $SbCl_3$ have two functions that are catalytically active and that are clearly demonstrated in the chemistry of 1,2-diarylethanes ($ArCH_2CH_2Ar$). The Lewis acid function of the melt can activate these substrates by generating benzylic cation intermediates by hydride abstraction (eq 29), while the redox function of the melt can produce radical cation intermediates by oxidation with Sb^{3+} (eq 30). The nature of the chemistry observed for $ArCH_2CH_2Ar$ depends significantly on the structure of the aryl group.

$$ArCH_2CH_2Ar + SbCl_2{}^+\cdot nSbCl_3 \rightleftarrows ArC^+HCH_2Ar + HSbCl_2\cdot nSbCl_3 \quad (29)$$

$$ArCH_2CH_2Ar + {}^1/_3Sb^{3+} \rightleftarrows ArCH_2CH_2Ar^{+\cdot} + {}^1/_3Sb \quad (30)$$

For DPE, which cannot be oxidized by Sb^{3+}, transalkylation is the reaction observed exclusively in these melts. This chemistry is a consequence of the ability of the Lewis acid function of the melt to generate the benzylic cation (eq 29) that is required for the selective cleavage of the benzylic (sp^2–sp^3) carbon–carbon bond. On the other hand, DAE is activated by the redox function of the melt (eq 30), which produces a radical cation that has many reaction pathways available. Several reaction pathways are not observed in these anhydrous metal halide media including intermolecular coupling, deprotonation at the benzylic carbon, and nucleophilic substitution. Instead the radical cation reacts by intramolecular coupling and by cleavage of the central (sp^3–sp^3) carbon–carbon bond. DNE undergoes a mixture of Lewis acid and redox-catalyzed reactions. Activation by eq 29 produces isomerization and transalkylation products, while oxidation of the dinaphthylethane isomers (eq 30) produces intramolecular cyclization products.

The 1,2-diarylethanes have often been used as model compounds for structural units in coal, although DPE has been most extensively studied. Thermolysis[15] and alkali metal reduction,[16] for example, give products resulting only from the initial cleavage of the central carbon–carbon bond. Our earlier work on coal model compounds demonstrated the ease with which organically bound hydrogen can be transferred in $SbCl_3$-rich melts. This study now shows that these melts can also induce carbon–carbon bond cleavage for 1,2-diarylethanes at the ethylenic sp^3–sp^3 bond (radical cation intermediate) and at the benzylic sp^2–sp^3 bond (benzylic carbenium ion intermediate). In the context of coal liquefaction in these melts, the radical cation cyclization pathway would be undesirable since a more refractory material is produced. However, the DAE chemistry illustrates that the proportion of radical cation cleavage to radical cation cyclization can increase dramatically with a modest increase in melt temperature.

On a broader scope, molten salts are potentially very attractive catalytic media for performing selective organic reactions. $SbCl_3$-rich melts have exhibited remarkable versatility because the strengths of both catalytic functions are capable of being reproducibly tuned by changes in melt composition, providing control over reaction rates and product selectivities.

Experimental Section

Materials. The procedures for the preparation and purification of the high purity melt constituents $SbCl_3$, $AlCl_3$, and BPCl have been described previously.[52] The KCl was purified by vacuum drying reagent grade material in the solid state followed by melting and bubbling first HCl and then argon (both high purity) through the melt.

DPE (Aldrich) and DNE (Frinton) were high quality reagents whose purity was confirmed by GC, HPLC, and ^1H NMR. DAE was synthesized from 9-anthraldehyde (Aldrich) with excess $LiAlH_4$ in THF according to the method of Schreiber and Emerson.[53] DAE was purified by multiple recrystallizations from toluene and characterized as follows: mp 319–320 °C dec (lit.[53] mp 314–316 °C); mass spectrum (70 eV), m/e 382 (M^+, 7), 192 (16), 191 (100), 190 (8), 189 (16), 165 (4); ^1H NMR (CS_2) δ 3.96 (s, 4, CH_2), 8.28 (d, (J = 8.5 Hz), 4, H_1), 7.40 (m, 8, $H_{2,3}$), 7.90 (d (J = 8.3 Hz), 4, H_4), 8.24 (s, 2, H_{10}); UV (MeOH), λ_{max} ($\epsilon \times 10^3$), 391 nm (18.0), 370 (14.7), 352 (8.3), 334 (4.2), 320 sh (2.0), 255 (152), 247 (168).

NMR Studies. The melt constituents and organic reagents were stored and loaded into the NMR tubes 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.

Reactions were studied in situ by ^1H NMR spectroscopy in 5-mm o.d. tubes (1-mm wall) that were sealed on a vacuum line under a reduced pressure of purified argon. Typically ~1 g of metal halide catalyst was employed, and the concentration of the organic substrate was 0.6–4.0 mol %. The ^1H NMR measurements were made at 80–130 °C on a Nicolet NT-200 Fourier transform spectrometer at 200.17 MHz. The chemical shifts were referenced externally to $(CH_3)_4NCl$ (δ 3.12) in $SbCl_3$, which was itself separately referenced to $(CH_3)_4Si$ in the melt.

ESR and CV. ESR studies were performed on melts in sealed flat cells by using procedures that have been described previously.[13] CV was performed in the glovebox, using the ambient temperature $SbCl_3$–$AlCl_3$–BPCl melts, in a glassy carbon crucible that also served as the working electrode. The counter electrode was a large area Pt foil contained in a separate compartment and isolated from the main electrolyte by a medium porosity Pyrex frit, and the reference electrode was $SbCl_3$–BPCl (liquid), $SbCl_3$ (solid)/Sb. Further details on equipment and methods are provided in ref 26.

General Reaction Procedure. Products were identified and quantitated from reactions performed in 10-mm o.d. Pyrex tubes

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(1-mm wall) with 4–10 g of melt constituents and substrate concentrations comparable to the NMR experiments. The tubes were loaded in the glovebox and sealed on a vacuum line under a reduced pressure of purified argon. For experiments in which tetralin or 12 M HCl were employed, these reagents were added externally to the glovebox by syringe under an argon purge before seal off. The reaction tube was rocked at about 0.2 Hz in an oil bath whose temperature could be reproducibly set and regulated to ±0.1 °C. At the conclusion of the heating period, the tubes were plunged in an ice bath and subsequently broken under a layer of 3 M HCl. The organics were recovered from the CH_2Cl_2 layer following a standard CH_2Cl_2/3 M HCl workup.

The products were analyzed by GC, HPLC, GC–MS, UV, and, when necessary, ^1H and ^{13}C NMR. A description of the equipment and procedures has been reported.[12,14] Quantitative analyses were determined by GC with the use of internal standards and by UV on samples collected by HPLC. Reaction products were also analyzed following several NMR experiments and were found to be identical with those of the larger scale experiments.

DAE Reaction. Compound 1. Compound 1 was obtained in highest yield from reactions performed in $SbCl_3$–10 mol % KCl melts. The DAE was added to a preformed $SbCl_3$–KCl mixture, and the reaction could be carried out either in Schlenk glassware or in a sealed tube with no discernible difference in the product mixture.

The reaction of 0.248 g (0.648 mmol) DAE in 10.00 g of $SbCl_3$–10 mol % KCl at 80 °C for 30 min produced 0.178 g (72%) of 1 as determined by HPLC–UV with a 50 × 0.94 cm Whatman Partisil M9-ODS 3 column with a $MeOH–H_2O$ (93:7) mobile phase. The anthracene and 9-methylanthracene products were quantitated by the same method. Compound 1 was isolated by fractional sublimation at 200–245 °C (~5 × 10^{-2} mmHg) followed by column chromatography on neutral alumina (Fisher, Activity I, 80–200 mesh) with hexane as eluent. In addition to the ^1H and ^{13}C NMR data described in the results section, 1 has been characterized as follows: UV (MeOH) λ_{max} ($\epsilon \times 10^3$) 395 nm (9.1), 374 (10.0), 355 (6.2), 338 (3.0), 324 sh (1.3), 260 (135); mass spectrum (70 eV), *m/e* 382 (M^+, 53), 383 (17), 303 (11), 289 (13), 192 (15), 191 (100), 175 (13), 152 (16), 151 (16).

DNE Reaction Products. Naphthalene, 2, and 3 were identified from a reaction of 0.100 g (0.354 mmol) of DNE in 4.050 g (17.76 mmol) of $SbCl_3$ after 2 h at 130 °C. GC–MS (30 m × 0.25 mm i.d. SE-52 capillary column) at 70 eV gives essentially identical mass spectra for DNE, 2, and 3: *m/e* 282 (M^+, 16), 283 (4), 142 (12), 141 (100), 139 (5), 115 (22). The isomer ratio of DNE, 2, and 3 was obtained by GC on a 10 ft × $^1/_8$ in. 3% Dexsil 300 column using authentic samples of DNE and 3 (provided by R. R. Chambers of ORNL) as standards. Quantitative analysis of naphthalene, DNE, 2, and 3 was performed by HPLC–UV.

Coupling products were determined from reactions carried out at a longer reaction period (24 h). The complex product mixture was identified primarily by capillary column GC–MS. In addition to the products described above, picene and benzo[*b*]chrysene (*m/e* 278) were identified from their mass spectra[54] and from GC coelution with standards (from Aldrich and Columbia Organics, respectively). Quantitative results were obtained from HPLC–UV and from GC with pyrene as an internal standard.

DPE Reaction Products. Products were obtained from a reaction of 0.192 g (1.05 mmol) of DPE in 6.888 g of preformed $SbCl_3$–10 mol % $AlCl_3$ that was run for 10 min at 100 °C (70% conversion). Benzene, 6, and 7 were identified by GC–MS and HPLC–UV as described previously[14] and quantitated by HPLC–UV or by GC (anthracene or diphenylmethane internal standard).

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Registry No. 1, 69469-58-5; 2, 83313-24-0; 3, 21969-45-9; 7, 95935-34-5; Ph^+CHCH_2Ph, 25836-78-6; $AlCl_3$, 7446-70-0; HCl, 7647-01-0; $SbCl_3$, 10025-91-9; BPCl, 1124-64-7; DPE, 103-29-7; DNE, 15374-45-5; DAE, 4709-79-9; $DAE^{+\cdot}$, 95977-51-8; $DNE^{+\cdot}$, 34475-81-5; 1-[*o*-(2-phenylethyl)phenyl]-2-phenylethane, 18888-80-7; 1-[*m*-(2-phenylethyl)phenyl]-2-phenylethane, 52995-87-6; 1-[*p*-(2-phenylethyl)phenyl]-2-phenylethane, 1985-58-6; 9-anthraldehyde, 642-31-9.

Supplementary Material Available: Cyclic voltammogram for DAE in $SbCl_3$–$AlCl_3$–BPCl (60:19:21 mol %) (1 page). Ordering information is given on any current masthead page.

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[54] Eight Peak Index of Mass Spectra, 2nd *Ed.*; Mass Spectrometry Data Centre: AWRE, Aldermaston, Reading, UK, 1974.