

Reaction of Areneselenenyl Chlorides and Alkenes. An Example of Nucleophilic Displacement at Bivalent Selenium¹

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The effect of substituents in the phenyl ring of both the electrophile and the alkene has been studied in the reaction of areneselenenyl chlorides and (*E*)- and (*Z*)-1-phenylpropenes. Electron-donating groups in both phenyl rings enhance the rate of reaction. Viewing this reaction as a nucleophilic displacement at bivalent selenium leads to a model that allows the possibility of reaction by a continuum of mechanisms. These mechanisms differ only in the relative amounts of C-Se bond making and Se-Cl bond breaking in the rate-determining transition state. From our data, it is concluded that C-Se bond making lags behind Se-Cl bond breaking in the rate-determining transition state.

The reactions of areneselenenyl chlorides and alkenes are usually considered to be electrophilic addition reactions.³ Viewed in this way, we can compare these reactions with the additions of other electrophiles such as arenesulfenyl chlorides, the halogens, and interhalogens.⁴ As a result of such comparisons, a two-step mechanism for the addition of areneselenenyl chloride to alkenes has been suggested similar to that proposed for the addition of arenesulfenyl chlorides.⁵ That is a rate-determining first step leading to the formation of a seleniranium ion⁶ followed by a second product-determining step.

However such a mechanism is not unique. Indeed if the reaction of areneselenenyl chlorides and alkenes is regarded as a nucleophilic displacement at bivalent selenium,⁷ several variations of this two-step mechanism can be envisioned. The first, analogous to the S_N1 mechanism at a saturated carbon atom, is shown in Figure 1a. A second, analogous to the S_N2 mechanism at a saturated carbon atom, is shown in Figure 1b. Finally an addition-elimination mechanism is shown in Figure 1c.

These three mechanisms differ in the relative amounts of C-Se bond making and Se-Cl bond breaking in the step or steps leading to the formation of the seleniranium ion. Thus Se-Cl bond breaking occurs before C-Se bond making in mechanism 1a. Both Se-Cl bond breaking and C-Se bond making occur in mechanism 1b, while C-Se bond making occurs before Se-Cl bond breaking in mechanism 1c. Thus these three, rather than being distinct mechanisms, are extremes of a common mechanism that differ in the timing of the covalency changes at selenium.

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Table I. Rate Constants for the Addition of 4-Substituted Benzeneselenenyl Chloride to (*Z*)- and (*E*)-1-Phenylpropene in Methylene Chloride at 25 °C

substituent	$k_2, M^{-1} s^{-1}$	
	<i>Z</i>	<i>E</i>
CH ₃ O	48.2 ± 0.5	98.2 ± 0.8
CH ₃	12.6 ± 0.3	22.5 ± 0.8
H	5.13 ± 0.09	7.88 ± 0.07
F	3.07 ± 0.06	5.03 ± 0.05
Cl	2.91 ± 0.08	4.28 ± 0.07
Br	2.43 ± 0.07	3.47 ± 0.06
CF ₃	0.583 ± 0.007	0.733 ± 0.009
NO ₂	0.291 ± 0.003	0.355 ± 0.004

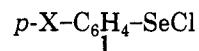
Table II. Rate Constants for the Addition of Benzeneselenenyl Chloride to a Series of Ring-Substituted (*Z*)- and (*E*)-1-Phenylpropenes in Methylene Chloride at 25 °C

substituent	$k_2, M^{-1} s^{-1}$	
	<i>Z</i>	<i>E</i>
4-C ₆ H ₅ O		122 ± 9
4-CH ₃ O	55.6 ± 0.8	444 ± 12
4-CH ₃	22.2 ± 0.9	33.4 ± 0.6
H	5.13 ± 0.07	7.88 ± 0.09
4-Cl	1.95 ± 0.06	3.82 ± 0.07
4-NO ₂		0.151 ± 0.005
3-NO ₂	0.079 ± 0.009	0.176 ± 0.007

To determine this timing and the charge distribution in the rate-determining transition state relative to the ground state, we have studied the effect of substituents in the phenyl ring of both the areneselenenyl chloride and (*E*)- and (*Z*)-1-phenylpropene. The results of this study and the mechanistic conclusions drawn from the data are the subject of this paper.

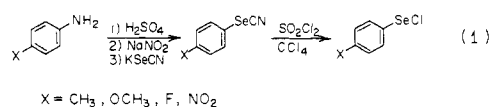
Results and Discussion

The areneselenenyl chlorides 1a, 1b, 1e, and 1h were



- a, X = OCH₃ e, X = F
 b, X = CH₃ f, X = Br
 c, X = H g, X = CF₃
 d, X = Cl h, X = NO₂

prepared by the reaction sequence shown in eq 1. The



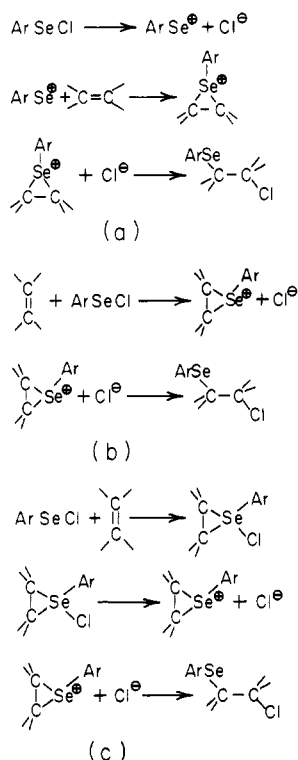
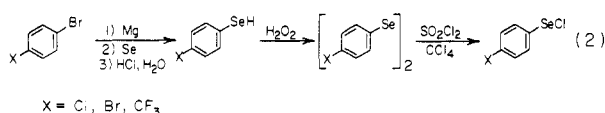


Figure 1. Three possible mechanisms for the reaction of areneselenenyl chlorides and alkenes.

others **1d**, **1f**, and **1g** were prepared by the sequence shown in eq 2. The rates of addition were determined by



measuring the decrease in the absorption of the areneselenenyl chlorides at 433 nm in anhydrous methylene chloride at 25 °C using a Durrum-Gibson stopped-flow spectrophotometer. All additions were found to exhibit second-order kinetics, first order in alkene and first order in areneselenenyl chloride to at least 80% completion of the reaction. The rate constants for the addition of a series of 4-substituted benzeneselenenyl chlorides to (*Z*)- and (*E*)-1-phenylpropenes are reported in Table I. The rate constants for the addition of benzeneselenenyl chloride to a series of ring-substituted (*Z*)- and (*E*)-1-phenylpropenes are reported in Table II.

The rate data given in Tables I and II were plotted against σ and σ^+ substituent constants.⁸ The values of ρ , ρ^+ , and their correlation coefficients are given in Table III. In an attempt to gain further information about the structure of the rate-determining transition state, the effect of substituents in the 4-position were separated into their polar and resonance contributions by means of the following dual substituent parameter equation.⁹

$$\log \frac{k}{k_0} = \rho_I \sigma_I + \rho_R \sigma_R$$

Values of ρ_I and ρ_R obtained by correlation against Taft values of σ_{R^0} , σ_R , and σ_{R^+} are given in Table IV. The best

Table III. Values of ρ and ρ^+ for Reactions of Areneselenenyl Chlorides and (*Z*)- and (*E*)-1-Phenylpropenes in CH₂Cl₂ at 25 °C

	ρ (<i>r</i>)	ρ^+ (<i>r</i>)
(<i>Z</i>)-ArCH=CHCH ₃ + C ₆ H ₅ SeCl	-2.91 (0.979)	-1.51 (0.958)
(<i>E</i>)-ArCH=CHCH ₃ + C ₆ H ₅ SeCl	-2.88 (0.962)	-1.91 (0.983)
(<i>Z</i>)-C ₆ H ₅ CH=CHCH ₃ + ArSeCl	-1.91 (0.970)	-1.39 (0.991)
(<i>E</i>)-C ₆ H ₅ CH=CHCH ₃ + ArSeCl	-2.17 (0.971)	-1.53 (0.993)

Table IV. Values of ρ_I , ρ_{R^0} , ρ_R , and ρ_{R^+} for Reactions of Areneselenenyl Chlorides and (*Z*)- and (*E*)-1-Phenylpropenes in CH₂Cl₂ at 25 °C

	(<i>Z</i>)-C ₆ H ₅ CH=CHCH ₃ + ArSeCl	(<i>E</i>)-C ₆ H ₅ CH=CHCH ₃ + ArSeCl	(<i>E</i>)-XC ₆ H ₄ CH=CHCH ₃ + C ₆ H ₅ SeCl
ρ_I	-1.73	-1.88	-1.88
ρ_R	-2.40	-2.67	-4.68
F^a	42.6	42.7	24.3
ρ_I	-1.79	-1.95	-2.16
ρ_{R^0}	-1.93	-2.15	-3.44
F^a	56.4	60.2	120
ρ_I	-1.70	-1.86	-2.16
ρ_{R^+}	-1.35	-1.51	-2.29
F^a	244	299	537

^a *F* test.

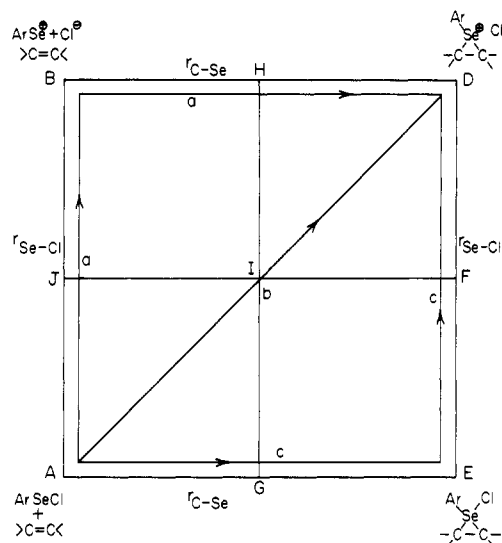


Figure 2. Reaction coordinate contour diagram for the first step in the reaction of areneselenenyl chloride and alkenes.

correlation is obtained using σ_I and σ_{R^+} values for three of the four reaction series. Such a correlation was not attempted for the reaction of benzeneselenenyl chloride and (*Z*)-1-(4-substituted-phenyl)propenes because rate data are available for only four compounds.

Our data establish that electron-donating groups in the phenyl ring of both the alkene and areneselenenyl chloride enhance the rate of reaction. This combination of substituent effects is consistent with positive charge at both the α -carbon of 1-phenylpropene and the selenium atom of the areneselenenyl chloride in the rate-determining transition state.

Additional insight into the mechanism of this reaction can be gained by incorporating the various mechanisms given in Figure 1 into the reaction-coordinate contour diagram shown in Figure 2.¹⁰ At corner A of the diagram

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Table V. Physical Properties

X	XC ₆ H ₄ SeH mp or bp, °C	(XC ₆ H ₄ Se) ₂ mp or bp, °C	XC ₆ H ₄ SeCN mp or bp, °C	XC ₆ H ₄ SeCl mp or bp, °C
Cl	54-56 (lit. ¹⁵ 57 °C)	85-87 (lit. ¹⁵ 87-88 °C)		118-120 ^a (lit. ¹⁵ 103-104 °C/4mm)
F			49-50 ^a	
Br	89-90 (lit. ¹⁸ 84 °C)	105 (lit. ¹⁸ 106-107 °C)		67-68 ^a
CF ₃	oil (lit. ¹⁶ 103 °C/4mm)	49-50 ^a		52 ^a
OCH ₃			59-60 ^a	55.5-57.5 ^a
CH ₃			53-54 (lit. ¹⁷ 51-52 °C)	97 ^a
NO ₂			62-63 ^a	

^a Satisfactory combustion analytical data were reported for these substances (C, H, Cl [where applicable]): ±0.4%.

is located the starting areneselenenyl chloride and alkene. The intermediate seleniranium ion and chloride ion are found at corner D. Breaking the Se-Cl bond of the areneselenenyl chloride corresponds to movement along the edge AB to form the selenium ion (ArSe⁺), chloride ion, and alkene.^{11a} Approach of the alkene to the areneselenenyl chloride without breaking the Se-Cl bond corresponds to movement along the edge AE to form the episelenurane at corner E. On this diagram, the S_N1-like mechanism (Figure 1a) is represented by path a. Path b represents an S_N2-like mechanism (Figure 1b), and path c represents the addition-elimination mechanism (Figure 1c).

Viewing the reactions of areneselenenyl chlorides and alkenes in this way suggests a continuum of mechanisms between two extremes, an S_N1-like mechanism (path a) and an addition-elimination mechanism (path c). Using such a reaction surface and the effect of substituents in the phenyl ring of both the areneselenenyl chloride and the alkene, we can estimate the location of the rate-determining transition state on this surface.

The values of ρ for the effect of substituents on the phenyl rings of both benzeneselenenyl chloride and the 1-phenylpropenes indicate that both the selenium and α -carbon atoms are positively charged in the transition state. In order to generate a positive charge on the selenium atom, substantial heterolytic cleavage of the Se-Cl bond must occur. In Figure 2 such bond breaking occurs only in the region bounded by the four lines BD, DF, FJ, and JB.^{11b} To generate a positive charge on the carbons of the alkene, substantial C-Se bond making must occur. This occurs in Figure 2 in the region described by the four lines GE, ED, DH, and HG. In the region described by the four lines HD, DF, FI, and IH, there will be positive charge at both selenium and carbon. This is the region in which the rate-determining transition state is located. Within this region any transition state whose structure has more Se-Cl bonding breaking than C-Se bond making is in accord with our data, because only in such a transition state can positive charge be generated on both the Se and α -carbon atoms.

There are insufficient data to allow energy contour lines to be placed on the diagram in Figure 2. Therefore it is impossible to state precisely the path of lowest energy from corner A to corner D. However, several facts concerning the reactions of compounds containing bivalent selenium allow us to limit the choices available. First, stable com-

plexes with bivalent selenium as the central electron-acceptor atom are known to exist.¹² Furthermore, oxidation of Se(II) to Se(IV) is known to occur easily in many compounds of bivalent Se.¹³

It is also known that arenesulfenyl chlorides do not ionize to form an arenesulfenium ion and a chloride ion.¹⁴ Areneselenenyl chlorides should behave in a similar manner. This suggests that corner B will be of high energy and path a will be unfavorable. A more favorable path is one that involves electron donation from the alkene to the areneselenenyl chloride. Thus any such path that leads to a transition state within the prescribed region of Figure 2 in which C-Se bond making lags behind Se-Cl bond making is in accord with our data.

Conclusion

Viewing the reaction of areneselenenyl chlorides and alkenes as nucleophilic displacement at bivalent selenium leads to a model that allows the possibility of reaction by a continuum of mechanisms. These mechanisms differ only in the relative amounts of C-Se bond making and Se-Cl bond breaking in the rate-determining transition state. From our data it is concluded that C-Se bond making lags behind the Se-Cl bond breaking in the rate-determining transition state of the addition of areneselenenyl chlorides to 1-phenylpropenes.

Experimental Section

All melting points are uncorrected. Microanalyses were carried out by A. G. Gygli Microanalysis Laboratory, Toronto. The (*Z*)- and (*E*)-1-(4-substituted-phenyl)propenes were prepared as previously reported.¹⁹ Methylene chloride was purified as previously reported.²⁰ Benzeneselenenyl chloride was obtained from Aldrich Chemical Co. and recrystallized from CH₂Cl₂, mp 63.7-64.5 °C (lit.²⁰ 64 °C). The rate data were obtained as previously described.²¹

Preparation of Areneselenenyl Chlorides via Grignard Reagent: General Procedure. 4-Substituted Benzeneselenol. To the Grignard reagent, prepared from 0.50 mol of the appropriately substituted bromobenzene and 12 g (0.50 mol) of Mg in 700 mL of anhydrous diethyl ether under a N₂ atmosphere, was added 38 g (0.48 mol) of black selenium powder at such a rate as to maintain gentle refluxing. After the addition of the selenium, the reaction mixture was stirred for another 20 min and poured over 600 g of cracked ice, and 75 mL of concentrated HCl was

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(11) (a) It is assumed that interatomic distances not explicitly indicated in Figure 2 will adjust to their most stable values. (b) The lines JF and GH are drawn arbitrarily midway along the edges AB and AE, respectively. Their actual locations will depend on the relative energies at corners A, B, D, and E. Changing the locations of these lines changes the sizes of the various regions but does not affect the basic argument.

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added slowly with stirring. After filtering, the layers were separated and the aqueous layer was extracted with diethyl ether. The organic layers were combined, dried over MgSO_4 , and filtered, and the diethyl ether was removed by rotary evaporation. The physical properties of the 4-substituted benzeneselenols are listed in Table V.

Bis(4-substituted-benzene) Diselenide. To 0.30 mol of 4-substituted benzeneselenol in 500 mL water was added 12.0 g (0.30 mol) of NaOH . To the mixture was added 225 mL of 3% hydrogen peroxide at such a rate that the temperature of the reaction mixture did not exceed 30 °C. After the addition of hydrogen peroxide, the reaction mixture was stirred overnight at room temperature. The crystals of diselenide were filtered and washed with warm water and then by distilled water until the filtrate was alkaline free. The physical properties of the bis(4-substituted-benzene) diselenides are listed in Table V.

4-Substituted Benzeneselenenyl Chlorides. To a solution of 0.25 mol of bis(4-substituted-benzene) diselenide in 400 mL of CCl_4 was added dropwise a solution of 0.25 mol of SO_2Cl_2 in 250 mL of CCl_4 . The reaction mixture was allowed to stand for 30 min at room temperature after addition of SO_2Cl_2 . The solvent was removed by rotatory evaporation. The resulting oil or solid was recrystallized from pentane. The physical properties of the 4-substituted benzeneselenenyl chlorides are given in Table V and the elemental analyses for all the new compounds were satisfactory.

Preparation of Areneselenenyl Chlorides via Arene Selenocyanates: General Procedure. 4-Substituted-benzene selenocyanates. To a solution of 0.10 mol of the appropriately substituted aniline in 85 mL of 20% H_2SO_4 cooled to 4 °C was added in portions with stirring 8.0 g of NaNO_2 . Sodium acetate was added until the pH of the reaction mixture was 6.0 and then a solution of 14.0 g (0.10 mol) of KSeCN in 150 mL of cold water was added slowly. The reaction mixture was stirred at room temperature for 48 h, filtered, and extracted with CH_2Cl_2 . The

CH_2Cl_2 layer was dried over MgSO_4 and the solvent removed by rotary evaporation leaving the solid selenocyanate. The melting points of the 4-substituted-benzene selenocyanates prepared in this study are given in Table V.

4-Substituted Benzeneselenenyl Chlorides. The 4-substituted-benzene selenocyanates were chlorinated with SO_2Cl_2 in CCl_4 by the same procedure used for bis(4-substituted benzene) diselenides. Attempts to isolate 4-fluorobenzeneselenenyl and 4-nitrobenzeneselenenyl chlorides were unsuccessful. Solutions of these areneselenenyl chlorides in CH_2Cl_2 for kinetic runs were prepared immediately after the chlorination reaction. The CCl_4 was removed from the reaction mixture under high vacuum to constant weight. A known volume of anhydrous CH_2Cl_2 was added, and the amount of areneselenenyl chloride was determined by titrating an aliquot with (*E*)-3-hexene.

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Registry No. 1a, 57878-19-0; 1b, 52178-47-9; 1c, 5707-04-0; 1d, 57878-20-3; 1e, 71912-36-2; 1f, 57878-21-4; 1g, 71912-37-3; 1h, 57878-23-6; (Z)-4- $\text{C}_6\text{H}_5\text{OC}_6\text{H}_4\text{CH}=\text{CHCH}_3$, 60319-64-4; (Z)-4- $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}=\text{CHCH}_3$, 25679-28-1; (Z)-4- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}=\text{CHCH}_3$, 2077-29-4; (Z)-4- $\text{ClC}_6\text{H}_4\text{CH}=\text{CHCH}_3$, 1879-52-3; (Z)-4- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}=\text{CHCH}_3$, 1879-54-5; (Z)-3- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}=\text{CHCH}_3$, 23281-57-4; (E)-4- $\text{C}_6\text{H}_5\text{OC}_6\text{H}_4\text{CH}=\text{CHCH}_3$, 60319-66-6; (E)-4- $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}=\text{CHCH}_3$, 4180-23-8; (E)-4- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}=\text{CHCH}_3$, 2077-30-7; (E)-4- $\text{ClC}_6\text{H}_4\text{CH}=\text{CHCH}_3$, 1879-53-4; (E)-4- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}=\text{CHCH}_3$, 1879-55-6; (E)-3- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}=\text{CHCH}_3$, 23204-79-7; (Z)-1-phenylpropene, 766-90-5; (E)-1-phenylpropene, 873-66-5.

Reactions with 3,1-Benzoxazin-4-ones. 3.¹ Reactions of 6,8-Dibromo-2-methyl-3,1-benzoxazin-4-ones with Amines

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We observed that the reaction of 6,8-dibromo-2-methyl-3,1-benzoxazin-4-one, **5**, with primary amines occurs very slowly in ethanol solution at room temperature and that the product is usually the corresponding 2-acetamido-3,5-dibromobenzamide, **6**. These results are in sharp contrast to the results reported for the corresponding reactions with 6-bromo-2-methyl-3,1-benzoxazin-4-one, **5'**. The latter occur very rapidly to give the corresponding *N*-(2-carboxy-4-bromophenyl)-*N'*-substituted-acetamidine intermediate, **4**, which undergoes cyclodehydration in solution (sometimes spontaneously) to give the corresponding *N*-substituted-2-methyl-6-bromoquinazolin-4-ones, **7'**. It was inferred from these observations that the qualitative difference in chemistry exhibited by **5** and **5'** is somehow attributable to the presence of the substituent in the 8-position of compound **5**.

In a recent series of publications,²⁻⁶ Errede et al. reinvestigated the reactions of 3,1-benzoxazin-4-ones **1** with amines. They reported that the products, ortho-substi-

tuted benzamides (**2**) and/or quinazolin-4-ones (**3**), were not formed sequentially (**3** from **2**) as was assumed by early investigators but rather were formed competitively via alternative pathways A and B as shown in Scheme I.

These authors showed that the precursors of **3** are the amidine salt intermediates **4**. These intermediates were isolated in >90% yield when R'' is aromatic (Table IV of ref 4 and Table I of ref 3) and when R'' is nonsterically hindered aliphatic amines (Table I of ref 5). They undergo cyclodehydration quantitatively even in aqueous solution at room temperature within a few minutes to a few hours. In contrast, the *o*-acetamidobenzamides, **2**, need temper-

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