5 mL of dry THF and filtered once more. The solution was concentrated under reduced pressure and distilled in vacuo to give 2.4 g (61%) of **20**: bp 74–76 °C (0.005 Torr); ^{11}B NMR (THF) δ 46.14 (monomer); ^{1}H NMR δ 0.27 (s, 3 H), 0.68 (d, J = 9.3 Hz, 1 H), 0.83 (t, J = 7.3 Hz, 3 H), 1.12 (s, 3 H), 1.23 (s, 3 H), 1.46 (sext, J = 7.3 Hz, 2 H), 1.6–2.08 (m, 7 H), 2.42 (m, 1 H), 2.95 (m, 5 H).

Reduction of Ketones with the BH_3 Complexes of *N*-Alkyl-10,10-dimethyl-5-aza-6-boratricyclo[7.1.1.0^{2,7}]undecanes (General Procedure). To a solution of 10 mmol of the appropriate azaborane in 20 mL of THF was added 14.5 mL of 0.58 M BH_3/THF (8.42 mmol) or 18.2 mL of 0.462 M BMS/THF (8.40 mmol) dropwise, and the resulting solution was stirred for 1 h at rt. A solution of 6.25 mmol of ketone in 12 mL of THF was added dropwise at either 0 °C or rt. The solution was stirred for 1 h or overnight depending upon the substrate. The reaction was quenched by the addition of 2 mL of MeOH–H_2O (1:1) and refluxed for 0.5 h with 4 mL of diluted HCl (1:1). The reaction mixture was subsequently saturated with solid NaCl and extracted with ether. The combined extracts were washed with water, saturated $NaHCO_3$ solution, and brine and dried (K_2CO_3). After evaporation of ether, the residue was subjected to Kugelrohr distillation to give the alcohol which was subjected to ^{1}H NMR shift studies (Eu(hfc)$_3$).

Acknowledgment. This work was supported by the National Institutes of Health (GM24517) and the University of California, Riverside, Committee on Research.

Supplementary Material Available: ^{1}H and ^{13}C NMR data for compounds **3**–**8** and ^{1}H and ^{13}C NMR spectra of compounds described in the Experimental Section (20 pages). Ordering information is given on any current masthead page.

Charge-Transfer Activation of Aromatic Hydrocarbons with Stannic Chloride

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Stannic chloride ($SnCl_4$) is a versatile Lewis acid that is especially useful for various types of electrophilic aromatic substitutions, including Friedel–Crafts alkylations with alkyl chlorides, chlorinations with chlorine, etc.[1-3] The catalytic activity of stannic chloride is usually attributed to its ability to activate the electrophile (RCl, Cl_2, etc.) by ligand (chloride) coordination.[4] It is thus noteworthy that there are varied reports of charge-transfer absorption bands when different aromatic hydrocarbons ArH are exposed to stannic chloride (that are not present with either $SnCl_4$ or the aromatic compound alone).[5,6] Spectrophotometric analyses have established (with the aid of Job's plots) the 1:1 stoichiometry for ArH–$SnCl_4$ in the formation of electron donor–acceptor or EDA complexes,[7] i.e.

$$ArH + SnCl_4 \underset{}{\overset{K_{EDA}}{\rightleftharpoons}} [ArH, SnCl_4] \qquad (1)$$

Table I. Charge-Transfer Spectra of Aromatic EDA Complexes with Stannic Chloride[a]

aromatic donor	IP[b] (eV)	λ_{max} (nm)	$h\nu_{CT}$ (eV)
1. mesitylene	8.42	299	4.15
2. naphthalene	8.12	326	3.80
3. pentamethylbenzene	7.92	322	3.85
4. hexamethylbenzene	7.85	340	3.65
5. 1,4-dimethylnaphthalene	7.78	348	3.56
6. 1-methoxynaphthalene	7.72	352	3.52
7. 9-bromoanthracene	7.47	408	3.04
8. anthracene	7.43	400	3.10
9. 2-*tert*-butylanthracene	~7.3	408	3.04
10. 9-methylanthracene	7.25	414	3.00
11. 9,10-dimethylanthracene	7.11	434	2.86

[a] In cyclohexane solution containing 0.01 M arene and 0.05 M $SnCl_4$ at 23 °C. [b] Ionization potential from ref 11.

The formation of [ArH, $SnCl_4$] in eq 1 is reminiscent of the series of 1:1 complexes observed between aromatic hydrocarbons and titanium tetrachloride.[8] Since both metal halides share catalytic properties in common,[9] the delineation of their behavior toward the same (aromatic) substrates would provide the comparative basis for chemical reactivity. Indeed, our recent spectroscopic and structural study of the charge-transfer (CT) structures of aromatic complexes between titanium tetrachloride[10] offers a ready format for the direct comparison of this related series of EDA complexes. Accordingly, we focus in this study on the chemical consequences of the charge-transfer excitation of aromatic EDA complexes with stannic chloride in the comparative light of the $TiCl_4$ analogues.[8]

Results

Charge-Transfer Spectra of Aromatic EDA Complexes with Stannic Chloride. The addition of $SnCl_4$ (dissolved in cyclohexane) to mesitylene immediately resulted in a bright yellow solution. With naphthalene an orange coloration developed, and the quantitative effects of these dramatic color changes are illustrated in Figure 1. The systematic spectral shifts of the new absorption bands for the various benzene and naphthalene donors, as listed in Table I, define the linear relationship $h\nu_{max} = 1.0IP - 4.62$ when the absorption maximum (ν_{max}) and the aromatic ionization potential (IP) are both expressed in eV.[11] Such a spectral behavior accords with Mulliken's prediction for charge-transfer excitation ($h\nu_{CT}$) in weak intermolecular complexes[12], i.e.

$$h\nu_{CT} = IP - EA - \omega \qquad (2)$$

Since stannic chloride is the acceptor in common, EA (electron affinity) is constant in eq 2, as is the electrostatic

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(2) De La Mare, P. B. D.; Ridd, J. H. *Aromatic Substitution. Nitration and Halogenation*; Butterworths: London, 1959.

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(5) Tsubomura, H. *Bull. Chem. Soc. Jpn.* **1954**, *27*, 1.

(6) (a) Satchell, D. P. N. *J. Chem. Soc.* **1960**, 4380 (b) Burkhardt, L. A.; Hammond, P. R.; Knipe, R. H.; Lake, R. R. *J. Chem. Soc. A* **1971**, 3789 and related papers. (c) Krauss, H. L.; Huttmann, H. Z. *Naturforsch.* **1963**, *18b*, 976; **1966**, *21b*, 490.

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0022-3263/92/1957-2956$03.00/0

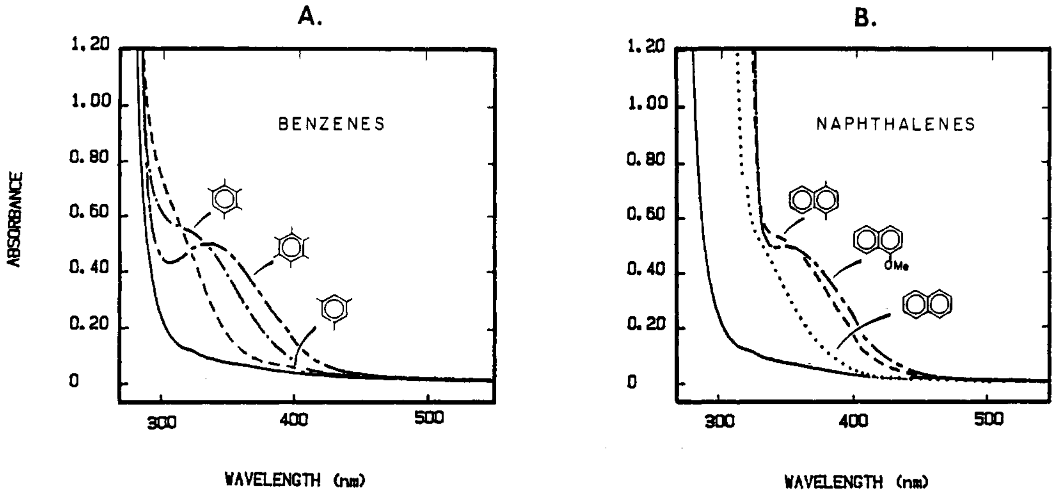


Figure 1. Charge-transfer spectra of the EDA complexes of stannic chloride with (A) benzene and (B) naphthalene donors (as indicated) in cyclohexane solution. The absorption spectrum (—) of stannic chloride alone in cyclohexane.

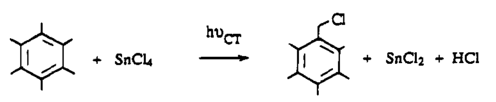
work term ω that can be approximated for the structurally related aromatic π-donors in Figure 1.

Owing to the high solubility of stannic chloride in moisture-free cyclohexane, the charge-transfer absorbance grew monotonically with increasing concentrations of the aromatic donor [ArH] according to the spectrophotometric relationship of Benesi and Hildebrand,[13] i.e.

$$\frac{[\mathrm{SnCl_4}]}{A_{\mathrm{CT}}} = \frac{1}{\epsilon_{\mathrm{CT}}} + \frac{1}{K_{\mathrm{EDA}}\epsilon_{\mathrm{CT}}[\mathrm{ArH}]} \qquad (3)$$

under the conditions in which $[\mathrm{SnCl_4}] \ll [\mathrm{ArH}]$, where A_{CT} is the molar absorbance and ϵ_{CT} is the extinction coefficient of the charge-transfer band at the monitoring wavelength (close to $\lambda_{\max}$).[14] The linear fit of the absorbance data was obtained by the method of least squares, and it yielded the formation constants $K_{\mathrm{EDA}} = 0.40$ and 1.3 $\mathrm{M^{-1}}$ (ϵ_{CT} 620 and 213 $\mathrm{M^{-1}\ cm^{-1}}$) for mesitylene and 1-methoxynaphthalene, respectively.[15] Such small values of K_{EDA}, irrespective of whether a benzene or a naphthalene donor was employed, indicate that the [ArH, $\mathrm{SnCl_4}$] complexes are uniformly weak. Thus, the first-order form of the Mulliken expression in eq 2 accurately expresses the energetics of the charge-transfer excitation.[12,16]

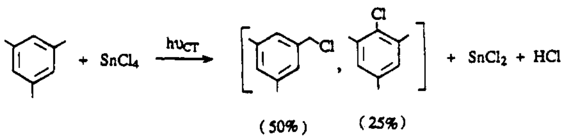
Charge-Transfer Photochemistry of Aromatic EDA Complexes with Stannic Chloride. The charge-transfer bands of all the [ArH, $\mathrm{SnCl_4}$] complexes lay in the visible spectral region and were distinctly separated from the ultraviolet tail of the $\mathrm{SnCl_4}$ absorption shown in Figure 1. As such, only the charge-transfer band of the EDA complex was selectively excited when cyclohexane solutions of ArH/$\mathrm{SnCl_4}$ pairs were deliberately exposed to filtered light with $\lambda > 350$ nm (see details in the Experimental Section). Under these conditions, a 0.06 M solution of hexamethylbenzene (HMB) containing a 10-fold excess of stannic chloride afforded pentamethylbenzyl chloride (95% yield) according to the stoichiometry



(4)

The reduced stannous chloride precipitated from solution as a fine colorless powder.[17] Essentially the same stoichiometric conversion of hexamethylbenzene occurred when a more concentrated (0.35 M) solution in cyclohexane was treated with 0.07 M $\mathrm{SnCl_4}$. Both solutions remained unchanged for prolonged periods if they were protected from adventitious light. Since the side-chain substitution in eq 4 only occurred upon the deliberate excitation of the charge-transfer absorption band of [HMB, $\mathrm{SnCl_4}$], it is hereafter referred to as *CT chlorination*.

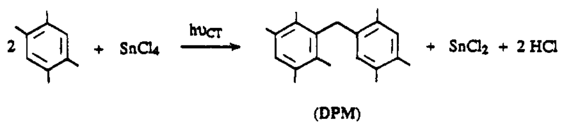
Charge-transfer chlorination according to eq 4 was not the sole photochemical process with the mesitylene EDA complex. Thus, the irradiation of 0.35 M mesitylene and 0.07 M $\mathrm{SnCl_4}$ in cyclohexane with $\lambda > 350$ nm yielded 3,5-dimethylbenzene chloride as the principal product, together with significant amounts of the ring-chlorinated 2-chloromesitylene, i.e.



(5)

The isomeric benzyl chloride (**BC**) and chlorobenzene (**CB**) in eq 5 clearly represented the competition between the (methyl) *side-chain* and the *nuclear* substitution, respectively, of mesitylene.

The exposure of the durene EDA complex with stannic chloride under the same photochemical conditions led to the dimeric hydrocarbon (**DPM**)[18] in high yields (85%), i.e.



(6)

together with minor amounts of 2,4,5-trimethylbenzyl chloride (5%) and 3-chlorodurene (3%). The diphenylmethane-type dimer **DPM** in eq 6 is related to decamethyldiphenylmethane (**DDM**)[19] obtained in low yield (5%) as a byproduct from the CT chlorination of hexamethylbenzene in eq 4. Since the aromatic dimerization in eq 6 also arises directly from charge-transfer excitation, it is hereafter referred to as *CT dimerization*.

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[13] Benesi, H. G.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.

[14] Foster, R. *Organic Charge-Transfer Complexes*; Academic: New York, 1969.

[15] See: Foster, R. *Molecular Complexes* **1974**, *2*, 107.

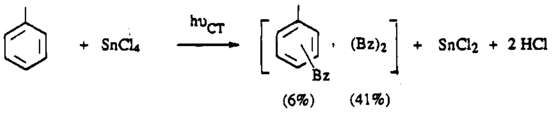
[16] Hanna, M. W.; Lippert, J. L. *Molecular Complexes* **1973**, *1*, 1.

[17] Compare: Phillip, W. H.; Marsik, S. J.; May, C. E. *U.S. Pat. Appl.* 527, 728, 1974; *Chem. Abstr.* **1975**, *83*, 211243h.

[18] See: Lau, W.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7100.

[19] Welch, C. M.; Smith, H. A. *J. Am. Chem. Soc.* **1951**, *73*, 4391.

Charge-transfer dimerization according to eq 6 was only a minor photoreaction of the toluene EDA complex with stannic chloride—the major dimeric hydrocarbon being bibenzyl, i.e.



(7)

where Bz = $C_6H_5CH_2$. The formation of bibenzyl as the head-to-head side-chain dimer (**BB**) was not an important process in the CT dimerization of durene (vide supra). However, **BB** was observed in small amounts (7%) with mesitylene as 3,3′,5,5′-tetramethylbibenzyl and in larger amounts (21%) with *p*-xylene as 4,4′-dimethylbibenzyl. The isomeric diphenylmethane (**DPM**) and bibenzyl (**BB**) in CT dimerization thus correspond to the side-chain and nuclear substitution, respectively, in CT chlorination. In addition to bibenzyl and benzyltoluene[20] as products of the CT dimerization of the toluene complex in eq 7, side-chain and nuclear chlorination were also observed in the form of benzyl chloride (30%) and chlorotoluene (16%). The isomeric composition of the latter was ortho (60%), para (40%), and meta (<1%). CT chlorination of *p*-xylene also resulted in the competition between side-chain and nuclear substitution in the form of *p*-xylyl chloride (54%) and 2-chloro-*p*-xylene (3%), respectively.

Charge-transfer chlorination and dimerization were also competing processes in the photoexcitation of the pentamethylbenzene EDA complex with stannic chloride. Side-chain chlorination yielded a mixture of tetramethylbenzyl chlorides in low yields (9%). Analogously, the CT dimerization of the pentamethylbenzene complex afforded a mixture of all three **DPM** dimers (78%) by GC–MS analysis, but they were not structurally characterized.

In order to examine the competition between CT chlorination and dimerization, the photoexcitation of the durene EDA complex was reexamined in the presence of chloride added as the tetra-*n*-butylammonium (TBA^+) salt. Indeed, the presence of 1.0 M TBA^+Cl^- during the CT excitation of 0.2 M durene and 0.45 M $SnCl_4$ in dichloromethane led to an increase in the yield of the ring-substituted 3-chlorodurene from 5 to 45% (the yield of 2,4,5-trimethylbenzyl chloride of 10% dropped to nil), mainly at the expense of the **DPM** dimer which decreased from 75% to 2% with a corresponding increase in **BB** dimer from nil to 41%.

The photoexcitation of the aromatic EDA complexes with stannic chloride uniformly resulted in the separation of stannous chloride as a fine white powder, as given in eqs 4–7. The precipitation of stannous chloride caused a considerable amount of light scattering which drastically reduced the photoefficiency of CT chlorination and dimerization. The scattered light also precluded the reliable measurement of the quantum yield (Φ). Nonetheless, we qualitatively judge from the photoconversion observed over a 24-h period that the intrinsic photoefficiency (i.e., in the absence of light scattering) for all processes was not high (Φ < 0.1).

Discussion

Spectroscopic studies establish the facile formation of a series of electron donor–acceptor complexes between the various aromatic donors (Table I) and stannic chloride according to eq 1 by the appearance of broad charge-transfer absorption bands (Figure 1) typical of intermolecular associations of the type described by Mulliken.[12,14] Such EDA complexes are clearly responsible for the array of photoproducts described in eqs 4–7, since they obtain only upon the specific irradiation of the charge-transfer absorption band. In order to account for how this complexion of products is formed, let us consider the spectral properties of the series of $SnCl_4$ complexes with reference to our earlier studies of the aromatic EDA complexes with titanium tetrachloride.[8,10] Thus, the linear variation of the CT transition energies ($h\nu_{CT}$) with the ionization potentials of the aromatic donors points to weak intermolecular interactions in the [ArH, $SnCl_4$] complexes that are characterized by the limited values of the formation constants $K_{EDA} < 2$ M^{-1}.[21] Most importantly, the direct correlation in Figure 2 of the CT transition energies for the $SnCl_4$ complexes with those previously measured for the aromatic EDA complexes with titanium tetrachloride[9] underscores their close structural relationship. Since the molecular structure of the $TiCl_4$ complex invokes a formal "halogen" bond[22] in its weak association with the aromatic donor as illustrated below (M = Ti), a similar charge-transfer structure pertains to the stannic chloride complex with M = Sn. Furthermore, the close response of the CT energies to the structural changes of the aromatic donors in Figure 2 also indicates that both series of EDA complexes undergo

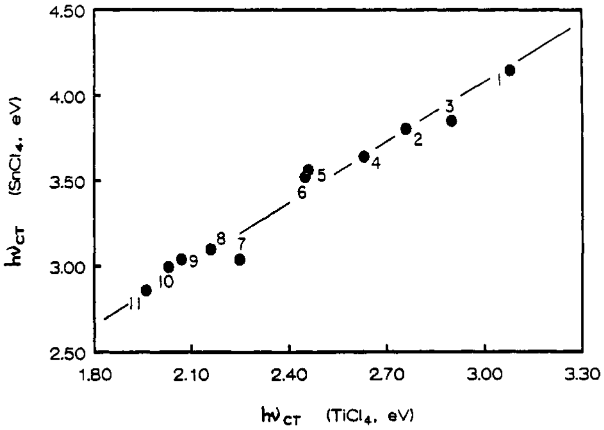
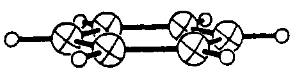
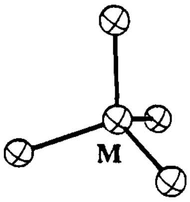


Figure 2. The direct correlation of the charge-transfer absorption bands of the EDA complexes of stannic chloride (ordinate) and titanium tetrachloride (abscissa) with the aromatic donors numbered in Table I.





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[20] As a mixture of ortho and para isomers.

[21] Briegleb, G. *Elektronen-Donator-Acceptor Komplexe*; Springer: Berlin, 1961. See also refs 14 and 16.

[22] Strieter, F. J.; Templeton, D. H. *J. Chem. Phys.* **1962**, *37*, 161. Strieter et al. presented the first example of halogen bonding in their X-ray crystallographic determination of the EDA complex of *p*-xylene and carbon tetrabromide. For related examples of halogen bonding based on X-ray crystallography and charge-transfer spectra of EDA complexes in the solid state and in solution, see: Blackstock, S. C.; Lorandt, J. P.; Kochi, J. K. *J. Org. Chem.* **1987**, *52*, 1451. Blackstock, S. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 2484.

Table II. Charge-Transfer Photochemistry of Aromatic EDA Complexes with Stannic Chloride[a]

	chlorination (%)		dimerization (%)	
aromatic donor	nuclear (CB)	side chain (BC)	bibenzyl (BB)	diphenylmethane (DPM)
hexamethylbenzene	0	95 (95)	0	5 (5)
pentamethylbenzene	6 (4)	9 (8)[b]	0	78 (84)[b]
durene	3 (1)	5 (3)	0	85 (95)[b]
mesitylene	25 (28)	50 (49)	7 (3)	11 (12)
p-xylene	3 (3)	54 (61)	21 (16)	13 (9)
toluene	16 (8)	30 (35)	41 (25)	6 (1)

[a] In cyclohexane solution containing 0.35 (0.06) M aromatic donor and 0.07 (0.65) M stannic chloride by irradiation with λ > 350 nm light at 23 °C. [b] Mixture of isomers.

essentially the same photoexcitation.[23] Indeed, the latter has been identified for the titanium complex as an intracomplex redox change, i.e.

$$[\mathrm{ArH, TiCl_4}] \xrightarrow{h\nu_{\mathrm{CT}}} [\mathrm{ArH^+, TiCl_4^-}] \qquad (8)$$

by the time-resolved spectral observation of transient ion radicals.[10] As such, the analogous formulation for the $SnCl_4$ complex leads to the reduced chlorotin anion, i.e.

$$[\mathrm{ArH, SnCl_4}] \xrightarrow{h\nu_{\mathrm{CT}}} [\mathrm{ArH^+, SnCl_4^-}] \qquad (9)$$

In the $TiCl_4$ complex, back electron transfer from the ion radical pair in eq 8 is facile, and the photostationary state in the charge-transfer process can be described as

Scheme I

$$\mathrm{ArH + TiCl_4} \overset{K_{\mathrm{EDA}}}{\rightleftharpoons} [\mathrm{ArH, TiCl_4}] \qquad (10)$$

$$[\mathrm{ArH, TiCl_4}] \underset{k_{-1}}{\overset{h\nu_{\mathrm{CT}}}{\rightleftharpoons}} [\mathrm{ArH^+, TiCl_4^-}] \qquad (11)$$

Consequently, no permanent photochemistry results, even upon the prolonged exposure of the EDA complex to light with sufficient energy to effectively populate the CT ion-pair state in eq 11. Thus, the efficiency of any photochemical transformation resulting from the chargetranfer excitation of $[\mathrm{ArH, TiCl_4}]$ is limited by the short lifetime of $\tau \sim 100$ ps that is dictated by the measured rates of back electron transfer from the ion radical pair in eq 11 of $k_{-1} \sim 10^{10}\ \mathrm{s^{-1}}$.[10] Since such fast rates lie in the Marcus inverted region for electron transfer,[24] the corresponding rate for $[\mathrm{ArH^+, SnCl_4^-}]$ in eq 9 is likely to be slower owing to the electron affinity of $SnCl_4$ which is substantially less than that of $TiCl_4$ by ~1.3 eV.[25] As such, the low quantum efficiencies for CT chlorination and dimerization in Table II can be reconciled with Scheme I by considering a "leakage" of the ion radical pair. Thus, an incomplete back electron transfer from the ion radical pair in eq 9 would lead to a (quasi) photostationary state in the charge-transfer activation of aromatic EDA complexes with stannic chloride that is modulated by the competition (k_1) from the followup process(es), i.e.

Scheme II

$$\mathrm{ArH + SnCl_4} \overset{K_{\mathrm{EDA}}}{\rightleftharpoons} [\mathrm{ArH, SnCl_4}] \qquad (12)$$

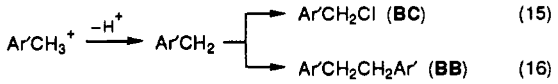
$$[\mathrm{ArH, SnCl_4}] \underset{k_{-1}}{\overset{h\nu_{\mathrm{CT}}}{\rightleftharpoons}} [\mathrm{ArH^+, SnCl_4^-}] \xrightarrow{k_1} \text{etc.} \qquad (13)$$

Since the ion radicals ArH^+ and $SnCl_4^-$ are by themselves labile species,[26,28] the extent to which either (or both) is diverted by alternate pathways (k_1) would render the back electron transfer (k_{-1}) in Scheme I to be less efficient, i.e., $\Phi = k_1/(k_1 + k_{-1}) > 0$. For example, the reduced acceptor $SnCl_4^-$ is formally a chlorostannate(III) anion, and like other coordinatively saturated paramagnetic species, it is expectedly labile to ligand dissociation,[27] i.e.

$$\mathrm{SnCl_4^-} \xrightarrow{k_1} \mathrm{SnCl_3 + Cl^-} \qquad (14)$$

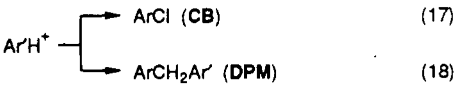
Indeed such a chloride heterolysis of the chlorostannate(III) intermediate can contribute to the followup steps in Scheme II. The resultant increase of k_1, coupled with the diminished importance of back electron transfer of $[\mathrm{ArH^+, SnCl_4^-}]$ is tantamount to an enhanced lifetime of the aromatic cation radical relative to that produced from the $TiCl_4$ complex in Scheme I.

The aromatic cation radicals derived from the (poly)methylbenzene donors ($Ar'CH_3$) pertinent to this study are known to be highly acidic and electrophilic species.[29] When the (poly)methylbenzene cation radicals suffer proton loss they generate benzyl radicals[30] which lead to side-chain substitution and the benzyl chlorides (**BC**) and bibenzyl dimers (**BB**) in Table II, i.e.



$$\mathrm{Ar'CH_3^+} \xrightarrow{-\mathrm{H^+}} \mathrm{Ar'CH_2} \begin{cases} \rightarrow \mathrm{Ar'CH_2Cl}\ (\mathbf{BC}) & (15) \\ \rightarrow \mathrm{Ar'CH_2CH_2Ar'}\ (\mathbf{BB}) & (16) \end{cases}$$

where $Ar'CH_3 \equiv ArH$.[31] Likewise, when the aromatic cation radicals undergo addition they can lead to nuclear substitution[29,32] and the chlorobenzenes (**CB**) and the diphenylmethane dimers (**DPM**) in Table II, i.e.



$$\mathrm{Ar'H^+} \begin{cases} \rightarrow \mathrm{ArCl}\ (\mathbf{CB}) & (17) \\ \rightarrow \mathrm{ArCH_2Ar'}\ (\mathbf{DPM}) & (18) \end{cases}$$

The nonuniform trends in the yields of the chlorinated products with systematic changes in the aromatic donor, as summarized in Table II, indicate that chlorine is introduced in side-chain (**BC**) and nuclear chlorination (**CB**) in eqs 15 and 17, respectively, by several competing pathways. Thus, the increased yields of 3-chlorodurene with added TBA^+Cl^- are consistent with the nucleophilic addition of chloride to the aromatic cation radical. The latter also accords with the isomeric distribution of chlo-

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rotoluenes that is akin to that observed during electrophilic chlorination.[33] Chlorine-atom transfer from either $SnCl_4$ or $SnCl_3$ (eq 14) to the benzylic radical would lead to stannous chloride.[34] Further studies are required to resolve the similar dichotomy that applies to the dimeric products **BB** and **DPM** in eqs 16 and 18, respectively.[18,26,29]

Experimental Section

Materials. Aromatic donors (commercial reagent-grade samples) were used as such or repurified as follows. Hexamethylbenzene (Eastman), durene (Aldrich), and pentamethylbenzene (Aldrich) were recrystallized from ethanol; mesitylene, *p*-xylene, and toluene were redistilled. Naphthalene (Allied), 1-methoxynaphthalene (Aldrich), 1,4-dimethylnaphthalene (Aldrich), anthracene (Aldrich, gold label), 9,10-dimethylanthracene (Aldrich), 9-bromoanthracene (Aldrich), and 2-*tert*-butylanthracene (Aldrich) were used as received. 9-Methylanthracene (Aldrich) was recrystallized from methanol. Stannic chloride (Matheson, Coleman and Bell reagent grade) was redistilled (bp 114 °C) according to standard procedures,[35] and the colorless liquid was stored in a Schlenk flask under an argon atmosphere prior to use. Cyclohexane (Aldrich) was distilled from sodium, and also stored in a Schlenk flask under an argon atmosphere. All subsequent manipulations with $SnCl_4$ were carried out with Schlenk techniques using an all-glass hypodermic syringe equipped with a Teflon (capillary) needle. Glassware was thoroughly dried in a 150 °C oven for at least 2 h and flushed with a stream of argon prior to use.

Determination of the Absorption Spectra and the Formation Constants of the Aromatic EDA Complexes with Stannic Chloride. In a typical experiment, a known amount of aromatic donor was added under an argon atmosphere to 3-mL aliquots of standard stock solutions (different concentrations) of $SnCl_4$ in cyclohexane. The solutions were then placed in a 1-cm quartz cuvette, and the absorbance was measured at the absorption maximum as well as at two other wavelengths close to the absorption maximum. From a plot of $[\text{arene}]/A_{CT}$ against $[SnCl_4]^{-1}$, the slope was estimated as $(K\epsilon_{CT})^{-1}$ and the intercept as ϵ_{CT}^{-1}. All plots were linear with a correlation coefficient of $r > 0.99$. Electronic spectra were recorded on a Hewlett-Packard 8450 diode-array spectrophotometer.

Charge-Transfer Photochemistry of Aromatic EDA Complexes with Stannic Chloride. The photochemical changes accompanying the charge-transfer excitation of the aromatic EDA complexes with stannic chloride were monitored by UV–vis spectroscopy. After a period of time, the reaction mixture was quenched with water, and the resulting extract was analyzed by quantitative gas chromatography using the internal standard method on a Hewlett-Packard 5890 chromatograph with a 12.5-m SE30 (cross-linked methylsilicone) capillary column. GC/MS measurements were carried out on a Hewlett-Packard 5890 chromatograph interfaced to a HP 5970 mass spectrometer (EI, 70 eV). Initially, a cyclohexane solution containing 0.06 M hexamethylbenzene and 0.65 M stannic chloride was irradiated with the focused beam from either a 500-W Osram (HBO-2L2) high-pressure Hg lamp or a 450-W Osram (XBO/OFR) mercury–xenon lamp. The light was passed through an IR water filter and a glass sharp cutoff filter (Corning CS-3 series) to remove light with $\lambda < 350$ nm. The temperature was maintained during the irradiation with the aid of a water bath. The monotonic decrease in the charge-transfer absorption band (Figure 1A) was followed for a 24-h period. The gas chromatography of the photolysate showed that it consisted of pentamethylbenzyl chloride (95% yield) by comparison with that of an authentic sample prepared from hexamethylbenzene and *N*-chlorosuccinimide. A small amount (5%) of decamethyldiphenylmethane,[19] but no decamethylbibenzyl, was observed. Equivalent results were obtained when the same solution was irradiated in a commercial chamber reactor [Rayonet RPR-100, New England Ultraviolet Co.] by utilizing the 3500-Å lamps which emitted an approximately Gaussian distribution of light with a half-band width of ±150 Å at 3520 Å. Accordingly, all the aromatic donors in Table II were treated in the chamber reactor by the standard procedures at both the high and low ratios of $[\text{Arene}]/[SnCl_4]$ given in Table I for a 24-h period. The products of side-chain chlorination (designated as **BC**) were independently prepared by the free-radical chlorination of the aromatic donor in carbon tetrachloride with sulfuryl chloride and benzoyl peroxide at 77 °C.[36] The products of nuclear chlorination (designated as **CB**) were either compared with commercial samples, or prepared for the aromatic donor via the ferric chloride-catalyzed chlorination with chlorine in carbon tetrachloride.[37] The bibenzyl dimers (**BB**) were significant only in the CT photochemistry of toluene, *p*-xylene, and mesitylene, and they were prepared by the free-radical dimerization of the aromatic donor with di-*tert*-butyl peroxide.[38] The diphenylmethane dimers (**DPM**)[19] of hexamethylbenzene, pentamethylbenzene, and durene were also available from previous studies.[18,29d,39] In each case, the product comparisons were carried out by GC–MS analysis. The charge-transfer photochemistry of 0.20 M pentamethylbenzene and 0.45 M $SnCl_4$ in dichloromethane afforded pentamethylchlorobenzene (45%) and a mixture of nonamethyldiphenylmethanes (53%), but in the presence of 1.0 M TBA^+Cl^- the yields of these products dropped to 13 and 0%, respectively, and a mixture of tetramethylbenzyl chlorides (33%) and octamethylbibenzyls (49%) was formed.

Stannic bromide (mp 31 °C) formed similar aromatic EDA complexes in cyclohexane (e.g., $h\nu_{CT} = 373$ and 392 nm for toluene and *p*-xylene). Prolonged irradiation under conditions similar to those described above yielded products of both side-chain and nuclear bromination, but the conversions were too low to warrant further studies.

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Registry No. Mesitylene·Cl_4Sn, 32870-87-4; naphthalene·Cl_4Sn, 35497-38-2; pentamethylbenzene·Cl_4Sn, 32870-85-2; hexamethylbenzene·Cl_4Sn, 32870-84-1; 1,4-dimethoxynaphthalene·Cl_4Sn, 139895-28-6; 1-methoxynaphthalene·Cl_4Sn, 139895-29-7; 9-bromoanthracene·Cl_4Sn, 139913-72-7; anthracene·Cl_4Sn, 35497-39-3; 2-*tert*-butylanthracene·Cl_4Sn, 139895-30-0; 9-methylanthracene·Cl_4Sn, 139895-31-1; 9,10-dimethylanthracene·Cl_4Sn, 139895-32-2; durene·Cl_4Sn, 32870-86-3; *p*-xylene·Cl_4Sn, 139895-33-3; toluene·Cl_4Sn, 36065-04-0.

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Synthesis of Chiral Functionalized *trans*-β-Isopropenyl-γ-(hydroxymethyl)-γ-butyrolactones[1]

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In connection with studies on the total synthesis of some members of the heliangolide family of sesquiterpenes,[2,3]

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