4.96%. The data to parameter ratio was 8.4:1.

9-Chloro-10-cyclopropylanthracene. Chlorine (1.55 mmol) was condensed into a 30-mL pressure tube containing 9-cyclopropylanthracene[14] (0.34 g, 1.6 mmol), anhydrous K_2CO_3 (0.22 g, 1.6 mmol), and 5 mL of carbon tetrachloride. The pressure tube was wrapped with aluminum foil and placed in a water bath maintained at 15 °C. After 1 h, the reaction mixture was filtered and the resulting filtrate concentrated on a rotary evaporator. The residue was purified by column chromatography (neutral alumina, 97:3 hexane-CH_2Cl_2). Recrystallization from ethanol afforded 0.25 g (65%) of the desired product, mp 117-118 °C; ^{1}H NMR ($CDCl_3$) δ 0.79 (m, 2 H, *cis*-cyclopropylmethylene H), 1.47 (m, 2 H, *trans*-cyclopropylmethylene H), 2.47 (m, 1 H, cyclopropylmethine), 7.51-7.61 (m, 4 H, 2-, 3-, 6-, and 7-H of anthryl), 8.69 (m, 2 H, 1- and 8-H of anthryl), 8.78 (m, 2 H, 4- and 5-H of anthryl); ^{13}C NMR ($CDCl_3$) δ 9.64 and 10.67 (cyclopropyl C), 121.78, 125.22, 126.29, 128.25, 128.65, 132.25 and 134.56 (anthryl C); MS (EI, 70 eV) *m/e* (relative intensity) 254 (14, M + 2), 252 (40, M^+), 217 (100), 215 (55), 202 (68), 108 (13), 101 (12), 95 (11). Anal. Calcd for $C_{13}H_{13}Cl$: C, 80.79; H, 5.15; Cl, 14.06. Found: C, 80.40; H, 5.19; Cl, 14.15. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a stoppered solution of the anthracene in acetonitrile. A single crystal of approximate dimensions 0.3 × 0.4 × 0.4 mm was chosen for this study. Crystal data for $C_{17}H_{13}Cl$: orthorhombic, space group $P2_12_12_1$ with a = 4.890 (2) Å, b = 14.698 (6) Å, c = 17.097 (7) Å, V = 1228.9 (9) Å^3, Z = 4, d_{calcd} = 1.366 g cm^{-3}, and fw = 252.7. A total of 1691 reflections were collected by the $\theta/2\theta$ scan method employing a 1.2° scan range (ω) and scan speeds varying from 3 to 15° min^{-1} in the 2θ range 3.5-45°. Of these, 1636 were unique with 1272 ($F > 3.0\sigma(F)$) observed reflections employed in the refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed at calculated positions and treated with a riding model with fixed isotropic U. A weighting scheme with ($w^{-1} = \sigma^2(F) + 0.0002F^2$) was employed in the refinement, and the data were corrected for extinction, yielding final R = 4.31% and R_W = 4.34%. The data to parameter ratio was 7.8:1.

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Supplementary Material Available: Labeled ORTEP plots, experimental details of the X-ray diffraction experiments, tables of final atomic positional parameters, atomic thermal parameters, and bond distances and angles from the X-ray structural determinations of the (2,4-dinitrophenyl)hydrazone of *p*-cyclopropylacetophenone, 4-cyclopropyl-1-naphthalenecarboxylic acid, and 9-chloro-10-cyclopropylanthracene (27 pages). Ordering information is given on any current masthead page.

The Use of Bis(4-chlorophenyl) Selenide/Lewis Acid Catalysts in the Electrophilic Chlorination of Toluene

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The electrophilic chlorination of toluene has been studied using bis(4-chlorophenyl) selenide/Lewis acids as catalysts. These catalysts generate ortho/para ratios which are considerably lower than those obtained using Lewis acids as catalysts with the ortho/para ratio decreasing as the reaction temperature increases in the range of -30 to 70 °C. The enhanced para selectivity observed using these catalysts has been ascribed to the intermediacy of a bis(4-chlorophenyl)selenium dichloride/Lewis acid complex which functions as a sterically hindered source of chlorine. Proton NMR studies in acetone-d_6 support the existance of bis(4-chlorophenyl)selenium dichloride/Lewis acid complexes which lose chlorine directly from the selenium atom. The loss of para selectivity as the reaction temperature decreases has been ascribed to an increase in the conversion of bis(4-chlorophenyl) selenide to bis(4-chlorophenyl)(4-methylphenyl)selenonium chloride, which does not function as a catalyst in this reaction. Although triarylselenonium chlorides are known to reductively eliminate to produce aryl chlorides, our studies have shown that only where the Lewis acid is aluminum(III) chloride does this occur. Subsequently, with the exception of aluminum(III) chloride, reductive elimination of bis(4-chlorophenyl)(4-methylphenyl)-selenonium chloride is not responsible for the high para selectivity observed under our conditions.

Introduction

The electrophilic chlorination of aromatic compounds such as toluene historically has involved the use of Lewis acid catalysts such as aluminum(III) chloride, iron(III) chloride, or antimony(V) chloride. These catalysts, in the case of toluene, generate a statistical mixture of *o*-chlorotoluene and *p*-chlorotoluene as well as minor amounts of *m*-chlorotoluene and polychlorotoluenes. In actual practice, the reaction appears to be quite complex with the product distribution varying widely depending on the reaction media, temperature, and nature of the chlorinating agent.[1-22] For example, Stock and Himoe[5]

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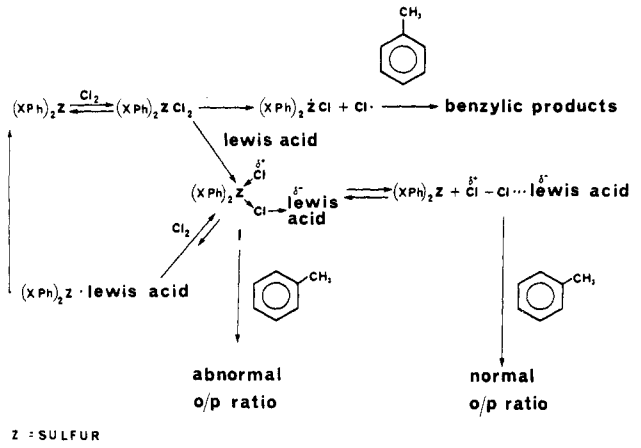
Scheme I. Previously Proposed Mechanism for the Chlorination of Toluene Using Diaryl Sulfide/Lewis Acid Catalysts



and Hugust and Ylla-Catalen[6] reported ortho/para ratios that varied from 0.52 to 2.27 as the solvent media for the reaction was changed. Direct chlorination using iron(III) chloride reportedly generates ortho/para ratios approaching 0.15 when 1 mol of toluene is reacted with 2 mol of iron(III) chloride at 50 °C.[17-19] Similar work was reported using other metallic chlorides such as $SbCl_5$, $TiCl_4$, $SnCl_4$, and $ZrCl_4$ as chlorinating agents.[20-22]

More recently, one of us (J.C.G.) reported that aromatic sulfides and selenides, when used with Lewis acids as co-catalysts, reduce the ortho/para ratio considerably to as low as 0.90.[23-25] This represents a significant increase in the yield of the para-chlorinated product which is the more important commercial product. Reduced ortho/para ratios have also been reported by others[26-30] using inorganic and organic sulfur compounds in conjunction with Lewis acids.

Previously, one of us (J.C.G.) proposed a mechanism involving the intermediacy of a sterically hindered diarylsulfonium dichloride/Lewis acid complex (I) as being responsible for the enhanced yield of *p*-chlorotoluene (Scheme I).[33] A similar mechanism was proposed by Nakayama[34] who obtained a reduced ortho/para ratio using phenoxanthine/antimony(III) chloride as the catalyst. Unfortunately, the sulfur intermediates proposed in this mechanism are unstable, preventing a closer study of the reaction by commonly used techniques such as ^1H NMR spectroscopy.

Diaryl selenides, on the other hand, which are known to yield diarylselenium dichlorides (II), possessing a trigonal-bipyramid structure with C_{2v} symmetry[35] similar to diarylsulfonium dichlorides (III),[36] are quite stable and can be studied by proton NMR spectroscopy. In this paper, we report the results of our investigation on the mechanism involved in the chlorination of toluene using bis(4-chlorophenyl) selenide/Lewis acid catalysts and the ortho/para ratios obtained.

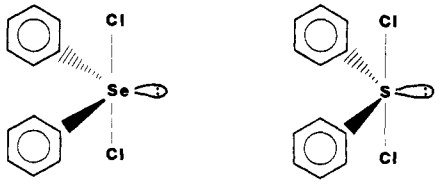
Table I. Summary of the Ortho/Para Ratios Obtained during the Catalyzed Chlorination of Toluene

temp, °C	$(ClPh)_2Se/AlCl_3$	$AlCl_3$	$(ClPh)_2Se/FeCl_3$	$FeCl_3$
-30	2.19	–	–	–
0	1.90	2.81	1.57	–
30	1.43	2.45	1.27	3.18
60	1.05	2.05	1.14	2.90

temp, °C	$(ClPh)_2Se/SbCl_3$	$SbCl_3$	$(ClPh)_2Se/SbF_3$	SbF_3	$(ClPh)_2Se/SbCl_5$	$SbCl_5$
-20	1.78	1.76	2.07	1.94	2.00	3.00
20	1.11	2.16	1.48	1.74	1.90	2.50
50	1.08	2.34	1.43	1.90	1.20	2.30
70	0.72	3.45	1.03	3.03	1.00	1.80

Table II. Percent Conversion of Bis(4-chlorophenyl) Selenide (IV) to Bis(4-chlorophenyl)(4-methylphenyl)selenonium Chloride (V) in the Bis(4-chlorophenyl) Selenide/Lewis Acid Catalyzed Chlorination of Toluene

	% triaryl compound (V) recovered as a function of the catalyst used				
temp, °C	$(ClPh)_2Se/AlCl_3$	$(ClPh)_2Se/SbCl_5$	$(ClPh)_2Se/FeCl_3$	$(ClPh)_2Se/SbCl_3$	$(ClPh)_2Se/SbF_3$
-30	82	–	–	–	–
-20	–	85	–	0	0
0	72	–	53	–	–
20	–	25	–	0	0
30	47	–	36	–	–
60	20	0	17	0	0



II III

Results and Discussion

Unlike the Lewis acid catalyzed chlorination of toluene, where the ortho/para ratio was observed to be higher and to change in an inconsistent fashion as the reaction temperature and Lewis acid is varied, the addition of bis(4-

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Scheme II. Potential Pathways Involved in the Reductive Elimination of Bis(4-chlorophenyl)(4-methylphenyl)selenonium Chloride in the Presence of Lewis Acids as Catalysts

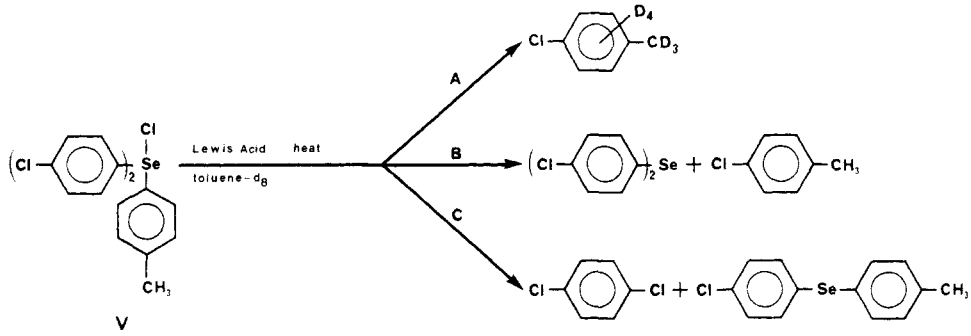
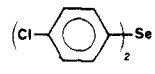


Table III. Analysis of the Products Obtained from the Reductive Elimination of Bis(4-chlorophenyl)(4-methylphenyl)selenonium Chloride (V) in Toluene-d_8

		chlorotoluene-d_7, %			chlorotoluene, %		
Lewis acid	temp, °C	ortho	para	o/p ratio	ortho	para	o/p ratio
$AlCl_3$	20	1.31	1.15	1.14	2.27	0.53	4.27
	50	2.51	2.42	1.04	16.10	48.60	0.33
$FeCl_3$	20	1.30	0.50	2.67	0.67	0.63	1.05
	50	1.16	0.38	3.09	0.44	0.48	1.09
$SbCl_5$	50	0.47	0.52	0.90	0.04	0.03	1.33
$SbCl_3$	50	0.06	0.09	0.59	nd[a]	0.02	na[b]
SbF_3	50	0.04	0.05	0.83	nd[a]	0.04	na[b]

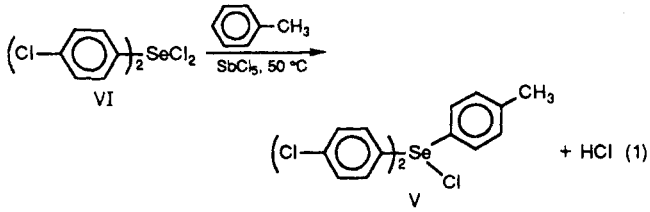
[a] nd = not detected. [b] na = not available.

chlorophenyl) selenide (IV) to the Lewis Acid generated reduced ortho/para ratios, which decreased consistently as the reaction temperature increased in the range of −30 to 70 °C regardless of which Lewis acid is used (Table I).



IV

Recovery of the selenide catalyst from the reaction mixtures where $AlCl_3$, $SbCl_5$, or $FeCl_3$ was used as the cocatalyst showed that the starting catalyst [bis(4-chlorophenyl) selenide (IV)] was being converted to bis(4-chlorophenyl)(4-methylphenyl)selenonium chloride (V). Identification of this compound was proven by instrumental analysis as well as its unequivocal synthesis as outlined in the Experimental Section. Analysis of the catalyst residue recovered after the reaction showed that the yield of bis(4-chlorophenyl)(4-methylphenyl)-selenonium chloride (V) decreased as the reaction temperature increased in a range of −30 to 60 °C when aluminum(III) chloride, antimony(V) chloride, or iron(III) chloride was used as the Lewis acid (Table II). No bis(4-chlorophenyl)(4-methylphenyl)selenonium chloride (V) was observed when antimony(III) chloride or antimony(III) fluoride was used as the Lewis acid catalyst in this temperature range. Since bis(4-chlorophenyl)selenium dichloride (VI) in toluene can be easily converted to bis(4-chlorophenyl)(4-methylphenyl)selenonium chloride (V) using a Lewis acid as the catalyst as shown in the synthetic section, it is likely that the same reaction occurs during the course of the chlorination reaction (eq 1). This implies



that bis(4-chlorophenyl)selenium dichloride (VI) must be present during the catalyzed chlorination of toluene. Attempts to chlorinate toluene using bis(4-chlorophenyl)(4-methylphenyl)selenonium chloride (V) have shown that this compound does not function as a catalyst in this reaction. Subsequently, the increase in the ortho/para ratio with decreasing temperature observed with $AlCl_3$, $FeCl_3$, and $SbCl_5$ appears to be caused by an increased conversion of bis(4-chlorophenyl) selenide (IV) to bis(4-chlorophenyl)(4-methylphenyl)selenonium chloride (V), thereby removing this cocatalyst from the reaction and generating ortho/para ratios approaching those obtained using Lewis acids alone (see Table I).

Since triarylsulfonium and -selenonium halides are reported to reductively eliminate, generating para-substituted aromatic compounds,[38] it is also possible that bis(4-chlorophenyl)(4-methylphenyl)selenonium chloride (V) can also reductively eliminate, generating *p*-chlorotoluene as outlined in Scheme II.

In order to test this hypothesis, bis(4-chlorophenyl)(4-methylphenyl)selenonium chloride (V) was unequivocally synthesized and reacted with Lewis acid catalysts $SbCl_5$, $SbCl_3$, SbF_3, $AlCl_3$, and $FeCl_3$ in toluene-d_8 as the solvent at 20 and/or 50 °C. Under our conditions, three results are possible as shown in Scheme II. If the reaction follows pathway a, no undeuterated chlorotoluene is formed indicating no reductive elimination. In pathway b, undeuterated chlorotoluene is observed, indicating reductive elimination of the triaryl compound (V). Finally, pathway c shows the presence of dichlorobenzene, indicating reductive elimination involving the chlorophenyl group of the triaryl compound (V). Although only the para isomers are shown in Scheme II, it should be realized that formation of the other isomers is also possible.

The results show that only $AlCl_3$ at 50 °C can effectively function as a catalyst in the reductive elimination of the

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Table IV. Chemical Shifts (ppm) Observed with Mixtures of Various Diarylselenium Compounds/Lewis Acid Complexes[a]

	no Lewis acid		$SbCl_3$		$SbCl_5$		SbF_3		$AlCl_3$	
diarylselenium compound	H_a	H_b	H_a	H_b	H_a	H_b	H_a	H_b	H_a	H_b
$(ClPh)_2SeCl_2$	8.11	7.69								
$(ClPh)_2SeCl_2\cdots SbX_5$					7.93 (multiplet)					
$(ClPh)_2SeCl_2\cdots SbX_3$			8.01 (quartet)	7.76	8.01 (quartet)	7.76	8.02 (quartet)	7.76	7.99	7.75
$(ClPh)_2Se\cdots SbCl_5$					8.01	7.76				
$(ClPh)_2Se$	7.41	7.46								
$(ClPh)_2Se\cdots SbX_3$			7.41	7.45	7.41	7.45	7.41	7.45	7.40	7.44

[a] Data in this table is based on 80- and 360-MHz studies.

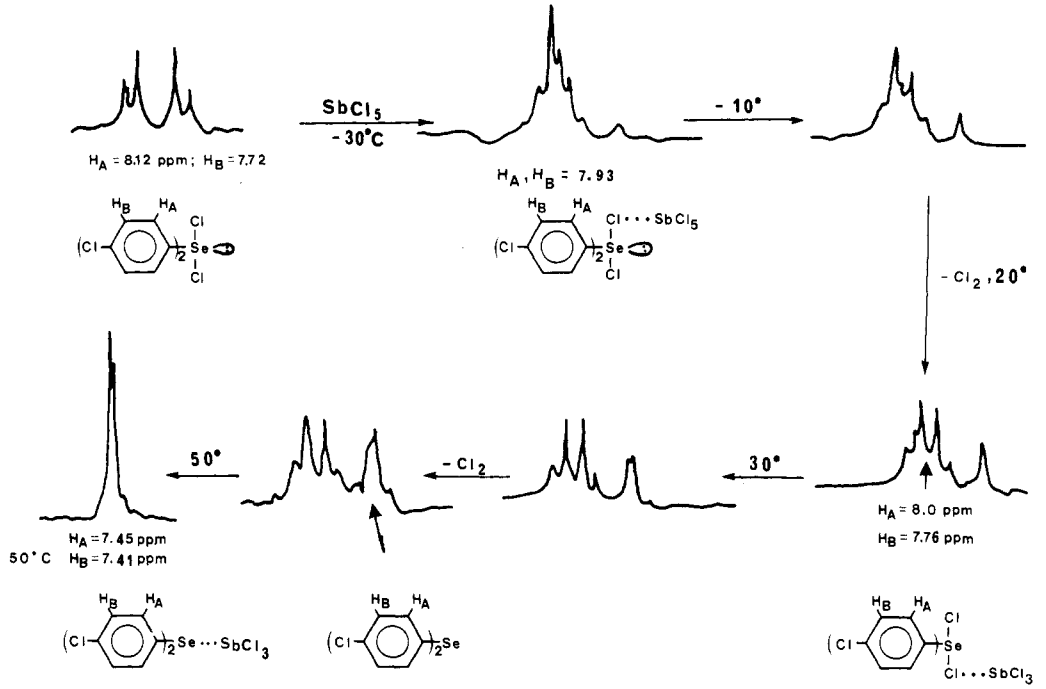


Figure 1. Proton NMR spectrum obtained after mixing equimolar amounts of bis(4-chlorophenyl)selenium dichloride (VI) and antimony(V) chloride at −30 °C and then heating mixture to 50 °C.

triaryl compound (V), yielding large amounts of the ortho and para-chlorinated products (Table III). The other catalysts, i.e. $FeCl_3$, $SbCl_5$, $SbCl_3$, and SbF_3, produce only minimal amounts of reductive elimination products. Minimal amounts of scrambling were also observed when using $AlCl_3$ as the Lewis acid catalyst as evidenced by the appearance of deuterated chlorotoluene products. Iron(III) chloride and antimony(V) chloride, which are capable of acting as chlorinating agents,[17-22] produced small amounts of chlorotoluene-d_7 as a result of the direct chlorination of the solvent by the Lewis acid catalyst. No dichlorobenzene was observed eliminating the participation of pathway c.

Unfortunately, chlorinations conducted using catalytic amounts of bis(4-chlorophenyl) selenide (IV) and $SbCl_3$ or SbF_3 did not produce the triaryl compound (V, Table II), despite the fact that the ortho/para ratio was observed to decrease as the reaction temperature increased as observed when $SbCl_5$, $AlCl_3$, or $FeCl_3$ was used as the Lewis acid (Table I). Lewis acids such as $SbCl_3$ and SbF_3, which exist in lower oxidation states, generate different results than $AlCl_3$, $FeCl_3$, and $SbCl_5$, which exist in fully oxidized valence states. Unlike the fully oxidized systems, which when used as the sole catalysts show a decrease in the ortho/para ratio with increasing reaction temperature, those catalysts existing in their lower oxidation states (SbF_3 and $SbCl_3$) show an increase in the ortho/para ratio with increasing reaction temperature (Table I).

In an attempt to further understand the reaction mechanism, we studied the interaction between equimolar mixtures of bis(4-chlorophenyl)selenium dichloride (VI) and Lewis acids in acetone-d_6 using ^1H NMR spectroscopy. The results which are summarized in Table IV and reproduced in Figures 1–4, show that bis(4-chlorophenyl)selenium dichloride (VI) forms a complex with antimony(V) chloride at −30 °C as evidenced by an upfield shift of the aromatic protons (H_a and H_b) from 8.11 and 7.69 ppm in the case of bis(4-chlorophenyl)selenium dichloride (VI) to a multiplet around 7.93 ppm. Within a short period of time, this multiplet resolves as a quartet centered at 8.01 and 7.76 ppm. Ultimately, this quartet shifts to a quartet at 7.41 and 7.45 ppm, which is identical with the field position and pattern exhibited by bis(4-chlorophenyl) selenide (IV) with or without Lewis acid (Figure 1). With the exception of the multiplet centered around 7.93 ppm, antimony(III) chloride, antimony(III) fluoride, and aluminum(III) chloride give identical ^1H NMR spectra when mixed in an equimolar ratio with bis(4-chlorophenyl)selenium dichloride (VI) (Table IV). The addition of antimony(V) chloride to bis(4-chlorophenyl) selenide (IV) at room temperature initially produced a quartet at 8.01 and 7.76 ppm (Figure 2), identical with that observed with bis(4-chlorophenyl)selenium dichloride (VI)/antimony(III) chloride (Figure 2), indicating that chlorine is transferred from the antimony atom and is lost directly from the selenide atom, not the Lewis acid. This information can

best be explained as shown in eq 2.

$$(ClPh)_2SeCl_2 + MX_5 \rightarrow (ClPh)_2SeCl_2\cdots MX_5 \xrightarrow{-Cl_2} (ClPh)_2SeCl_2\cdots MX_3 \xrightarrow{-Cl_2} (ClPh)_2Se\cdots MX_3 \quad (2)$$

where M = Al, Sb; X = Cl, F (except MX_5 where M = Sb and X = Cl)

When antimony(III) fluoride is used as the Lewis acid, a long-lived equilibrium appears to exist between two complexes presumed to be VII and VIII as shown in eq 3 (Figure 3). This equilibrium is not observed in the case

$$\underset{\text{VII}}{(ClPh)_2SeCl_2\cdots SbF_3} \qquad \underset{\text{VIII}}{(ClPh)_2Se\cdots SbF_3Cl_2} \quad (3)$$

of $SbCl_3$, implying an increased stability of and slower release of chlorine from the antimony(III) fluoride versus the antimony(III) chloride system (Figure 4).

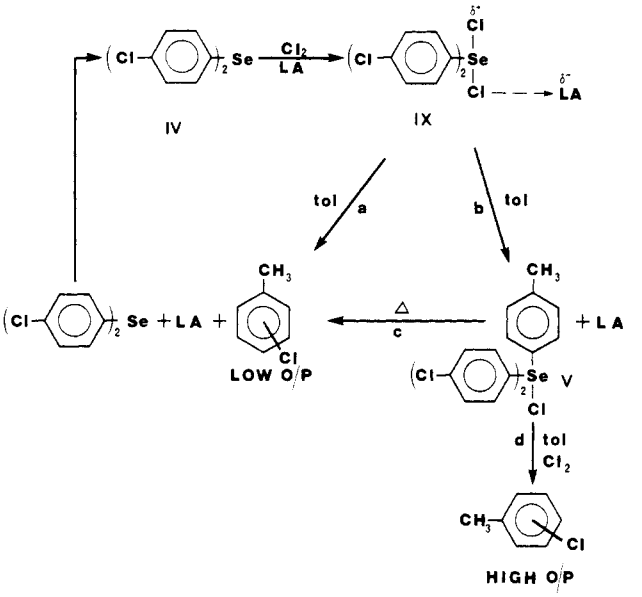
Since the ^1H NMR studies at room temperature show that bis(4-chlorophenyl)selenium dichloride (VI)/Lewis acid complexes convert over an 8-h period to bis(chlorophenyl) selenide (IV)/Lewis acid complexes (Figure 1), it might be argued that these complexes could not exist at temperatures higher than room temperature where the catalytic chlorination reaction is commonly conducted. However, we have observed that bis(4-chlorophenyl)selenium dichloride (VI) decomposes over a 24-h period at room temperature in the absence of Lewis acid in acetone-d_6, and it appears that acetone-d_6 is a poor solvent for evaluating the stability of these complexes. Studies in toluene-d_8 have shown that bis(4-chlorophenyl)selenium dichloride (VI) has increased stability in this solvent. Unfortunately, bis(4-chlorophenyl)selenium dichloride (VI)/Lewis acid complexes are not readily soluble in toluene-d_8 at room temperature, and this solvent could not be used in the NMR studies.

Assignment of the protons in the ^1H NMR spectra can be explained as follows: The lone pair of electrons in the diarylselenium dichloride trigonal-bipyramidal structure is strongly polarized toward the electronegative chlorine atoms. A partial positive charge may then develop around the selenium atom, resulting in the deshielding of the "H_a" protons in the chlorophenyl group. Free rotation of these groups allows the four aromatic protons to exhibit equivalent chemical shifts. When the Lewis acid is added, it complexes with one of the chlorines, polarizing the electrons toward the Lewis acid, inducing a partially positive charge in the chlorine atoms. The selenium's lone pair of electrons is then no longer polarized toward the halogens, and a higher electron density concentrates around the selenium. The "H_a" protons then become more shielded than before and absorb at higher field.

Based on the evidence accumulated to date, we propose the mechanism shown in Scheme III for the electrophilic chlorination of toluene and presumable other neutral aromatic compounds using diaryl selenides/Lewis acids as cocatalysts.

According to this mechanism, a complex (IX) forms between bis(4-chlorophenyl)selenium dichloride (VI) and the Lewis acid (IX) which, depending on the Lewis acid and reaction temperature, can react with toluene by either pathway a or b. Pathway a, which involves an attack by toluene on a sterically hindered complex (IX) containing a positively charged chlorine, generates low ortho/para ratios. Pathway b, which involves an attack by toluene on the selenium atom of complex IX, generates triarylselenonium chloride (V), effectively removing the selenide from a catalytic role in the reaction leaving the Lewis acid as the sole catalyst and generating higher ortho/para ratios. When using aluminum(III) chloride as the Lewis

Scheme III. Proposed Mechanism for the Chlorination of Toluene Using Bis(4-chlorophenyl) Selenide (IV)/Lewis Acid Catalysts



acid catalyst, the triaryl compound (V) can reductively eliminate at higher temperatures (e.g. 50 °C) via pathway c to produce low ortho/para ratios, thereby enhancing the yield of the para-chlorinated product.

Conclusions

The evidence to date implicates a sterically hindered diarylselenium dichloride/Lewis acid complex (IX) which is responsible for the low ortho/para ratios obtained during the chlorination of toluene. During the course of the chlorination reaction, the diaryl selenide (IV) may be converted, depending on the Lewis acid catalyst ($SbCl_5$, $AlCl_3$, $FeCl_3$) and on the reaction temperature, to a triarylselenonium chloride (V). This compound effectively removes the modifying influence of the diaryl selenide catalyst, generating higher ortho/para ratios that are consistent with the use of Lewis acids as the sole catalysts. Under certain conditions, such as when using aluminum(III) chloride as the cocatalyst at 50 °C, the bis(4-chlorophenyl)(4-methylphenyl)selenonium chloride (V) may reductively eliminate, generating large amounts of the para product, thereby enhancing the ortho/para ratio. Those Lewis acid cocatalysts which do not exist in their highest valence state ($SbCl_3$, SbF_3) appear to react differently than the other Lewis acid cocatalysts. Despite the fact that these Lewis acids complex with the diarylselenonium dichloride (VI) as evidenced by ^1H NMR data, they do not form bis(4-chlorophenyl)(4-methylphenyl)selenonium chloride (V) at temperatures as low as −20 °C. In addition, the addition of the diaryl selenide reverses the trend in the ortho/para ratios observed with these Lewis acid catalysts whereas diaryl selenide only enhances the trend in the ortho/para ratios observed with Lewis acid catalysts which are in their highest oxidation state ($AlCl_3$, $FeCl_3$, $SbCl_5$). It is also interesting that antimony(III) chloride, which one predicts should be converted to antimony(V) chloride during the chlorination reaction, does not generate the same ortho/para ratio as antimony(V) chloride. In addition, it is observed that the lowest ortho/para ratios were obtained using bis(4-chlorophenyl) selenide (IV)/antimony(III) chloride as the catalyst and that this ortho/para ratio was significantly lower than that obtained using bis(4-chlorophenyl) selenide (IV)/antimony(V)

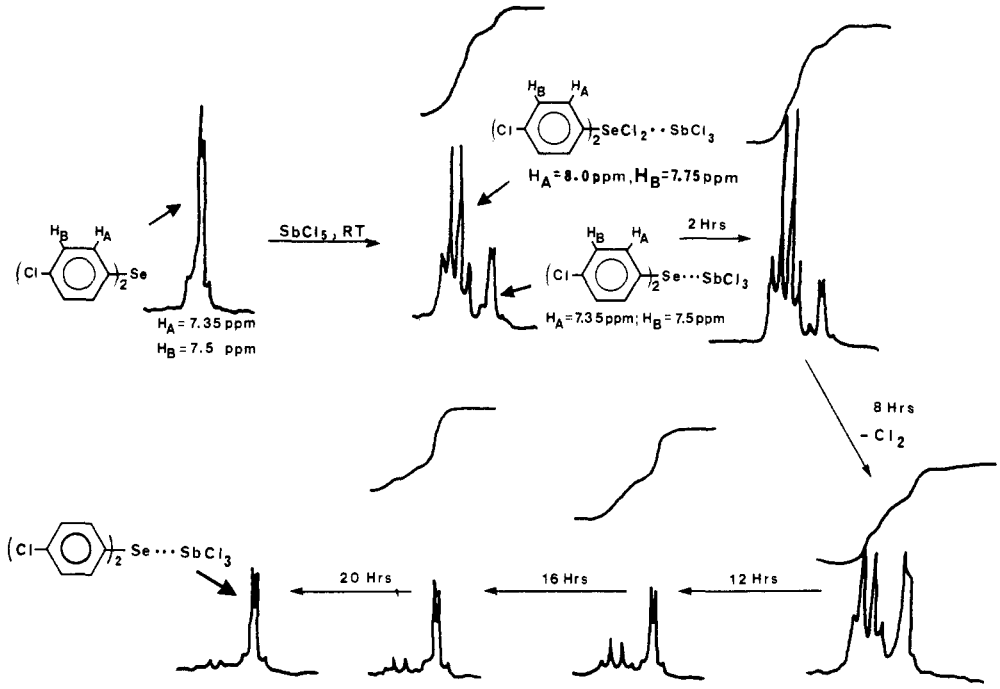


Figure 2. Proton NMR spectrum obtained after mixing equimolar amounts of bis(4-chlorophenyl)selenide (IV) and antimony(V) chloride at room temperature.

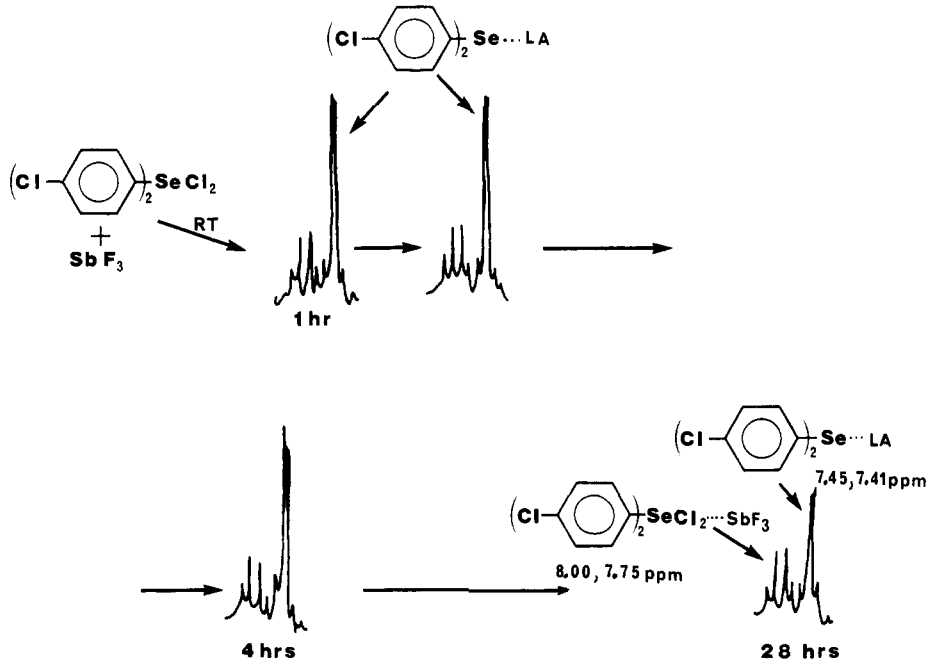


Figure 3. Proton NMR spectra obtained after mixing equimolar amounts of bis(4-chlorophenyl)selenium dichloride (VI) with antimony(III) fluoride at room temperature.

chloride as the catalyst. This data certainly suggests that antimony(III) chloride is not converted to antimony(V) chloride during the course of the chlorination reaction.

Experimental Section

Melting points were determined using a Mel-Temp apparatus. All melting points are uncorrected. Infrared spectra were obtained using an IBM Model 44 FTIR spectrophotometer. NMR and mass spectra were obtained using a FT 80A Varian or a Brucker FT 360 spectrophotometer and a Finnigan Model 4021 mass spectrophotometer, respectively. Gas chromatographic analysis was performed using a Varian Model 90-P with a 20 ft × $^1/_4$ in. 10% DC-QF-1 silicone on stainless steel column at 70 °C on thermal detector or a Hewlett-Packard Model 5890 GC using a 30-m DB-5 capillary column. All commercial compounds used in this research were of good quality and were used without further purification. All solvents used in this study were anhydrous.

Bis(4-chlorophenyl) Selenide (IV).[37] Leicester's method was used with modification, as follows: 28 g (0.50 mol) of potassium hydroxide powder was mixed with 20 g (0.25 mol) of selenium powder in a 250-mL Erlenmeyer flask. This mixture was heated in an oil bath at 140 °C until a thick, dark red homogeneous liquid was obtained. Ice water was then added slowly to the red liquid in a 500-mL flask. The solution was kept in an ice bath until used. Separately, a solution prepared from 27.0 g of 37% hydrochloric acid and 15.8 g (0.125 mol) of *p*-chloroaniline was cooled to −5 °C and diazotized with an aqueous solution of 10.8 g (0.125 mol) of sodium nitrite with ice being added to the reaction mixture during the diazotization reaction in order to keep the temperature below 5 °C. The resulting diazotized solution was added slowly into the previously prepared potassium selenide solution with stirring. When all the diazotized solution had been added, the resulting mixture consisted of a red aqueous

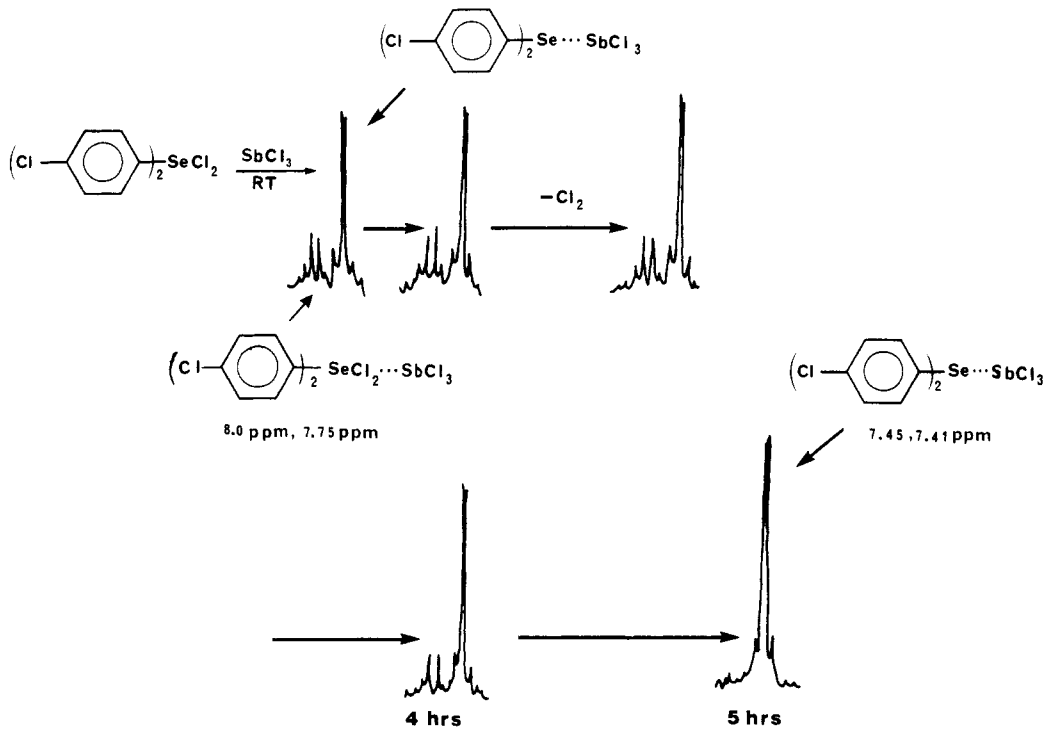


Figure 4. Proton NMR obtained after mixing equimolar amounts of bis(4-chlorophenyl)selenium dichloride (VI) with antimony(III) chloride at room temperature.

layer and a dark, oily layer. The red aqueous layer was decanted from the dark, oily layer, heated to boiling, and then poured back into the oily layer with continuous stirring. This treatment converts the selenium from the red colloidal form into the more easily filterable black form. Finally, the aqueous layer was extracted three times with 20-cm^3 portions of chloroform. The chloroform was then evaporated, and the resultant solids were recrystallized from hot methanol and charcoal several times. Silvery, light-yellow crystals of bis(4-chlorophenyl) selenide (IV) were obtained in 25% yield. The mp was 95–96 °C. (lit.[37] mp 96–97 °C.).

Bis(4-chlorophenyl)selenium Dichloride (VI). Five grams (0.165 mol) of bis(4-chlorophenyl) selenide (IV) was dissolved in 50 mL of anhydrous carbon tetrachloride in a 125-mL three-neck round-bottom flask. The flask was equipped with a thermometer, a condenser fitted with a calcium chloride drying tube, and a chlorine gas inlet. The reaction vessel was cooled to −15 °C to −20 °C. Chlorine gas, dried by passing through a concentrated sulfuric acid solution, was bubbled into the reaction vessel. The dichloride precipitated from the solution after 1 h reaction time. After filtration and washing three times with anhydrous carbon tetrachloride, white/grayish crystals (V) were obtained in 71% yield. The mp was 174–176 °C. ^1H and ^{13}C NMR (360 MHz) data and the mass spectrum were consistent with the structure of the compound.[1-3]

Synthesis of Bis(4-chlorophenyl)(4-methylphenyl)-selenonium Chloride (V). Two grams (5.36×10^{-3} mol) of bis(4-chlorophenyl)selenium dichloride (VI) was dissolved in 9.86 g (35.13 mL) of anhydrous toluene and placed in a round-bottom flask equipped with a stirring bar and fitted with a condenser. To this solution was added 1.50 grams (6.57×10^{-3} mol) of antimony(V) chloride, and the temperature was decreased to 10 °C. The grayish-brown precipitate, which formed over a 4-h period, was filtered and washed with diethyl ether. When dry, the solid bis(4-chlorophenyl)(4-methylphenyl)selenonium chloride, obtained in 58% yield, was found to have a melting point of 184–186 °C. ^1H and ^{13}C NMR (360 MHz) data and mass spectra were consistent with the structure of the compound.[1-3]

Chlorination Procedure. The following is an example of the experimental procedure used in the catalytic chlorination of toluene: 5 mmol of Lewis acid and 5.0 mmol (1.5 g) of bis(4-chlorophenyl) selenide (IV) were dissolved in 0.5 mol (46 g) of anhydrous toluene in a three-neck round-bottom flask equipped with a thermometer, a condenser fitted with a calcium chloride drying tube, a magnetic stirring bar, and a chlorine gas inlet. Chlorine gas, which was dried by passing through a concentrated sulfuric acid solution, was bubbled into the reaction vessel at a flow rate of 5.75 (±2%) g/h for 4 h. A small amount of the reaction mixture was removed periodically and analyzed by GC and GC/MS; the remainder was worked up according to the following procedures. The temperature during the reaction was controlled where necessary using a thermowatch. Percent conversions varied considerably, depending on temperature and catalyst, with the ortho/para ratios remaining reasonably constant during the initial stages of the reaction. In the latter stages, the ortho/para ratio tended to decrease slightly as monochlorinated products were converted to di- and trichlorinated products. For additional details, the reader is referred to the original thesis.[1-3]

Analysis of Reaction Mixture. The analyses of the reaction mixture was accomplished using GC, GC/MS, and ^1H NMR spectroscopy. Isomer ratios were determined using a Hewlett-Packard Model 5890 GC with 30-m DB-5 capillary columns or, in limited instances, a Varian Model 90P GC using a 20 ft × $^1/_4$ in. 10% DC-QF-1 silicone column, and programmed temperatures. (Initial temperature was 50 °C for 15 min, and then increased to 250 °C at a rate of 15 °C/min and held at that temperature for 15 min.)

Reaction Mixture Workup. Any precipitated solid was filtered out of the reaction mixture and allowed to air-dry prior to proton NMR analysis. The liquid portion of the reaction mixture was extracted with water in order to remove any bis(4-chlorophenyl)(4-methylphenyl)selenonium chloride (V). The water layer was then extracted with chloroform, which was allowed to evaporate. The solid residue was dissolved in deuterated acetone (acetone-d_6) for NMR analysis.

Reductive Elimination Procedure. The following is an example of the conditions used for the reductive elimination reactions: 2.3 mmol (1.0 g) of bis(4-chlorophenyl)(4-methylphenyl)selenonium chloride (V) was added to 0.046 mol (4.6 g) of deuterated toluene (toluene-d_8) in the presence of 2.3 mmol of a Lewis acid in a 100-mL three-neck round-bottom flask equipped with a thermometer and a condenser. The solution was allowed to react with stirring for 4 h at 20 °C or 50 °C, and the products were analyzed using GC and GC/MS techniques.

^1H NMR Conditions. The following is an example of the conditions used for the ^1H NMR studies: 0.1 g (3.3×10^{-4} mol) of bis(4-chlorophenyl)selenium (IV) was dissolved in acetone-d_6, 0.4 mL (3.3×10^{-4} mol) of antimony(V) chloride was added, and

the mixture was shaken in a test tube. The ^1H NMR of the sample was run at different intervals of time. In the case of low temperature studies, a 0.1-g sample (2.69×10^{-4} mol) of bis(4-chlorophenyl)selenium dichloride (VI) was dissolved in about 1 mL of acetone-d_6, which had been previously cooled to −50 °C. An equimolar amount of antimony(V) chloride was then added. A portion of the contents was transferred to a NMR tube. The whole operation was performed in a glovebag filled with nitrogen gas, and the NMR tube was always kept in a mixture of isopropyl alcohol and liquid nitrogen at −50 °C. The NMR tube was sealed, and the ^1H NMR spectra were run at the required temperatures which varied from −30 °C to 50 °C.

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Asymmetric Synthesis Using Tartrate Ester Modified Allylboronates. 1. Factors Influencing Stereoselectivity

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A detailed study of the factors that influence the enantio- and diastereoselectivity of the reactions of tartrate allylboronate **1** with chiral and achiral aldehydes is reported. The stereoselectivity of these reactions is sensitive to variables such as reaction temperature (best results invariably are obtained at −78 °C), solvent (toluene is best for aliphatic aldehydes; THF is preferred for aromatic aldehydes), and moisture (use of molecular sieves is recommended to maintain an anhydrous reaction environment), but not on the structure of the tartrate ester. Tartrate allylboronate **1** has been found to be exceptionally reactive compared to other, previously studied allylboronates, and even the reactions of very hindered substrates (e.g., pivalaldehyde) are complete within several hours at −78 °C. An improved method for synthesis of **1** is described that involves the reaction of allylmagnesium bromide with $(iPrO)_3B$ followed by aqueous hydrolysis and esterification with DIPT. Yields of **1** are considerably higher (65–76%) by using this new procedure, and the crude reagent so prepared may be used directly in allylboration experiments. A simple method for standardizing solutions of **1** is described. Finally, the absolute stereochemistry of five homoallylic alcohols (**5a–e**) were assigned by correlation with epoxy alcohols prepared via the Sharpless asymmetric epoxidation. The results of these correlations are in complete agreement with the stereochemical picture presented in our 1985 publication.

The reactions of allyl- and crotylmetal reagents with chiral carbonyl compounds are of considerable interest in the context of acyclic diastereoselective synthesis.[2,3] Studies from several laboratories have shown that allyl- and crotylboron reagents are particularly attractive as enolate surrogates for the aldol-like construction of the 1,3-dimethyl-2-hydroxy and 1,3-diol units that occur with high frequency in macrolide, ansamycin, and other natural products of propiogenic/acetogenic biosynthetic origin.[3-7] Like the aldol reaction, however, double asymmetric synthesis using chiral reagents is often necessary to achieve synthetically useful levels of aldehyde diastereofacial selectivity.[3,8,9] The chiral allylboron reagents developed by Hoffmann[4] and Brown[5] are noteworthy in this respect, as are the highly enantioselective allylmetal reagents recently introduced by Masamune, Reetz, Hoppe, Riediker, and Corey, among others.[6]

We have contributed the diisopropyl tartrate modified allyl- and crotylboronates **1–3** to this rapidly evolving field.[7] These readily accessible and synthetically convenient reagents exhibit good to excellent enantioselectivity with achiral aliphatic aldehydes and, more importantly, function

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