arrangement–alkylation sequence by alkylaluminum reagents followed by the introduction of the second alkyl groups to the resulting ketimines by allylic or propargylic Grignard reagents. The synthesis of 2-allyl-2-methylazacycloheptane (**88**) is illustrative. To a solution of cyclohexanone oxime mesylate (**11**) (191 mg, 1 mmol) in methylene chloride (5 mL) at −78 °C was added trimethylaluminum (1 mL of a 2 M toluene solution, 2 mmol). After 5 min, the reaction mixture was allowed to warm to 0 °C and stirred for 30 min. The solution was cooled to −78 °C and treated with allylmagnesium bromide (1.67 mL of a 1.2 M ethereal solution, 2 mmol) at −78 °C for 5 min and at 0 °C for 1 h. Then the mixture was poured onto a 10% NaOH solution (30 mL), shaken well, and centrifuged to remove the white gel. Extractive workup with methylene chloride, followed by column chromatography on silica gel (i-$PrNH_2$–ether, 1:50), furnished 2-allyl-2-methylazacycloheptane (**88**) (92 mg, 60% yield) as a colorless oil: TLC, R_f 0.57 (i-$PrNH_2$–ether–CH_2Cl_2, 1:20:20); ^1H NMR (CCl_4) δ 5.37–6.17 (1 H, m, $CCH{=}C$), 4.70–5.13 (2 H, m, $C{=}CH_2$), 2.43–2.80 (2 H, m, CH_2N), 2.03 (2 H, d, J = 7.5 Hz, $C{=}CCH_2$), 1.23–1.77 (8 H, br s, $(CH_2)_4$), 1.07 (1 H, br s, NH), 0.93 (3 H, s, CH_3).

Anal. Calcd for $C_{10}H_{19}N$: C, 78.37; H, 12.50. Found: C, 78.37; H, 12.21.

In case of α-propargylation, excess propargyl Grignard reagents (4 equiv) are required with prolonged reaction time (>4 h). Other examples of the reaction are listed in Table VI and the physical properties and analytical data for α,α-dialkylamines are given in Table X.

Acknowledgment. This research was supported by the Naito Science Foundation and the Yamada Science Foundation.

Registry No. (*E*)-**1**, 85027-95-8; (*E*)-**1** oxime, 10341-75-0; **2**, 85027-96-9; (*E*)-**3**, 59073-50-6; (*E*)-**4**, 85027-97-0; (*E*)-(±)-**5**, 85027-98-1; (*Z*)-(±)-**6**, 85027-99-2; (±)-**7**, 85028-00-8; (±)-**8**, 85028-01-9; **9**, 10442-97-4; **9** oxime, 1192-28-5; (*E*)-(±)-**10**, 85028-02-0; (*E*)-(±)-**10** oxime, 85028-03-1; **11**, 80053-69-6; **11** oxime, 100-64-1; **12**, 17512-84-4; (*E*)-(±)-**13**, 85028-04-2; (*E*)-(±)-**13** oxime, 85027-98-1; **14**, 80053-71-0; **14** oxime, 2158-31-8; **15**, 80053-73-2; **15** oxime, 946-89-4; **16**, 80053-72-1; (*E*)-(±)-**17**, 85114-16-5; **18**, 85028-05-3; **19**, 19766-29-1; (±)-**20**, 85028-06-4; **21**, 39488-50-1; **22**, 85028-07-5; **23**, 85028-08-6; **24**, 85028-09-7; **25**, 85028-10-0; **26**, 85048-06-2; (±)-**27**, 85028-11-1; (*E*)-**28**, 85028-12-2; (*E*)-**29**, 85028-13-3; (*E*)-**30**, 85028-14-4; (*E,E*)-**31**, 85028-15-5; **32**, 85028-16-6; **33**, 85028-17-7; (*E*)-**34**, 85028-18-8; (*E*)-**35**, 85028-19-9; **36**, 29376-34-9; **37**, 32504-26-0; **38**, 85028-20-2; **39**, 85028-21-3; **40**, 23579-36-4; **41**, 85028-22-4; **42**, 85028-23-5; **43**, 85028-24-6; (*E*)-L-**44**, 37886-68-3; (*E*)-**45**, 85028-25-7; (*E*)-**45** oxime, 68253-35-0; (*E*)-**46**, 85028-26-8; (*E*)-**46** oxime, 68253-36-1; (±)-**47**, 85028-27-9; (±)-**48**, 85028-28-0; (±)-**49**, 85028-29-1; (±)-**50**, 85028-30-4; (±)-**51**, 85028-31-5; *cis*-(±)-**52**, 85048-07-3; *trans*-(±)-**52**, 85048-08-4; **53** (isomer 1), 85081-37-4; **53** (isomer 2), 85081-38-5; (2*S*-*trans*)-**54**, 85081-39-6; (±)-**55**, 85028-32-6; (±)-**56**, 85028-33-7; **57**, 295-03-4; (±)-**58**, 85048-09-5; **59**, 768-52-5; **60**, 103-69-5; (±)-**61**, 85028-34-8; (±)-**62**, 85048-10-8; (±)-**63**, 85028-35-9; **64**, 635-46-1; (±)-**65**, 85028-36-0; (±)-**66**, 3238-60-6; **67**, 39190-95-9; **68**, 68170-79-6; (±)-**69**, 80053-78-7; (±)-**70**, 62400-71-9; (*E*)-(±)-**70** oxime, 80053-79-8; (±)-**72**, 55785-29-0; (±)-**72**·HCl, 55785-30-3; (±)-**73**, 85028-37-1; (±)-**74**, 55950-19-1; (±)-**75**, 85081-40-9; (±)-**76**, 62400-72-0; (±)-**77**, 62446-08-6; (±)-**78**, 85028-38-2; (±)-**80**, 80053-67-4; (±)-**81**, 28720-60-7; (±)-**82**, 83019-10-7; *cis*-(±)-**82**, 83019-09-4; (*E*)-(±)-**83**, 83019-14-1; (*E*)-(±)-**84**, 83019-15-2; (±)-**85**, 83019-11-8; (±)-**86**, 63950-16-3; **87**, 85028-39-3; (±)-**88**, 85028-40-6; (±)-**89**, 85028-41-7; (±)-**90**, 85028-42-8; (±)-**91**, 85028-43-9; (±)-**92**, 85028-44-0; (±)-**93**, 85028-45-1; **94**, 85028-46-2; (±)-**95**, 85028-47-3; **96**, 85028-48-4; **97** (isomer 1), 85028-49-5; **97** (isomer 2), 85028-50-8; **98**, 85028-46-2; (±)-**99**, 85028-51-9; Me_2AlSEt, 81701-35-1; $Me_2AlSCH_2CH{=}CH_2$, 85028-52-0; Me_2AlSPh, 36896-63-6; Me_2AlSBu-*t*, 60699-27-6; Me_2AlS-2-pyridyl, 85028-53-1; $Me_2AlS(CH_2)_6SAlMe_2$, 85028-54-2; $Me_2AlSeMe$, 67132-62-1; *i*-$Bu_2AlSePh$, 85028-55-3; DIBAH, 1191-15-7; MeSSMe, 624-92-0; PhCN, 100-47-0; PhSeSePh, 1666-13-3; $CuCl_2$, 7447-39-4; Pr_3Al, 102-67-0; $Et_2AlCH_2CH{=}CH_2$, 18760-02-6; $H_2C{=}CHCH_2MgBr$, 1730-25-2; Et_2AlCl, 96-10-6; cyclopentanone, 120-92-3; 1-undecene, 821-95-4.

Molten Salt Catalysis. Selective Bond Cleavage Reactions for Some α,ω-Diphenylalkanes in $SbCl_3$ Melts

A. C. Buchanan, III,* A. S. Dworkin, and G. P. Smith

Contribution from the Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830. *Received September 23, 1982*

Abstract: The chemistry of the α,ω-diphenylalkanes, $C_6H_5(CH_2)_nC_6H_5$ [n = 1–4], in highly purified anhydrous $SbCl_3$ and $SbCl_3$–10 mol % $AlCl_3$ melts has been investigated from 100 to 130 °C by in situ ^1H NMR spectroscopy and by quench and separation techniques. These substrates, which are often used to model the aliphatic chains that link aromatic and hydroaromatic clusters in coal, are found to undergo selective cleavage of the sp^2–sp^3 bond. For n = 1 and 2 products are formed via a transaralkylation reaction, while for n = 3 and 4 the cleavage results in the selective production of only benzene and either indan (n = 3) or tetralin (n = 4). Toluene is also reactive in $SbCl_3$–$AlCl_3$, and typical transalkylation chemistry is observed. The relative rates for reaction in the aprotic $SbCl_3$ melts are in the order $PhCH_2Ph \gg Ph(CH_2)_2Ph \sim Ph(CH_2)_3Ph \sim Ph(CH_2)_4Ph \gg PhCH_3$. These relative reactivities, the discovery that $SbCl_3$–10 mol % $AlCl_3$ is a much more active catalytic medium than $SbCl_3$ alone, and the product distributions can be explained by a mechanism in which the rate-determining step involves the generation of a benzylic cation as the key reactive intermediate by hydride abstraction by $SbCl_2^+$ in the melt. This research provides new insights into the mechanism by which an aprotic molten salt medium catalyzes bond cleavage reactions for the α,ω-diphenylalkanes at temperatures substantially below those required for thermolysis. In addition, the mechanism is discussed in relation to mechanisms proposed for the transalkylation reactions of alkylbenzenes, which normally employ strong protic acid catalysts.

Recent interest in molten salt catalysis has stemmed from reports that molten metal halides such as SbX_3 (X = Cl, Br, I),[1] BiX_3 (X = Cl, Br),[1] AsI_3,[1] ZnX_2 (X = Cl, Br),[2] ZnI_2,[3,4] and ZnX_2–CuX (X = Cl, I)[4], which are relatively weak Lewis acids (particularly those based on Sb, As, and Bi), are very active catalysts for hydrocracking coal. When used in massive amounts, these catalysts are not only efficient at depolymerizing and liquefying coal, but also distinguish themselves from conventional

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[1] Wald, M. M. U.S. Patent 3 542 665, 1970.

[2] (a) Zielke, C. W.; Struck, R. T.; Evans, J. M.; Costanza, C. P.; Gorin, E. *Ind. Eng. Chem. Process Des. Dev.* **1966**, *5*, 151, 158. (b) Zielke, C. W.; Klunder, E. B.; Maskew, J. T.; Struck, R. T. *Ibid.* **1980**, *19*, 85. (c) Struck, R. T.; Zielke, C. W. *Fuel* **1981**, *60*, 795.

[3] (a) Loth, R. A. U.S. Patent 3 790 468, 1974. (b) Loth, R. A.; Wald, M. M. U.S. Patent 3 790 469, 1974.

[4] Ida, T.; Nomura, M.; Nakatsuji, Y.; Kikkawa, S. *Fuel* **1979**, *58*, 361.

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hydrocracking catalysts in their ability to produce gasoline directly with a high specificity.

Our research in molten salt catalysis has been directed toward attaining a mechanistic understanding of how selected organic compounds (chosen to model some of the structural units present in coal) react at moderate temperatures in highly purified melts. Earlier studies of polycyclic aromatic hydrocarbons and hydroaromatics in anhydrous $SbCl_3$-based melts have shown these melts to be extremely active catalysts for a variety of hydrogen redistribution reactions at surprisingly low temperatures, 80–130 °C.[5-9] This research has revealed that $SbCl_3$ melts possess a previously unrecognized redox functionality, and reactions have been observed which involve $SbCl_3$ as an oxidant in both a catalytic[5-7] and stoichiometric[8,9] fashion. Further evidence for the ability of $SbCl_3$ melts to oxidize arenes to radical cations has come from electron spin resonance spectroscopy.[10] Most recently we have found that tetralin can selectively hydrogenate arenes which are oxidizable by $SbCl_3$ in a reaction that is catalyzed by $SbCl_3$ melts at only 80 °C.[7]

The α,ω-diphenylalkanes, $C_6H_5(CH_2)_nC_6H_5$, model another important structural feature of coal, namely, the aliphatic chains which form the linkages that join aromatic or hydroaromatic clusters.[11] The cleavage of these aliphatic linkages has been investigated by a number of thermochemical,[12-15] reductive,[16] and oxidative methods[17,18] particularly for the case of 1,2-diphenylethane. In addition, the powerful Lewis acid $AlCl_3$ has been shown to cause extensive dealkylation, isomerization, and fragmentation reactions for some diphenylalkanes,[19,20] analogous to its effect on alkylbenzenes.[21]

There has been no previous study of the chemistry of this important class of model compounds in a molten salt medium consisting of one of the hydrocracking catalysts described above. It has been reported that cyclohexane solutions of α,ω-diphenylalkanes are unreactive in the presence of about 10 wt % $ZnCl_2$ even at 325 °C[20] (perhaps due to the greatly reduced activity of this type of catalyst when it is not present in massive amounts as a solvent). We have now investigated the behavior of a series of α,ω-diphenylalkanes, $C_6H_5(CH_2)_nC_6H_5$ [n = 1–4], in melts consisting of pure, anhydrous $SbCl_3$ or $SbCl_3$–10 mol % $AlCl_3$. The current study is of fundamental interest in terms of understanding how organic compounds are activated by $SbCl_3$ in the melts. Photoelectron spectroscopy[22] and mass spectrometry[23] measurements indicate that the first two members of the series, diphenylmethane and 1,2-diphenylethane, have identical first ionization potentials which are comparable to that of toluene. The relatively high oxidation potentials of these compounds compared to those of polycyclic aromatics[24] places them beyond the range of the oxidizing power of $SbCl_3$, and thus, the α,ω-diphenylalkanes cannot be activated by oxidation to radical cations by Sb^{3+} in the melt. Any reactivity observed for these diphenylalkanes at the low temperatures employed (100–130 °C) must then reflect a different functionality of the $SbCl_3$ molten salt catalyst.

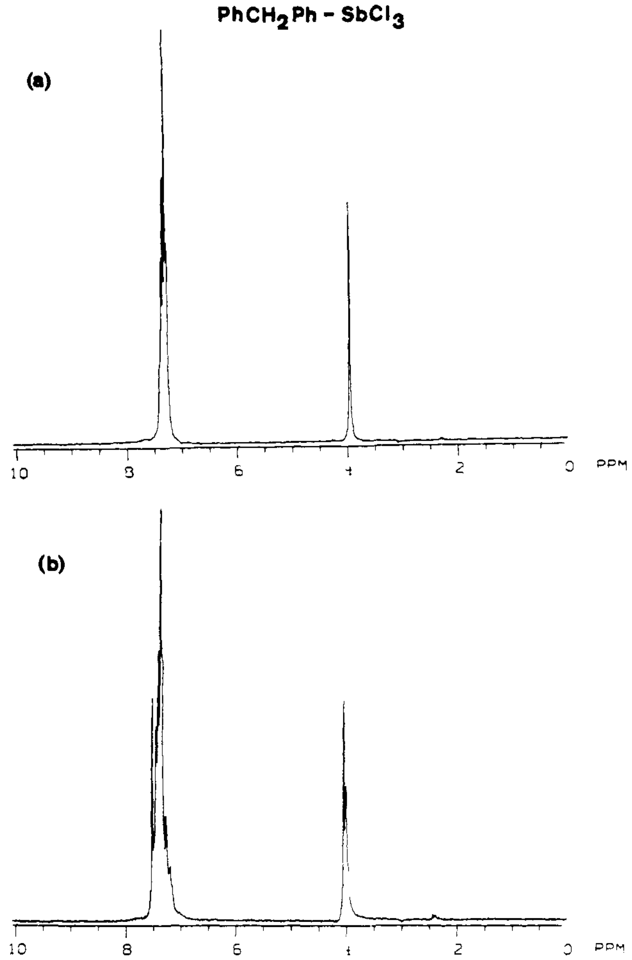

Figure 1. ^1H NMR spectrum of an $SbCl_3$ melt containing DPM: (a) initial spectrum at 100 °C; (b) spectrum after heating for 2 h at 130 °C.

Table I. Reaction of DPM in $SbCl_3$[a]

temp, °C	run time, min	% DPM conversion	% organics[b] recovered	isomer distbn 1 (% o-, m-, p-)	1/2 mole ratio
100	20	1	100	20, 20, 60	[c]
110	45	14	100	12, 31, 57	17
130	45	35	98	6, 47, 47	4.6
130	120	56	87	5, 54, 41	3.2

[a] DPM was 3 mol % in $SbCl_3$. [b] Includes unreacted DPM, benzene, 1, and 2. Benzene was found as a major product in each run amounting to 23–25 wt % (49–54 mol %) of the DPM reacted. [c] 2 was not detected.

Results

Diphenylmethane (DPM) in $SbCl_3$. A solution of DPM in a highly purified, anhydrous $SbCl_3$ melt exhibits an initial ^1H NMR

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

(6) Buchanan, A. C., III.; Dworkin, A. S.; Smith, G. P.; Buchanan, M. V.; Olerich, G. *Fuel* **1981**, *60*, 694.

(7) Buchanan, A. C., III.; Dworkin, A. S.; Smith, G. P. *J. Org. Chem.* **1982**, *47*, 603.

(8) Buchanan, A. C., III.; Dworkin, A. S.; Smith, G. P. *J. Am. Chem. Soc.* **1980**, *102*, 5262.

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

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

(11) Deno, N. C.; Curry, K. W.; Jones, A. D.; Keegan, K. R.; Rakitsky, W. G.; Richter, C. A.; Minard, R. D. *Fuel* **1981**, *60*, 210 and references therein.

(12) Poutsma, M. L. *Fuel* **1980**, *59*, 335.

(13) Miller, R. E.; Stein, S. E. *J. Phys. Chem.* **1981**, *85*, 580.

(14) Collins, C. J.; Raaen, V. F.; Benjamin, B. M.; Maupin, P. H.; Roark, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 5009.

(15) Vernon, L. W. *Fuel* **1980**, *59*, 102.

(16) (a) Collins, C. J.; Hombach, H.-P.; Maxwell, B.; Woody, M. C.; Benjamin, B. M. *J. Am. Chem. Soc.* **1980**, *102*, 851. (b) Collins, C. J.; Hombach, H.-P.; Maxwell, B. E.; Benjamin, B. M.; McKamey, D. *Ibid.* **1981**, *103*, 1213.

(17) Trahanovsky, W. S.; Brixius, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 6778.

(18) Wiberg, K. B.; Evans, R. J. *Tetrahedron* **1960**, *8*, 313.

(19) Roberts, R. M.; Khalaf, A. A.; Greene, R. N. *J. Am. Chem. Soc.* **1964**, *86*, 2846.

(20) Taylor, N. D.; Bell, A. T. *Fuel* **1980**, *59*, 499.

(21) Roberts, R. M.; Baylis, E. K.; Fonken, G. J. *J. Am. Chem. Soc.* **1963**, *85*, 3454.

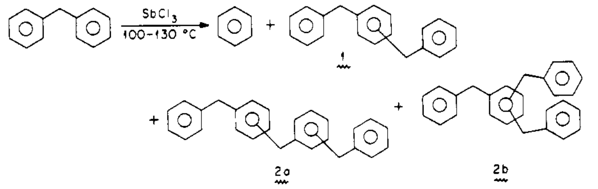
(22) Pignataro, S.; Mancini, V.; Ridyard, J. N. A.; Lempka, H. J. *J. Chem. Soc., Chem. Commun.* **1971**, 142.

(23) Pignataro, S.; Mancini, V.; Innorta, G.; Distefano, G. *Z. Naturforsch. A* **1972**, *27A*, 534.

(24) Rao, C. N. R.; Basu, P. K.; Hegde, M. S. *Appl. Spectrosc. Rev.* **1979**, *15*, 1.

spectrum at 100 °C of the molecular DPM (Figure 1a). There is no evidence for any complex formation with the solvent, which has been reported in the solid state[25] but with the complex apparently dissociating on melting. At 130 °C, DPM is observed to react as indicated in particular by the gradual growth of a peak at 7.5 ppm (the chemical shift for benzene in the melt) and by the broadening and splitting of the aliphatic methylene peak at 4.0 ppm (Figure 1b). The spectrum in Figure 1b was obtained after 2 h of heating at 130 °C, and subsequent chemical analysis showed that 56% of the DPM had reacted. The NMR spectrum suggests that the reaction products are structurally similar to DPM.

Analysis of the product mixture by GC, GC-MS, HPLC, UV, and NMR shows that DPM has reacted to form benzene, *o*-, *m*-, and *p*-benzyldiphenylmethane (**1**), and five of the nine possible isomers of dibenzyldiphenylmethane (**2a** and **2b**), as shown in eq 1. The overall reaction is a transaralkylation, the transfer of an aryl-substituted alkyl group, analogous to the much studied transalkylation chemistry of alkylbenzenes.[26-31]



(1)

Results of product analyses from reactions performed under different conditions are summarized in Table I. At the lowest DPM conversion (1%), the reaction products are completely represented by benzene and **1**. The high selectivity for the production of the para isomer of **1** is not generally observed in transalkylation reactions for alkylbenzenes, where production of the meta isomer usually dominates.[26,27,29,31] However, the isomer distribution is sensitive to reaction conditions and to steric effects with bulkier alkyl groups favoring para substitution.[26,31]

As the reaction conditions become more vigorous, DPM conversion increases and the formation of **2** becomes increasingly more important. Furthermore, the amount of organics accounted for by benzene, **1**, **2**, and unreacted DPM decreases with increasing DPM conversion. It appears that at higher conversions, polybenzyl oligomers larger than **2** are produced. The change in the isomer distribution of **1** with increasing DPM conversion probably reflects not only changes due to increasing temperature and isomerization but also changes due to the different reactivity of these isomers toward further transaralkylation.

An important feature of the transaralkylation reaction for DPM in $SbCl_3$ is the need for excess $SbCl_3$ to be present. If, for example, $SbCl_3$ is dissolved at 10 mol % concentration in DPM, no reaction is observed even after 2 h at 130 °C. As shown in Table I, under the same conditions if DPM is dissolved at 3 mol % concentration in $SbCl_3$, DPM reacts readily with a 56% conversion. The importance of having $SbCl_3$ present as a continuous melt rather than separated solute molecules for catalytic activity has been observed previously.[7]

Initial rate measurements on the DPM–$SbCl_3$ reaction were made at low conversions ($\sim$10%) where the occurrence of secondary reactions is unimportant and the products consist only of benzene and **1**. The initial rates at 110 °C were measured as a function of DPM concentration which was varied by a factor of 36 from 0.028 to 1.02 M. A log–log plot of initial rates vs. initial DPM concentration is shown in Figure 2 and yields a kinetic order of 1.0 for DPM from the slope. A first-order dependence on substrate concentration has also been measured for the transalkylation reaction of ethylbenzene in $GaBr_3$–HBr.[30]

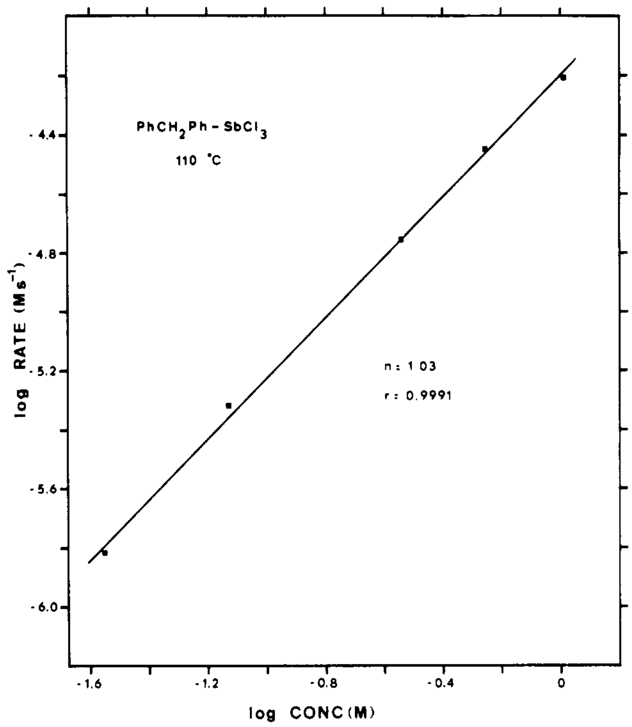
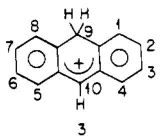


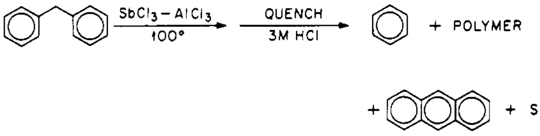
Figure 2. Initial rates of reaction of DPM in $SbCl_3$ as a function of initial DPM concentration.

DPM in $SbCl_3$–$AlCl_3$. The reaction behavior of DPM in an $SbCl_3$–10 mol % $AlCl_3$ melt was also examined for comparison with the chemistry of the larger diphenylalkanes in this medium (vide infra). The ^{1}H NMR spectrum of a melt of DPM in $SbCl_3$–$AlCl_3$ at only 100 °C shows that, within 20 min, essentially all of the DPM has reacted. The spectrum is dominated by the large peak at 7.5 ppm for benzene. Surprisingly, the spectrum of the 9-anthracenium ion (**3**) is also observed. The spectrum of **3** has been measured previously in $SbCl_3$–$AlCl_3$[8] and is characterized by a singlet at 4.9 ppm for the two aliphatic methylene hydrogens and a low-field shifted resonance at 9.6 ppm for H_{10}.



3

Following hydrolysis of the melt, analysis of the organics gives only two main products, benzene (42 wt %) and anthracene (15%), as shown in eq 2. Products **1** and **2** are not found in the mixture, and in fact, the majority ($\sim$37%) of the remaining organics are not detected by GC but appear as highly condensed polymeric materials by HPLC. In addition, antimony metal is identified as a reaction product, indicating that the reaction is no longer purely catalytic with regard to $SbCl_3$.



(2)

The addition of 10 mol % $AlCl_3$ to the $SbCl_3$ melt has generated a much more active catalyst, causing extensive reaction of DPM, **1**, and **2** to form benzene and higher oligomers. The unexpected formation of **3** in the melt can be explained by reaction of the ortho isomer of **1** in this melt and will be discussed later.

1,2-Diphenylethane (DPE). DPE is found to be much less reactive in $SbCl_3$ than DPM. The ^{1}H NMR spectrum of an $SbCl_3$

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(25) Perkampus, H.-H.; Sondern, C. *Z. Naturforsch. A* **1981**, *36A*, 362.

(26) Brown, H. C.; Smoot, C. R. *J. Am. Chem. Soc.* **1955**, *78*, 2176.

(27) McCaulay, D. A.; Lien, A. P. *J. Am. Chem. Soc.* **1957**, *79*, 5953.

(28) (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.

(29) Schriesheim, A. *J. Org. Chem.* **1961**, *26*, 3530.

(30) (a) Streitwieser, A.; Reif, L. *J. Am. Chem. Soc.* **1960**, *82*, 5003. (b) *Ibid.* **1964**, *86*, 1988.

(31) Roberts, R. M.; Roengsumran, S. *J. Org. Chem.* **1981**, *46*, 3689.

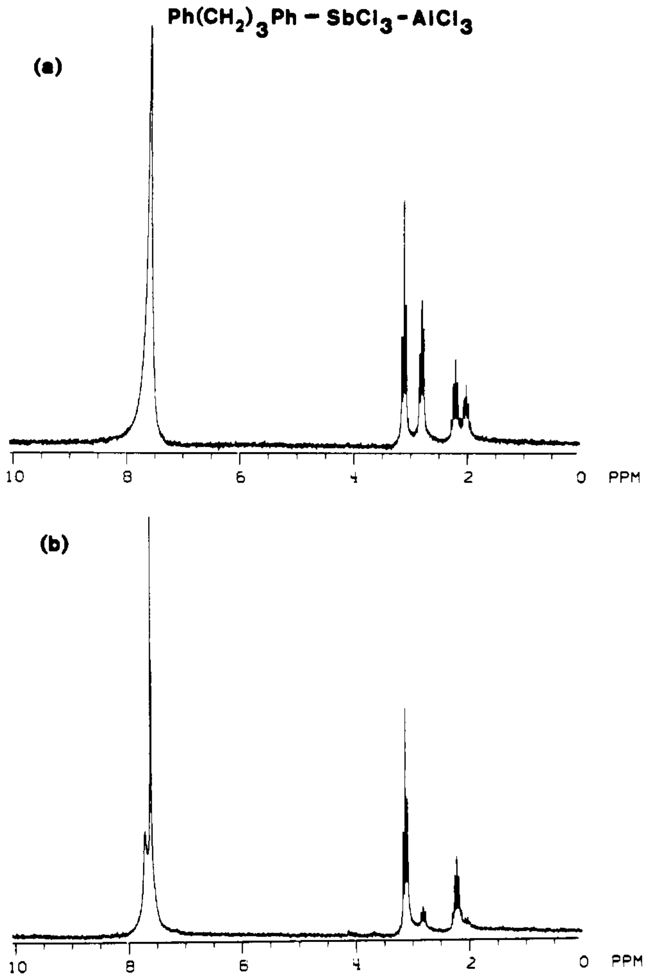
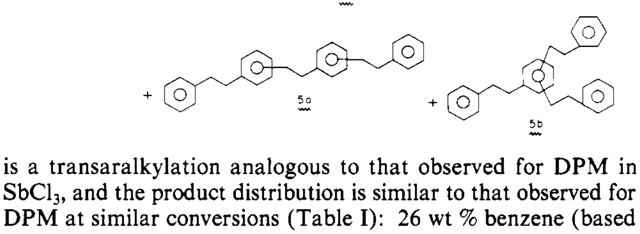


Figure 3. ^{1}H NMR spectrum at 100 °C of an $SbCl_3$-10 mol % $AlCl_3$ melt containing DPP: (a) after heating for 6 min; (b) after heating for 30 min.

melt containing DPE shows no evidence for reaction after 2 h at 130 °C. One observes only a clean spectrum of DPE, which is characterized by a singlet at 3.05 ppm for the aliphatic protons and a multiplet at 7.3–7.5 ppm for the aromatic protons. Hydrolysis of this melt results in a 100% recovery of DPE.

If, instead, DPE is dissolved in a $SbCl_3$–10 mol % $AlCl_3$ melt, the NMR shows that DPE reacts rapidly at 100 °C. This is manifested in the rapid growth of the peak at 7.5 ppm for benzene and the splitting of the singlet at 3.06 ppm into at least four peaks from 3.02 to 3.09 ppm. As in the case of DPM in $SbCl_3$, the NMR spectra indicate that the reaction products are structurally similar to the starting material. Product analysis shows that after 10 min at 100 °C nearly 63% of the DPE has reacted. The major products are benzene, *o*-, *m*-, and *p*-(2-phenylethyl)-1,2-diphenylethane (**4**), and four isomers of the next higher disubstituted homologue (**5a** and **5b**), as shown in eq 3. The overall reaction



(3)

is a transaralkylation analogous to that observed for DPM in $SbCl_3$, and the product distribution is similar to that observed for DPM at similar conversions (Table I): 26 wt % benzene (based on DPE reacted), an *o*-, *m*-, *p*-**4** ratio of 2, 71, 27, and a mol ratio of **4**:**5** of 3.0. Benzene, **4**, **5**, and unreacted DPE account for 84% of the organics with the remaining organics probably in the form of polymeric materials larger than **5**.[32] The observed cleavage of the sp^2–sp^3 bond for DPE is very selective with no products detected resulting from the cleavage of the central sp^3–sp^3 bond.

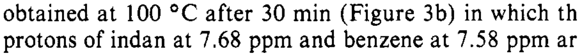
If DPE is reacted in $SbCl_3$–$AlCl_3$ under more severe conditions (130 °C, 1 h), the transaralkylation reaction described by eq 3 is still observed with a 92% conversion of DPE. However, benzene, **4**, and **5** make up only 50% of the organics with the remainder being in the form of higher polymers.

In order to obtain a better comparison of the relative reactivities of DPM and DPE, an $SbCl_3$ melt containing DPE was heated at 130 °C for 168 h. Only 12% of the DPE reacted during this time, and the same products are identified as in the reaction in $SbCl_3$–$AlCl_3$ (eq 3).[33] For DPM in $SbCl_3$ at 130 °C, a similar conversion is found after 10 min. Therefore, DPM is more reactive than DPE in $SbCl_3$ by a factor of about 1×10^3 at 130 °C.

The DPE results also show the dramatic effect that 10 mol % $AlCl_3$ has on the catalytic activity of the $SbCl_3$ melt. Compared with the 12% conversion of DPE in $SbCl_3$ at 130 °C for 168 h, a similar conversion is found in $SbCl_3$–$AlCl_3$ at 100 °C after about 1 min. Thus the rate of transaralkylation of DPE in $SbCl_3$–10 mol % $AlCl_3$ at 100 °C is greater than that in $SbCl_3$ at 130 °C by a factor of approximately 1×10^4.

1,3-Diphenylpropane (DPP). The ^{1}H NMR spectrum of a melt of DPP in $SbCl_3$ (like DPE in $SbCl_3$) shows no evidence for any reaction after heating for up to 2 h at 130 °C. When DPP is dissolved in an $SbCl_3$–10 mol % $AlCl_3$ melt at 100 °C, the NMR shows that DPP reacts rapidly in this medium. The spectrum obtained after 6 min at 100 °C is shown in Figure 3a. The multiplets centered at 2.75 and 2.01 ppm are due to the protons on the carbons α and β to the aromatic ring in DPP. The multiplets at 3.11 and 2.21 ppm are due to the corresponding α and β protons of indan, which was subsequently found to be a major product of the reaction. The resonances for the aromatic protons overlap to form a broad peak at 7.6 ppm.

Analysis of the products shows that DPP reacted to form only two major products, benzene and indan, in equimolar amounts as shown in eq 4. Interestingly, no products are detected which would be expected from a transaralkylation analogous to that observed for DPM and DPE (eq 1 and 3, respectively). DPP appears to be of comparable reactivity to DPE with a 53% conversion obtained after 6 min at 100 °C and 77% conversion after 20 min (DPE gave 63% conversion after 10 min at 100 °C in $SbCl_3$–$AlCl_3$). At near quantitative conversions of DPP, the stoichiometry described by eq 4 still accounts for better than 97% of the organics. This can be seen from the clean NMR spectrum obtained at 100 °C after 30 min (Figure 3b) in which the aryl protons of indan at 7.68 ppm and benzene at 7.58 ppm are now resolved. As with the other diphenylalkanes this selective reaction again results in cleavage of only sp^2–sp^3 bonds and can be understood by a mechanism analogous to that for the transaralkylation of DPM and DPE.



(4)

1,4-Diphenylbutane (DPB). DPB is found to react in a fashion similar to DPP. In $SbCl_3$–10 mol % $AlCl_3$ at 100 °C, the resonances for the protons α and β to the aromatic rings at 2.69 and 1.65 ppm, respectively, are observed to rapidly give way to new resonances at 2.86 and 1.79 ppm. These new resonances correspond to the α and β aliphatic protons of tetralin. Product analysis indicates that DPB has reacted slightly faster than DPP with a 51% conversion after 3 min at 100 °C. Only two major products are found, benzene and tetralin, in equimolar quantities. As in the case of DPP, there are no products resulting from a transaralkylation reaction. Even at quantitative conversions, the bond cleavage reaction for DPB is extremely selective and described by eq 5.

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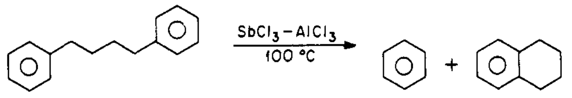
(32) In one GC–MS, two peaks were observed with *m*/*e* of 494 which could correspond to the next oligomer beyond **5**.

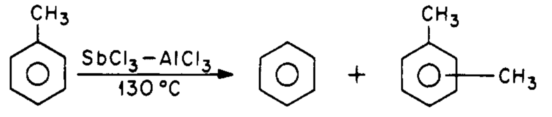
(33) Isomer distribution for **4** is (*o*-, *m*-, *p*-) 14, 39, 47, and the mol ratio of **4**:**5** is 4.0.



(5)

Toluene. The chemistry of toluene in $SbCl_3$–10 mol % $AlCl_3$ was examined in order to determine if the anhydrous melt could catalyze a transalkylation reaction for an alkylbenzene. This type of reaction is normally performed with strong protonic acid catalysts such as $AlBr_3$–HBr,[26,29,31] $GaBr_3$–HBr,[30] and BF_3–HF.[27] Moreover, a comparison of relative reactivities of DPM, DPE, and toluene provides useful information in considering mechanisms for transalkylation.

Toluene is found to be even less reactive than DPE, with the NMR spectrum showing no reaction for toluene in $SbCl_3$–$AlCl_3$ at 100 °C after 1 h. At 130 °C toluene is observed to react slowly, and product analysis following heating for 3.2 h shows only a 12% conversion of toluene according to the transalkylation reaction described by eq 6. At this conversion, only benzene and xylenes are found as products.[34]

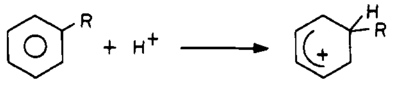


(6)

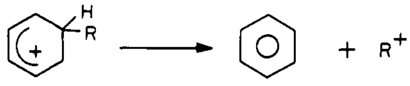
For comparison with the DPE reaction in $SbCl_3$–$AlCl_3$, toluene was heated at 100 °C for 79 h. A 70% conversion of toluene is obtained,[35] and at this higher conversion, mesitylene (1,3,5-trimethylbenzene) is also observed as a major product in addition to benzene and xylene. For DPE in $SbCl_3$–$AlCl_3$ at 100 °C this level of conversion occurs after about 12 min. These data demonstrate that toluene is much less reactive (by about 4×10^2) than DPE in $SbCl_3$–$AlCl_3$.

Discussion

Mechanisms of Transalkylation. Three principal mechanisms have been proposed to explain the chemistry of transalkylation for alkylbenzenes with strong protic acid catalysts.[36] These include transalkylation via dealkylation–alkylation (eq 7–9), via nucleophilic displacement (eq 10 and 11), and via benzylic cations (eq 12–14). The proton-initiated dealkylation–alkylation mechanism has been found to be appropriate for transalkylations in which a secondary or tertiary alkyl cation can be formed.[36-38] Isomerization of the 2-pentyl group in the transalkylation of 2-phenylpentane provided good evidence for the formation of a free alkyl carbenium ion intermediate.[37]



(7)



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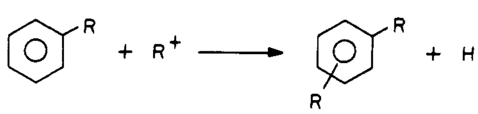
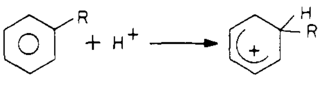


(9)

On the other hand in transalkylation reactions of primary alkylbenzenes, the alkyl group is transferred without isomerization.[26,27,30,31] It is generally believed, therefore, that transalkylation reactions for primary alkylbenzenes, in which a primary carbenium ion would have to be formed in eq 8, do not occur by the dealkylation–alkylation mechanism. Under more vigorous conditions, however, primary alkylbenzenes have been observed to undergo dealkylation (cracking) reactions which also involve isomerization and fragmentation of the incipient free cation.[21,28b,36]

One mechanism that has been proposed to explain the lack of alkyl group rearrangement in the transalkylation of primary alkyl benzenes is the nucleophilic displacement mechanism shown in eq 10 and 11.[26,27,38] In this mechanism the ipso proton complex



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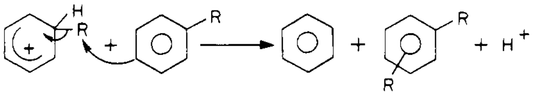
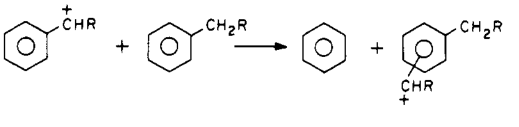


(11)

formed in eq 10 undergoes a S_N2-type attack at the benzylic carbon in the rate-determining step (eq 11) rather than dissociate to form the free cation. However, Streitwieser and Reif[30] showed that the transalkylation of ethylbenzene in $GaBr_3$–HBr was first order in ethylbenzene and, from a thorough kinetic study of isotopically labeled and optically active molecules, that the transalkylation was actually proceeding via the benzylic cation route (eq 12–14). In this mechanism, the generation of a

(12)



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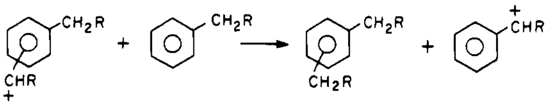

(14)

steady-state concentration of the benzylic cation is rate determining (eq 12) and is initiated by catalytic quantities of carbenium ions. For ethylbenzene the carbenium ion initiator is believed to be derived from protonation of styrene present as an impurity. Once the reaction is initiated, it proceeds by means of a cation chain mechanism (eq 13 and 14). Subsequently, much evidence has accumulated to support this mechanism for transalkylation of primary alkylbenzenes including the rare isolation of a substituted diphenylmethane intermediate before the production of benzene[28] (an intermediate in the composite eq 13) and the expected rate enhancement effects due to added carbenium ion initiators.[19,28]

$SbCl_3$-Catalyzed Reactions of α,ω-Diphenylalkanes. The chemistry of the α,ω-diphenylalkanes in $SbCl_3$ melts provides an interesting comparison with the transalkylation chemistry of alkylbenzenes under typical protic acid conditions in that the current study was performed under anhydrous, aprotic conditions with highly purified catalysts. The actual role of the catalyst will be discussed later. The chemistry of the diphenylalkanes in the aprotic $SbCl_3$ melts seems best represented by a benzylic cation mechanism analogous to the generally accepted mechanism for primary alkyl benzenes. The dealkylation–alkylation mechanism of eq 7–9 would involve primary cations and, thus, seems unlikely under these mild conditions. Furthermore, if fully developed primary cations were formed one would expect to find products resulting from isomerization of, or hydride abstraction by, these cations as has been previously observed.[19,20,37-39] The clean formation of **1** and **2** from DPM, **4** and **5** from DPE, indan from DPP, and tetralin from DPB strongly suggests that free phenyl alkyl cations are not formed.

The nucleophilic displacement mechanism (eq 10 and 11) seems equally unlikely. The first order kinetics observed for DPM in

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[34] The *m*- and *p*-xylenes were not resolved by GC with the columns employed. A (meta + para):ortho ratio of 7.9 was found.

[35] For comparison, Schriesheim found a similar conversion in $AlBr_3$–HBr at 110 °C after about 2 h.[29]

[36] Poutsma, M. L. *ACS Mongr. No. 171*, **1976**, 437.

[37] Burwell, R. L.; Shields, A. D. *J. Am. Chem. Soc.* **1955**, *77*, 2766.

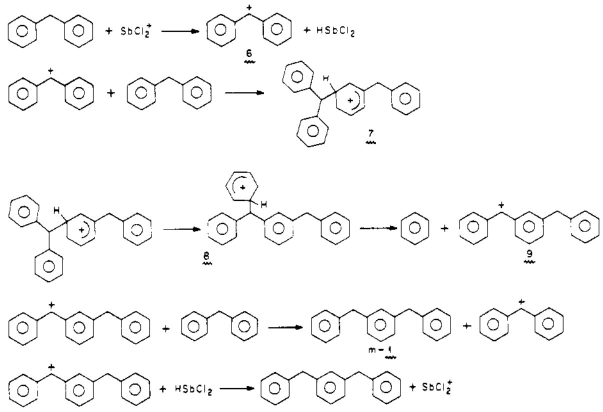
[38] McCauley, D. A.; Lien, A. P. *J. Am. Chem. Soc.* **1953**, *75*, 2411.

[39] Roberts, R. M.; Han, Y. W. *J. Am. Chem. Soc.* **1963**, *85*, 1168.

$SbCl_3$ is inconsistent with a nucleophilic displacement step (eq 11) being rate determining. Furthermore, the large difference in relative rates for the substrates in $SbCl_3$ melts, i.e., DPM $\gg$ DPE $\sim$ DPP $\sim$ DPB $\gg$ toluene, suggests that a direct displacement mechanism is unlikely. In particular the fact that DPM reacts 10^3 times faster than DPE in $SbCl_3$ is difficult to reconcile with this mechanism. Any rate enhancement expected for DPM relative to DPE based on electronic considerations would be greatly nullified by a much more sterically crowded transition state.

The chemistry of the diphenylalkanes and toluene in $SbCl_3$ melts can be explained readily by a mechanism analogous to eq 12–14 in which the rate-determining step is the generation of a steady-state concentration of the corresponding benzylic cation. The relative rates for the reaction of these compounds in $SbCl_3$ melts (vide supra) is exactly that predicted based on the stabilities of the corresponding benzylic cations, namely $PhC^+HPh \gg PhC^+HCH_2Ph \sim PhC^+H(CH_2)_2Ph \sim PhC^+H(CH_2)_3Ph \gg PhC^+H_2$.

A mechanism for the transaralkylation reaction of DPM and DPE is shown in eq 15–19 for the particular case of DPM and for the production of the meta isomer of **1**. The initiation step is a hydride abstraction which results in the benzylic cation **6** (eq 15). The key catalytic question of what species in the melt is affecting the hydride abstraction and how the addition of $AlCl_3$ enhances the catalytic activity of the $SbCl_3$ will be addressed below. Once cation **6** is generated it can react to give the observed products by the generally proposed transalkylation cation chain mechanism (eq 16–18). As noted earlier, products resulting from deprotonation of intermediate cations such as **7** are generally not observed, and no such products were identified in the DPM or DPE reactions. The isomers of **1** can then react further in an analogous manner to produce more benzene and higher oligomers such as **2**.



(15)

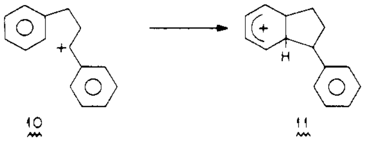
(16)

(17)

(18)

(19)

The production of benzene and indan from DPP and benzene and tetralin from DPB in $SbCl_3$–$AlCl_3$ can also be explained by a similar sequence of reactions as shown for the case of DPP. Once the benzylic cation of DPP, **10**, is formed in the rate-limiting step, this cation can either undergo an intermolecular reaction with another molecule of starting material (analogous to eq 16 for DPM) leading ultimately to transaralkylation products, or it can undergo an intramolecular reaction as represented in eq 20.



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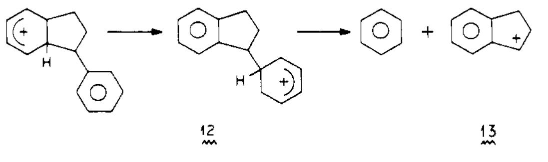
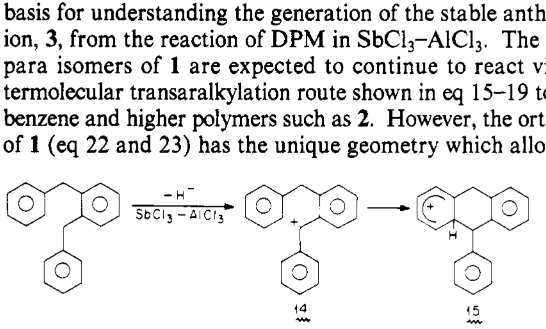


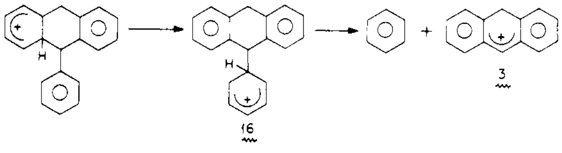
(21)

Cation **11** can then react as shown in eq 21 to produce benzene and the cation precursor to indan, **13**. For DPP and DPB in which stable five- and six-membered rings can be formed, this cyclialkylation path is observed exclusively.

The chemistry of DPP and DPB in $SbCl_3$–$AlCl_3$ provide the basis for understanding the generation of the stable anthracenium ion, **3**, from the reaction of DPM in $SbCl_3$–$AlCl_3$. The meta and para isomers of **1** are expected to continue to react via the intermolecular transaralkylation route shown in eq 15–19 to produce benzene and higher polymers such as **2**. However, the ortho isomer of **1** (eq 22 and 23) has the unique geometry which allows cation



(22)



(23)

14 to undergo the intramolecular cyclization reaction as was found for DPP and DPB. In contrast to the comparable cation, **13**, in the DPP reaction (and the corresponding tetralyl cation in the DPB reaction), cation **3** is stable in the $SbCl_3$–$AlCl_3$ molten salt, which allows it to be characterized by ^1H NMR spectroscopy. Hydrolysis of the melt leads to deprotonation of **3** and the production of anthracene.

The formation of such large amounts of **3** (15% based on recovered anthracene) clearly shows that the key hydride abstraction step in the $SbCl_3$–$AlCl_3$ molten salt cannot be due to "impurity" initiators. In fact, the identification of antimony metal as a reaction product following hydrolysis of the melt further indicates the involvement of $SbCl_3$ in this stoichiometric hydride abstraction.[40]

Role of $SbCl_3$. As shown in the previous section, the chemistry of the α,ω-diphenylalkanes in $SbCl_3$ melts is satisfactorily described by a mechanism involving the generation of the benzylic cation as the key reactive intermediate, analogous to the transalkylation reactions for primary alkylbenzenes. For alkylbenzenes with the typical strong protic acid catalysts employed such as $GaBr_3$–HBr, $AlBr_3$–HBr, BF_3–HF, the exact nature of the hydride abstracting moiety (in the absence of added initiators) is not well established but presumably derives from the protonation of an alkene impurity.[30]

As opposed to the strong acid catalysts described above, $SbCl_3$ is a notoriously weak Lewis acid.[41] However, in the molten state $SbCl_3$ is weakly ionized, as modeled by eq 24, with a reported

$$2SbCl_3 \rightleftarrows SbCl_2^+ + SbCl_4^- \qquad (24)$$

ionization constant, K_i, at 99 °C ranging from 3×10^{-11} [42] to 2×10^{-8} M^2.[43] The modest Lewis acid functionality of the melt resides in the chloride-deficient antimony cation, $SbCl_2^+$. The effect of adding $AlCl_3$, a strong chloride ion acceptor, to the melt is to greatly enhance the Lewis acidity of the medium by reacting completely with $SbCl_3$ to produce $SbCl_2^+$ according to eq 25. For

$$SbCl_3 + AlCl_3 \rightarrow SbCl_2^+ + AlCl_4^- \qquad (25)$$

an $SbCl_3$–10 mol % $AlCl_3$ melt the result is an increase in $SbCl_2^+$ concentration by a factor of 10^4–10^5 compared to that in a neat

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(40) Of course for the other reactions described, which are purely catalytic in $SbCl_3$, no antimony metal could be found.

(41) Olah, G. A. In "Friedel-Crafts and Related Reactions"; G. A. Olah, Ed.; Interscience: New York, 1963; Vol. 1, pp 853–858.

(42) Baughan, E. C. In "The Chemistry of Nonaqueous Solvents"; Lagowski, J. J. Ed.; Academic Press: New York, 1976; Vol. IV, pp 145–146.

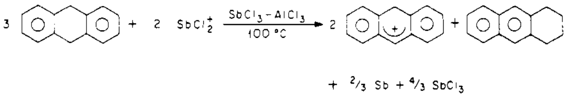
(43) Bauer, D.; Texier, P. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1968**, *266*, 602.

$SbCl_3$ melt (as estimated from the range of K_i values at 99 °C and using eq 24 and 25).

Recent evidence from Raman spectroscopy[44] and electrical conductivity measurements[45] on $SbCl_3$ and $SbCl_3$–$AlCl_3$ melts indicates that the model presented in eq 24 and 25 is oversimplified. Discrete ions such as $SbCl_2^+$ do not appear to exist freely in the melts, but instead are strongly complexed to neutral $SbCl_3$ molecules (or chains) through chlorine bridge bonds. However, for the purposes of the present discussion, $SbCl_2^+$ will be used to model the chloride-deficient antimony species that is acting as the Lewis acid in $SbCl_3$ and $SbCl_3$–$AlCl_3$ melts.

Hydride abstraction by $SbCl_2^+$ appears to be the key step by which the diphenylalkanes are activated in $SbCl_3$ melts, as shown in eq 15 for the case of DPM. The observation that $SbCl_3$ must be present as a continuous melt rather than separated solute molecules in order to have an active catalyst is consistent with this premise. The greatly enhanced catalytic activity of the $SbCl_3$ melt upon addition of 10 mol % $AlCl_3$ was evidenced by the fact that the rate of transaralkylation for DPE in $SbCl_3$–$AlCl_3$ at 100 °C was much faster ($\sim 10^4$) than in $SbCl_3$ at 130 °C. This effect can now be explained by the greatly increased concentration of $SbCl_2^+$ upon addition of 10 mol % $AlCl_3$ that promotes the hydride abstraction from DPE in the rate-determining step.[46]

As described earlier, the generation of large quantities of the anthracenium ion, **3**, in $SbCl_3$–$AlCl_3$ by means of eq 22 and 23, and the identification of antimony metal as a reaction product following hydrolysis of the melt strongly suggests the involvement of $SbCl_2^+$ as a hydride abstractor in a stoichiometric fashion. The ability of $SbCl_3$ based melts to act as hydride abstracting agents has been observed previously in cases where the resulting cations are stable.[9] The hydroaromatics, 9,10-dihydroanthracene and 5,12-dihydronaphthacene, produce stable arenium ions by hydride abstraction in $SbCl_3$–10 mol % $AlCl_3$ melts at 100 °C as shown in eq 26 for the dihydroanthracene.[9] Again hydrolysis of the melt produces stoichiometric quantities of antimony metal (and anthracene from the arenium ion). Therefore, there is ample evidence to support the proposal that the Lewis acid, $SbCl_2^+$ (in its complexed form), is acting as the hydride-abstracting reagent that initiates the catalytic reactions for the diphenylalkanes.



(26)

In these catalytic reactions it is possible that the hydride abstraction by $SbCl_2^+$ is only an initiation step which sets up a cationic chain mechanism as shown in eq 15–18 for DPM with eq 16–18 forming the propagation steps. However, it is likely that the $SbCl_2^+$ has a more involved role in the reactions acting as a hydride transfer agent in the melt, and that steps such as eq 19 are also important in the generation of products.

Selectivity of Bond Cleavage. Bond cleavage reactions for the α,ω-diphenylalkanes have received recent attention in an effort to understand how these types of aliphatic linkages can be broken in the liquefaction of coal. The sp^2–sp^3 bonds are difficult to break in typical thermal conversions. For example, DPM, for which the dissociation energy of the sp^2–sp^3 bond is 89 kcal/mol,[47] is completely stable at 400 °C. On the other hand DPE, whose central sp^3–sp^3 bond is much weaker at 62 kcal/mol,[47] readily reacts at 400 °C by cleavage of this central bond.[12,13] Since DPE has both types of bonds, it has been the prototypical model compound for most investigations. Moreover, reactions which produce radical anion[16] or radical cation[17] intermediates for DPE, although drastically lowering the temperatures at which bond cleavage reactions take place, still yield a total selectivity for cleavage of the sp^3–sp^3 bond.

In contrast, $SbCl_3$ melts catalyze reactions for the α,ω-diphenylalkanes at low temperatures (100–130 °C) in which only products resulting from the cleavage of the sp^2–sp^3 carbon–carbon bonds are observed. This unusual selectivity arises from the ability of the catalyst to generate benzylic cations by hydride abstraction which ultimately leads to the cleavage of the phenyl–alkyl bond.

Summary

Although molten $SbCl_3$ is known to be an unusually selective catalyst for hydrocracking coal, little fundamental research had been done previously on the chemistry of organic substrates in this medium. In our earlier studies of polycyclic aromatic hydrocarbons in $SbCl_3$ melts, a variety of novel reactions were discovered in which arene radical cations, produced through oxidation by Sb^{3+} in the melt, were the key reactive intermediates.

The present study of the α,ω-diphenylalkanes, which are not oxidized to radical cations by Sb^{3+}, shows the Lewis acid functionality of the melt playing the key catalytic role. The selective bond cleavage reactions observed result from the ability of $SbCl_2^+$ in the catalytic medium to generate benzylic cation intermediates by hydride abstraction. For DPM and DPE with one and two carbon linkages, the result is disproportionation of the diphenylalkane. For DPP and DPB with three and four carbon linkages that can lead to stable cyclic products, the result is cleavage of the diphenylalkane into two smaller compounds.

The chemistry in $SbCl_3$ melts of larger, oxidizable polycyclic aromatics connected by aliphatic linkages is currently under investigation. This research could provide insight into the relative importance of the redox and Lewis acid functionalities of this remarkable catalyst.

Experimental Section

Reagents. $SbCl_3$ (Alfa, 99.5%) was purified by refluxing with Sb_2O_3 and Sb metal under pure argon, followed by subliming at 40 °C under dynamic vacuum as previously described.[48] This material was further purified by a second sublimation and then by repeated zone refining. The resulting $SbCl_3$ was a colorless solid which produced clear, colorless melts.

$AlCl_3$ was prepared from zone-refined aluminum metal (Cominco Products, Inc., 99.9999%) and specially prepared HCl according to published procedures[49] and yielded a colorless solid.

DPM (Aldrich), DPE (Aldrich), DPP (Pfaltz and Bauer), and toluene (Fisher) were reagents of the highest available quality. DPB was provided by M. L. Poutsma of Oak Ridge National Laboratory. The purity of the organic substrates was confirmed by GC, HPLC, and ^1H NMR spectroscopy.

Manipulation of Reagents. The purified metal halides were stored and loaded into the NMR or reaction 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. Transfers of DPE and DPB were also performed in the glovebox while DPM, DPP, and toluene were added to the NMR or reaction tube outside the glovebox by means of a calibrated syringe while the tube was being purged with argon.

NMR Studies. Reactions were studied by in situ ^1H NMR spectroscopy in 5-mm o.d. tubes (1-mm wall) which were sealed on a vacuum line under a reduced pressure of purified argon. The concentration of the organic substrate in the melt was 3.0–3.3 mol % (0.3–0.4 M), and typically, 0.14 mmol of the diphenylalkane in 0.9–1.0 g of the metal halide catalyst was employed.

The ^1H NMR measurements were made at 100–130 °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.

Product Separation and Identification. Products were identified and quantitated from larger scale reactions performed in 10-mm o.d. pyrex tubes (1-mm wall) which were sealed on a vacuum line under a reduced

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(44) (a) Huglen, R.; Mamantov, G.; Begun, G. M.; Smith, G. P. *J. Raman Spectrosc.* **1980**, *9*, 188. (b) Aliotta, F.; Maisano, G.; Micali, N.; Migliardo, P.; Vasi, C.; Wanderlingh, F.; Triolo, R.; Smith, G. P. *J. Chem. Phys.* **1982**, *76*, 3987.

(45) Petrovic, C.; Mamantov, G.; Sørlie, M.; Lietzke, M. H.; Smith, G. P. *J. Phys. Chem.* **1982**, *86*, 4598.

(46) The rate enhancement for DPE at a common temperature, e.g., 100 °C, should be greater than 10^4. This rate enhancement corresponds roughly to the calculated increase in $SbCl_2^+$ concentration of 10^4–10^5.

(47) McMillen, D. F.; Ogier, W. C.; Ross, D. S. *Prepr., Div. Fuel Chem., Am. Chem. Soc.* **1981**, *26*, 181.

(48) Sørlie, M.; Smith, G. P. *J. Inorg. Nucl. Chem.* **1981**, *43*, 931.

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

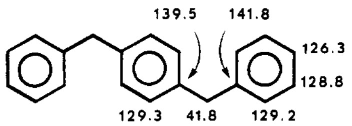
pressure of purified argon. The substrate concentrations were similar to those used in the NMR experiments, and typically 1 mmol of the diphenylalkane was employed. The reaction tube was rocked at about 0.2 Hz in an oil bath whose temperature could be reproducibly set and regulated to ±0.1 °C. At the conclusion of the heating period, the tubes were allowed to cool to room temperature and then broken under a layer of 3 M HCl. The organics were extracted into CH_2Cl_2, and the entire mixture was filtered. The CH_2Cl_2 layer was separated, washed with 3 M HCl, and dried over $MgSO_4$. Following filtration, the CH_2Cl_2 layer was concentrated by distillation at 39 °C under argon.

The organic products were analyzed by GC, HPLC, GC–MS, UV and, where applicable, by ^1H and ^{13}C NMR spectroscopy. GC measurements were made on a Bendix 2200 chromatograph with flame ionization detection. Separations were made on a 10 ft × $^1/_8$ in. column packed with either 3% Dexsil 300 or 10% SP-2100 on Supelcoport. HPLC was performed on a Waters liquid chromatograph with UV detection at 254 nm. Separations were made on a 50 × 0.94 cm ID Whatman Partisil M9-ODS-3 column with a $CH_3OH–H_2O$ mobile phase. UV spectra were obtained on HPLC fractions with a Cary 14 spectrophotometer. GC–MS spectra were measured with a Hewlett-Packard 5985 GC–mass spectrometer using electron impact ionization at 70 eV. Chromatographic separations were made on a 30 m × 0.25 mm i.d. glass capillary column coated with OV-101 liquid phase. Antimony metal was reacted with a 3:1 $HCl–HNO_3$ (v/v) mixture, and the resulting solution was analyzed with an Instrumentation Laboratory atomic absorption spectrometer.

Quantitative analyses were performed by GC with the use of internal standards. In addition, benzene, unreacted diphenylalkane, indan, tetralin, and anthracene were collected by HPLC in amounts determined from their UV spectra. In a few cases, the reaction products were also analyzed following the NMR experiments and were found to be identical with those identified from the larger scale reactions.

DPM Reaction: Compounds 1 and 2. The ortho isomer of **1** was identified from its 70-eV mass spectrum: *m/e* (rel intensity) 258 (M^+, 59), 259 (13), 181 (17), 180 (100), 179 (92), 178 (33), 167 (56), 166 (16), 165 (62), 152 (19), 91 (10). The mass spectrum of the ortho isomer is unique in that the molecular ion undergoes a rearrangement with concomitant loss of a molecule of benzene as observed earlier in the 15-eV spectrum of the ortho isomer.[50]

The meta and para isomers of **1** were found to give nearly identical mass spectral fragmentation patterns characterized principally by loss of the benzyl radical. The 70-eV mass spectrum of the meta isomer is as follows: 258 (M^+, 57), 259 (12), 168 (13), 167 (100), 166 (13), 165 (43), 152 (16), 91 (15). The mass spectrum of the para isomer: 258 (M^+, 48), 259 (12), 168 (13), 167 (100), 166 (14), 165 (39), 152 (16), 91 (12). In order to distinguish the meta and para isomers, one of the isomers (the para, vide infra) was collected by HPLC from a reaction mixture from which the benzene and unreacted DPM had been removed by vacuum distillation. About 1 mg of the isomer was collected, dissolved in 60 μL of CD_2Cl_2, and transferred to a 1.7-mm o.d. NMR tube. The ^{13}C NMR spectrum was then obtained on a JEOL FX-90Q spectrometer, using a $^{13}C/^1H$ dual microprobe system and an internal ^2H lock. The $^{13}C/^1H$ spectrum was measured at 22.50 MHz, and the chemical shifts were referenced to the CD_2Cl_2 ^{13}C resonance at δ 53.74 [relative to $(CH_3)_4Si$]. The observed spectrum was readily assigned to the para isomer of **1**:



The three major isomers of **2** gave very similar mass spectra with fragmentation patterns characteristic of oligomeric polybenzyls.[50] The mass spectrum of the first isomer: *m/e* 348 (M^+, 74), 349 (24), 270 (20), 258 (14), 257 (67), 180 (28), 179 (46), 178 (26), 168 (13), 167 (100), 166 (31), 165 (86), 152 (18), 91 (31). The mass spectrum of the second isomer: *m/e* 348 (M^+, 62), 349 (19), 270 (12), 258 (18), 257 (79), 180 (10), 179 (27), 178 (22), 168 (13), 167 (100), 166 (25), 165 (71), 152 (17), 91 (32). The mass spectrum of the third isomer: *m/e* 348 (61), 349 (20), 258 (23), 257 (100), 179 (16), 178 (14), 167 (56), 166 (19), 165 (47), 152 (12), 91 (19).

DPE Reaction: Compounds 4 and 5. The assignments of the mass spectra obtained for the ortho, meta, and para isomers of **4** were based on the assumption that the isomers of **4**, on the same GC column, eluted in the same order as the isomers of **1**. The mass spectrum of the ortho isomer: *m/e* 286 (M^+, 51), 287 (11), 196 (16), 195 (100), 194 (19), 180 (16), 179 (13), 178 (12), 167 (20), 165 (21), 117 (25), 91 (28). The mass spectrum of the meta isomer: *m/e* 286 (M^+, 52), 287 (11), 196 (16), 195 (100), 167 (26), 165 (16), 115 (10), 104 (15), 103 (12), 91 (65), 78 (15), 65 (24). The mass spectrum of the para isomer: 286 (M^+, 34), 287 (8), 196 (16), 195 (100), 91 (6).

The three predominant isomers of **5** gave the following mass spectra: for the first isomer, *m/e* 390 (M^+, 16), 391 (5), 300 (24), 299 (100), 207 (12), 195 (12), 193 (13), 178 (10), 105 (26), 91 (23); for the second isomer, *m/e* 390 (M^+, 97), 391 (30), 299 (17), 208 (12), 207 (36), 196 (13), 195 (85), 194 (10), 193 (46), 180 (14), 179 (22), 178 (27), 167 (28), 165 (29), 153 (13), 129 (14), 119 (44), 117 (20), 115 (15), 105 (50), 91 (100); for the third isomer, *m/e* 390 (M^+, 68), 391 (21), 299 (30), 207 (27), 196 (14), 195 (100), 193 (37), 178 (12), 167 (14), 165 (14), 119 (24), 105 (33), 104 (22), 91 (94).

Rate Measurements on DPM–$SbCl_3$ Reaction. The kinetic order with respect to DPM was determined by the method of initial rates. The influence of DPM concentration on the initial rate was measured over the range of 0.028–1.02 M. The samples were prepared as described earlier with DPM that had been vacuum distilled. The reactions were run to 10–11% conversion at 110.5 °C (temperature reproducibility, ±0.1 °C) and then quenched by plunging the reaction tube into an ice bath. Following workup of the reaction mixture, the unreacted DPM was quantitated by multiple analyses using both GC, with DPE as an internal standard and corrections made for differences in detector response, and UV spectroscopy following HPLC separation. The reaction rates resulting from these measurements are believed to be accurate to ±10%. The kinetic order with respect to DPM was determined from the slope of a linear regression analysis of the log–log plot of initial rates vs. initial DPM concentration. The slope obtained was 1.03 ± 0.03 with a correlation coefficient of 0.9991.

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Registry No. $C_6H_5CH_2C_6H_5$, 101-81-5; $C_6H_5(CH_2)_2C_6H_5$, 103-29-7; $C_6H_5(CH_2)_3C_6H_5$, 1081-75-0; $C_6H_5(CH_2)_4C_6H_5$, 1083-56-3; $SbCl_3$, 10025-91-9; $AlCl_3$, 7446-70-0; toluene, 108-88-3.

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[50] Lüderwald, I.; Montaudo, G.; Przybylski, M.; Ringsdorf, H. *Makromol. Chem.* **1974**, *175*, 2423.